SYNTHESIS AND CHARACTERIZATION OF LACUO3 AND CECUO3 PEROVSKITES AND YTTRIUM OR POTASSIUM-PROMOTED PEROVSKITE FOR SELECTIVITY, LONGEVITY AND KINETIC STUDIES OF ETHANOL DRY REFORMING



اونيۇرسىيتي مليسىيا قهغ السلطان عبدالله UNIVERSITI MALAYSIA PAHANG AL-SULTAN ABDULLAH

DOCTOR OF PHILOSOPHY

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Thesis submitted in fulfillment of the requirements for the award of the degree of Doctor of Philosophy AL-SULTAN ABDULLAH

Faculty of Chemical and Process Engineering Technology

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ABSTRAK

Etanol dan karbon dioksida ialah bahan mentah lestari yang berpotensi bagi penghasilan singas menerusi tindak balas pembentukan semula kering. Tembaga ialah salah satu daripada mangkin-mangkin bukan adi yang aktif untuk tindak balas tersebut tetapi mudah ternyahktif akibat sinter dan penumpukan karbon pada suhu tindak balas yang tinggi. Penyokong yang kuat dan stabil terhadap haba dari struktur perovskite lanthanum atau cerium serta agen pengoksidaan seperti yttrium atau potassium adalah penyelesaian yang berpotensi untuk menyelesaikan masalah mangkin berasaskan tembaga tersebut. Oleh itu, objektif kajian ini adalah untuk menyedia dan menyiasat sifat kimia-fizikal, menguji ketermemilihan dan ketahanan mangkin, menilai tukaran berdasarkan pelbagai nisbah suapan dan suhu tindak balas, dan menentukan parameter kinetik dalam tindak balas EDR. Kaedah sol-gel telah digunakan untuk menyediakan sampel-sampel mangkin berdasarkan komposisi perovskite disimbolkan sebagai A_{1-x}B_xCuO₃ di mana x diubah dari 0 ke 1 dengan sela sebanyak 0.25. Mangkin terturun dan telah diguna kemudian dicirikan menggunakan kaedah BET, XRD, TPR, FTIR, SEM, Spektroskopi Raman, dan TEM. Aktiviti mangkin dalam EDR diuji menggunakan satu sistem reaktor tiub beraliran pada suhu-suhu tindak balas dari 948 ke 1073 K dan nisbah-nisbah CO₂:C₂H₅OH dari 2.5 hingga 1 di bawah tekanan atmosfera, dengan tekanan separa karbon dioksida dan etanol dari 20 hingga 70 kPa. Kesan promosi logam disiasat secara bertahap, bermula dengan A (lanthanum atau cerium) tanpa B (yttrium atau potassium). Jelas, LaCuO₃ menunjukkan luas permukaan 60 kali lebih besar daripada CeCuO₃ namun ia menurun kira-kira 50% selepas tindak balas EDR, lebih banyak filamen karbon bersaiz nano dari imej SEM dan TEM, struktur kristal perovskite dan oksida logam lebih besar dan banyak sebelum dan selepas tindak balas. Spektra Raman juga menunjukkan kehadiran karbon pada CeCuO₃ lebih banyak. Kedua-dua mangkin mempunyai dua suhu penurunan dan mangkin kedua mempunyai suhu penurunan yang lebih tinggi. LaCuO₃ kelihatan lebih aktif dan ujian EDRnya menghasilkan tukaran, hasilan dan nisbah H₂/CO yang lebih tinggi. Khususnya, tukaran CO₂ dan C₂H₅OH bertambah masing-masing kepada 86% dan 30% dengan suhu tindak balas yang meningkat dari 923 ke 1073 K. Ketika tindak balas EDR, nisbah H₂/CO sentiasa melebihi 1 disebabkan oleh tindak balas penyahhidrogenan etanol dan ini sesuai untuk sintesis F-T. Promosi yttrium and potassium ke atas mangkin perovskite melebihi 25% tidak menambah-baik tindak balas EDR. La_{0.75}Y_{0.25}CuO₃ menunjukkan aktiviti tertinggi, bersamaan dengan LaCuO3, dan menunjukkan ketahanan terhadap deposit karbon selama 72 jam dalam aliran pada nisbah suapan stoikiometri dan 1023 K, lebih baik daripada mangkin berasaskan kobalt dan zirconia. Persamaan kadar Langmuir-Hinshelwood mencadangkan kedua-dua bahan tindak balas sama-sama terjerap pada tapak tunggal mangkin La_{0.75}Y_{0.25}CuO₃ dengan tenaga pengaktifan kira-kira 102.24 kJ mol⁻¹. Keseluruhannya, LaCuO₃ dan La_{0.75}Y_{0.25}CuO₃ merupakan mangkin terbaik yang disediakan yang mempunyai deposit karbon yang rendah, ketahanan dan aktiviti yang tinggi dalam tindak balas EDR.

ABSTRACT

Ethanol and carbon dioxide are potential, sustainable feedstocks for syngas productions via ethanol dry reforming (EDR) reaction. Copper is one of the active, non-noble catalysts for this reaction, but prone to deactivation due to sintering and carbon deposition at high reaction temperatures. A strong and thermally stable support of perovskite structure from lanthanum or cerium and oxidating agent like yttrium or potassium are potential solution for the Cu-based catalyst problems. Therefore, the objectives of this study were to prepare and investigate the physicochemical properties of the catalysts, evaluate their selectivity and longevity, assess conversions based on various feed ratios and reaction temperatures, and determine kinetic parameters in the EDR reaction. The citric sol-gel method was employed to prepare the catalysts based on the perovskite compositions denoted as A₁- $_{x}B_{x}CuO_{3}$, where x was varied from 0 to 1 within 0.25 interval. A represents lanthanum or cerium, and B is yttrium or potassium. The reduced and spent catalysts were characterized using BET, XRD, TPR, FTIR, SEM, Raman Spectroscopy, and TEM methods. The catalyst activity in the EDR reaction was tested in a flow tubular reactor system at reaction temperatures ranging from 948 to 1073 K and CO₂:C₂H₅OH ratios from 2.5 to 1 under atmospheric pressure, with partial pressures of CO₂ and ethanol varying from 20 to 70 kPa. The promotion effect was investigated stepwise, starting with the support of A (lanthanum or cerium) without B (yttrium or potassium). Notably, LaCuO₃ exhibited better characteristics of surface area 60 times larger than CeCuO₃ despite of a drop by 50% after the EDR reaction, more carbon nanofilament in TEM and SEM images, greater crystallinity of perovskite and metal oxides in the XRD results before and after the reaction. Raman spectra also confirmed the carbon presence more in the CeCuO₃ catalysts. Both catalysts exhibited two reduction temperatures, with the latter being higher. Thus, LaCuO₃ appeared more active, resulting in higher conversion, product yield, and an elevated H₂/CO ratio during the EDR test. Specifically, the CO₂ and ethanol conversions increased to 86% and 30%, respectively, as the reaction temperature rose from 923 to 1073 K. During the EDR reaction, the H2/CO ratio always remained a higher value than unity due to the occurrence of the ethanol dehydrogenation reaction, which is suitable for F-T synthesis. The promotion of yttrium and potassium loading higher than 25% onto the perovskite catalysts did not improve the EDR reaction performance. La0.75Y0.25CuO3 exhibited the highest catalytic activity, equivalent to LaCuO3, and showed resistance to coke deposition for 72 h on stream at a stoichiometric ratio and 1023 K. These results are better than those achieved with cobalt-based catalyst and zirconiabased catalyst. Additionally, La_{0.75}Y_{0.25}CuO₃ had a lower carbon composition in EDX result compared to LaCuO₃. The Langmuir-Hinshelwood rate expression suggests that both reactants (C_2H_5OH and CO_2) are associatively adsorbed on a single site catalyst, with a corresponding activation energy of approximately 102.24 kJ mol⁻¹ on La_{0.75}Y_{0.25}CuO₃. Overall, LaCuO₃ and La_{0.75}Y_{0.25}CuO₃ are the best perovskite catalysts prepared that had low carbon deposition, longevity and high activity in the EDR reaction.

TABLE OF CONTENT

DECLARATION

TITI	LE PAGE	
ACK	NOWLEDGEMENTS	ii
ABS	TRAK	iii
ABS	TRACT	iv
ТАВ	LE OF CONTENT	V
LIST	TOF TABLES	xi
LIST	TOF FIGURES	xii
LIST	T OF SYMBOLS	xvi
LIST	T OF ABBREVIATIONS	xviii
LIST	T OF APPENDICES	xix
СНА	PTER 1 INTRODUCTION	1
1.1	Overview UMPSA	1
1.2	Problem Statement	3
1.3	اونيۇرسىينى مليسىيا قهغ الس Objectives of Research	4
1.4	Scope of Study	5
1.5	Thesis organization	5
СНА	PTER 2 LITERATURE REVIEW	7
2.1	Overview	7
2.2	Pursuit of Clean Energy	7
2.3	Ethanol Feedstock	9
2.4	Syngas Production	10
	2.4.1 Steam Reforming	11
	2.4.2 Partial Oxidation	12
	2.4.3 Autothermal reforming	12

	2.4.4	Dry Reforming	13
2.5	Perovs	skite	23
	2.5.1	Structure of Perovskite	25
	2.5.2	Classification of Perovskites	26
	2.5.3	Perovskite Catalysts in Reforming Reaction.	27
2.6	Promo	otion to Perovskite Catalyst	35
2.7	Cataly	vst Deactivation	41
2.8	Reacti	on mechanism and kinetic study of ethanol dry reforming	45
	2.8.1	Power Law Model	45
	2.8.2	Langmuir-Hinshelwood Model	47
2.9	Concl	uding remarks	48
СНА	PTER 3	METHODOLOGY	50
3.1	Overv	iew UMPSA	50
3.2	Mater	ials	52
3.3	Cataly	اونيۇرسىيتى مليسيا قھغ st Preparation Method	53
3.4	Cataly	vst Characterisation Methods	56
	3.4.1	X-ray Diffraction Analysis	56
	3.4.2	Temperature-Programmed Reduction	57
	3.4.3	Scanning Electron Microscopy Energy Dispersive X-ray	57
	3.4.4	Transmission Electron Microscopy	57
	3.4.5	Fourier Transform Infrared Spectroscopy	58
	3.4.6	X-ray Photoelectron Spectroscopy	58
	3.4.7	Raman Spectroscopy	58
	3.4.8	Brunauer-Emmett-Teller	58
3.5	Ethan	ol Dry Reforming Reaction	59

	3.5.1	Gas Chromatography	60
	3.5.2	Ethanol Dry Reforming Reaction Parameters	61
3.6	Prelin	inary Works	62
	3.6.1	Blank Test Results	62
	3.6.2	Transport Resistance Estimations	62
	3.6.3	Thermodynamics Analysis	69
3.7	Concl	uding Remarks	70

CHAPTER 4 TRIOXIDE PEROVSKITE OF COPPER AND LANTHANUM OR CERIUM: CATALYST CHARACTERIZATION AND ETHANOL DRY REFORMING REACTION STUDY

ЕТН	ANOL I	DRY REFORMING REACTION STUDY	72
4.1	Overv	riew	72
4.2	Cataly	vst Characterization	72
	4.2.1	Surface Area and Pore Size	72
	4.2.2	X-ray diffraction of LaCuO ₃ and CeCuO ₃ catalyst	73
	4.2.3	Temperature Programmed reduction	74
	4.2.4	Fourier Transform Infrared Spectroscopy	76
	4.2.5	Raman spectroscopy ABDULLAH	77
4.3	Ethan	ol Dry Reforming Reaction	78
	4.3.1	Effect of Reaction Temperature	78
	4.3.2	Effect of feed ratio	82
	4.3.3	Effect of ethanol partial pressure	85
	4.3.4	Effect of CO ₂ partial pressure	86
4.4	Post-F	Reaction Characterization	89
	4.4.1	Surface Area and Pore Size	89
	4.4.2	X-Ray Diffraction	89
	4.4.3	Fourier Transform Infrared Spectroscopy	90

	4.4.4	Scanning and Transmission Electron Microscopy	91
	4.4.5	X-ray photoelectron spectroscopy	93
	4.4.6	Raman spectroscopy	95
4.5	Concl	uding Remarks	96
CHA ONT	PTER 5 O LACI	5 EFFECT OF YTTRIUM AND POTASSIUM PROMOTION UO3 PEROVSKITE CATALYST	97
5.1	Overv	iew	97
5.2	Effect	of Yttrium Promotion	97
	5.2.1	X-Ray Diffraction	98
	5.2.2	Fourier Transform Infrared Spectroscopy	99
	5.2.3	Hydrogen Temperature Programmed Reduction	100
	5.2.4	Ethanol Dry Reforming	101
5.3	Yttriu	m-Promoted LaCuO ₃ after the EDR Reaction	105
	5.3.1	X-ray Diffraction	105
	5.3.2	Fourier-Transform Infrared Spectroscopy	106
	5.3.3	X-Ray Photoemission Spectroscopy (XPS) HANG	107
	5.3.4	Scanning electron microscopy – Energy Dispersive X-Ray	109
5.4	Effect	of potassium promotion	111
	5.4.1	X-Ray Diffraction	112
	5.4.2	Fourier Transform Infrared Spectroscopy	113
	5.4.3	Temperature Programmed Reduction	114
	5.4.4	Ethanol Dry Reforming	115
5.5	Potass	sium-Promoted LaCuO3 Catalyst After Reaction	119
	5.5.1	X-ray Diffraction	119
	5.5.2	Fourier-Transform Infrared Spectroscopy	120
	5.5.3	X-Ray Photoemission Spectroscopy	121

	5.5.4	Scanning Electron Microscopy with Energy Dispersive X-Ray	122
5.6	The L	ongevity Tests on the Yttrium and Potassium promoted LaCuO ₃ .	125
5.7	Post-I	Longevity Test Characterization	129
	5.7.1	X-ray Diffraction	129
	5.7.2	Scanning Electron Microscopy with Energy Dispersive X-Ray.	130
	5.7.3	X-Ray Photoemission Spectroscopy	132
5.8	Concl	uding Remarks	133
CHA	PTER 6	5 KINETICS STUDY	134
6.1	Overv	iew	134
	6.1.1	Power Law Model	134
	6.1.2	Langmuir-Hinshelwood Model	137
	6.1.3	Concluding Remarks	143
		UMPSA	
CHA	PTER 7	CONCLUSION AND RECOMMENDATIONS	144
7.1	Concl	او نيو رسيتي ملسبا قمع السلطان عيداللم	144
7.2	Recon	nmendation RSITI MALAYSIA PAHANG	145
		AL-SULTAN ABDULLAH	
	REFF	CRENCES	147
APPH	ENDIX	A CALCULATION OF CATALYST PREPARATION	163
APPF	ENDIX	B TRANSPORT RESISTANCE CALCULATIONS	168
B.1 R	esistanc	e of External Mass Transfer	168
B.2 In	ternal (Intraparticle) Mass transfer Resistance	172
B.3 E	xternal	Heat Transfer Resistance	173
B.4 In	iternal H	Ieat Transfer Resistance	175
B.5 E	ffect of	wall and Radial Heat Dispersion	176

APPENDIX C GRAPHS OF ISOTHERMAL ADOSRPTION FOR BET	
SURFACE ANALYSES.	178
C.1 Isothermal Adsorption of LaCuO ₃	178
C.2 Isothermal Adsorption of CeCuO ₃	179
APPENDIX D CALIBRATION CURVE	180
D.1 Calibration Curve for Syringe Pump	180
D.2 Calibration Curve for Mass Flow Controller (MFC)	181
D.3 Calibration Curve of GC Analysis	183



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LIST OF TABLES

Table 2.1 Advantages and disadvantages of reaction processes for syngas	15
	13
Table 2.2 Synopsis of earlier studies in the EDR reactions.	18
Table 2.3 Goldshmidt tolerance factor on various perovskite structures with examples	24
Table 2.4 Synopsis on the perovskite catalysts involved in reforming processes of ethanol, methanol and glycerol.	30
Table 2.5 Synopsis of K-promoted perovskite catalysts	36
Table 2.6. Synopsis of study on Y-promoted perovskites	38
Table 2.7 Deactivation of catalyst	41
Table 2.8 Catalyst poisons in typical processes	44
Table 3.1 List of materials used for catalyst preparation and experiment	52
Table 3.2. List of gases for GC analyses	53
Table 3.3 Amount of the chemicals used for the 5 g of catalyst preparation.	55
Table 3.4 Standard gas information	60
Table 3.5 properties employed in the calculation of transport resistance	63
Table 3.6 Summary of thermodynamics of the EDR reaction	69
Table 4.1 BET Analysis Results	72
Table 4.2 Crystallite size of the LaCuO ₃ catalyst.	74
Table 4.3 Crystallite size of the CeCuO ₃ catalyst.	74
Table 4.4 Parameters of sigmoid equation for yields	80
Table 4.5 BET Analysis Results MALAYSIA PAHANG	89
Table 5.1 Size of Crystallites for Each Catalyst	98
Table 5.2 Size of Crystallites for Each Catalyst	112
Table 6.1 Rate of Reactions for Various Pressures of Reactants	135
Table 6.2 Kinetics parameters of the reactant of La _{0.75} Y _{0.25} CuO ₃ catalyst based the power law model.	136
Table 6.3 Kinetic parameters calculated from L-H rate expressions for $La_{0.75}Y_{0.25}CuO_3$ catalyst	140
Table 6.4 Summary of kinetic parameter computed from L-H rate expression over catalysts	142

LIST OF FIGURES

Figure 2.1 Global primary energy consumption in 2021	8
Figure 2.2 Global emission of CO ₂ from fossil fuels until 2020	9
Figure 2.3 Various application of syngas	11
Figure 2.4 Basic perovskite structure of CaTiO ₃	24
Figure 2.5 Perovskite structural frame positions of atoms.	26
Figure 2.6 Classification of perovskite structures	27
 Figure 2.7 coke formation on a supported metal catalyst (Ochoa, Bilbao, Gayubo, & Castaño, 2020): (i) carbon chemisorption or physisorption blocking the access to reactants; (ii) metal particle encapsulation; (iii) pore plugging; (iv) degradation of catalyst structure by carbon filament. (v) FESEM analysis revealed coke filament on the catalyst after methane dry reforming. 	43
Figure 2.8 Theoretical models of crystallite growth due to sintering: (A) Ostwald ripening; (B) small particle migration.	44
Figure 2.9 Langmuir – Hinshelwood reaction mechanism (A) and (B) are reactants; (P) is product (Rousseau et al., 2009).	47
Figure 3.1 The flowchart of steps in methodology in accordance with the objectives	51
Figure 3.2 The steps in preparing catalysts by the sol-gel method.	54
Figure 3.3 Bragg's law for XRD measurement	56
Figure 3.4 Schematic diagram of the EDR reactor setup	59
Figure 3.5 Individual steps of a heterogeneous catalytic reaction. Source (Mitchell, 2007)	63
Figure 3.6 Change of Gibbs free energy for all EDR reactions at various temperatures	69
Figure 4.1 XRD patterns of reduced (a) LaCuO ₃ (b) CeCuO ₃ catalysts.	73
Figure 4.2 TPR characterisation of (a) LaCuO ₃ (b) CeCuO ₃ catalysts.	76
Figure 4.3 FT-IR of LaCuO ₃ and CeCuO ₃ freshly reduced catalysts	77
Figure 4.4 Raman spectroscopy of Fresh LaCuO3 and CeCuO3 catalysts	78
Figure 4.5 Effect of reaction temperatures of LaCuO ₃ and CeCuO ₃ from 998-1073 K; $P_{C2H5OH} = P_{CO2} = 20$ kPa.	79
Figure 4.6 Effect of reaction temperature w.r to H_2 & CO yield and H_2 /CO ratio of LaCuO ₃ and CeCuO ₃ catalyst from 998 to 1073 K, $P_{CO2} = P_{C2H5OH} = 20$ kPa.	81
Figure 4.7 The effect of reaction temperature to CH_4 yield using the LaCuO ₃ and $CeCuO_3$ catalysts under the reactant pressures, $P_{CO2} = P_{C2H5OH} = 20$ kPa.	82
Figure 4.8 Effect of feed ratio on the CO ₂ conversion by LaCuO ₃ and CeCuO ₃ catalysts.	83

Figure 4.9 Effect of feed ratio with regard to H ₂ & CO yields and H ₂ /CO ratio of LaCuO ₃ and CeCuO ₃ catalysts.	84
Figure 4.10 effect of molar ratio w.r to CH ₄ yield of LaCuO ₃ and CeCuO ₃ catalysts.	85
Figure 4.11 Effect of ethanol partial pressure of C_2H_5OH on ethanol and carbon dioxide conversions at $P_{CO2} = 20$ kPa at 1023 K.	86
Figure 4.12 Effect of ethanol partial pressure of H_2/CO and CH_4/CO ratios at P_{CO2} = 20 kPa at 1023 K.	86
Figure 4.13 Effect of CO ₂ partial pressure of C ₂ H ₅ OH and CO ₂ conversions at $P_{ethanol} = 20$ kPa at 1023 K.	88
Figure 4.14 Effect of CO ₂ partial pressure of H_2 and CO Yields at $P_{C2H5OH} = 20$ kPa at 1023 K.	88
Figure 4.15 Effect of CO ₂ partial pressure of H_2/CO ratios at $P_{CO2} = 20$ kPa at 1023 K.	89
Figure 4.16 XRD of LaCuO ₃ and CeCuO ₃ spent catalysts	90
Figure 4.17 FTIR spectrums of (a) LaCuO ₃ and (b) CeCuO ₃ spent catalysts.	91
Figure 4.18 SEM-EDX images for (a) LaCuO ₃ and (b) CeCuO ₃ catalysts and TEM images for (c) LaCuO ₃ and (d) CeCuO ₃ catalysts after the EDR reaction.	93
Figure 4.19 XPS characterisation of (a) $LaCuO_3$ and (b) $CeCuO_3$ catalysts	95
Figure 4.20 Raman spectroscopy of LaCuO ₃ and CeCuO ₃ spent catalysts	96
Figure 5.1 X-ray diffraction spectrums of fresh La _{0.75} Y _{0.25} CuO ₃ , La _{0.50} Y _{0.50} CuO ₃ , La _{0.25} Y _{0.75} CuO ₃ and YCuO ₃ Catalysts	99
Figure 5.2 FTIR spectrums of fresh La _{0.75} Y _{0.25} CuO ₃ , La _{0.50} Y _{0.50} CuO ₃ , La _{0.25} Y _{0.75} CuO ₃ and YCuO ₃ Catalysts.	100
Figure 5.3 TPR of fresh La $_{0.75}Y_{0.25}CuO_3$, La $_{0.50}Y_{0.50}CuO_3$, La $_{0.25}Y_{0.75}CuO_3$ and YCuO_3 Catalysts.	101
Figure 5.4 Time on stream of the reactant conversions for the yttrium-promoted perovskite catalysts at $PC2H5OH = PCO2 = 20$ kPa and 1023K.	103
Figure 5.5 Time on stream of (a) H_2 and (b) CO_2 Yields for the yttrium-promoted perovskite catalysts at $PC2H5OH = PCO2 = 20$ kPa and 1023K	103
Figure 5.6 Time on stream of product ratios the yttrium-promoted pervoskite catalysts at $PC2H5OH = PCO2 = 20$ kPa and 1023 K	104
Figure 5.7 The EDR activity: (a) reactant conversions, (b) product selectivities, (c) product yields and (d) product ratios at $P_{C2H5OH} = P_{CO2} = 20$ kPa and 1023 K.	105
Figure 5.8 XRD analyses of the spent $La_{0.75}Y_{0.25}CuO_3$, $La_{0.50}Y_{0.50}CuO_3$, $La_{0.25}Y_{0.75}CuO_3$ and YCuO ₃ catalysts.	106
Figure 5.9 FTIR analyses of the spent $La_{0.75}Y_{0.25}CuO_3$, $La_{0.50}Y_{0.50}CuO_3$, $La_{0.25}Y_{0.75}CuO_3$ and $YCuO_3$ catalysts.	107

Figure 5.10 XPS analyses of the spent (a) $La_{0.75}Y_{0.25}CuO_3$, (b) $La_{0.50}Y_{0.50}CuO_3$ and (c) $La_{0.25}Y_{0.75}CuO_3$ catalysts.	108
Figure 5.11 SEM analyses of the spent (a) $YCuO_3$, (b) $La_{0.25}Y_{0.75}CuO_3$, (c) $La_{0.50}Y_{0.50}CuO_3$, (d) $La_{0.75}Y_{0.25}CuO_3$ catalysts.	109
Figure 5.12 EDX topography analyses of the spent (a) $YCuO_3$, (b) $La_{0.25}Y_{0.75}CuO_3$, (c) $La_{0.50}Y_{0.50}CuO_3$, (d) $La_{0.75}Y_{0.25}CuO_3$ catalysts.	111
Figure 5.13 XRD analysis of La_{0.75}K_{0.25}CuO_3, La_{0.50}K_{0.50}CuO_3, La_{0.25}K_{0.75}CuO_3 and KCuO_3	113
Figure 5.14 FTIR analysis of $La_{0.75}K_{0.25}CuO_3$, $La_{0.50}K_{0.50}CuO_3$, $La_{0.25}K_{0.75}CuO_3$ and $KCuO_3$	114
Figure 5.15 TPR analysis of La_{0.75}K_{0.25}CuO_3, La_{0.50}K_{0.50}CuO_3, La_{0.25}K_{0.75}CuO_3 and $KCuO_3$	115
Figure 5.16 Conversions of C ₂ H ₅ OH and CO ₂ from the EDR reactions for 8 h of TOS using potassium-promoted perovskite catalysts.	116
Figure 5.17 Yields of H ₂ and CH ₄ from the EDR for 8 h of TOS using the potassium-promoted perovskite catalysts.	117
Figure 5.18 Ratios of the EDR products for 8 h of TOS using the potassium- promoted perovskite catalysts.	117
Figure 5.19 The activity of potassium-based perovskite catalyst $P_{CO2} = P_{C2H5OH} =$ 20 kPa and 1023 K: (a) $C_2H_5OH \& CO_2$ conversion (b) H_2 , CO and CH ₄ Selectivity (c) H_2 , CO and CH ₄ Yield (d) H_2/CO and CH ₄ /CO product ratio.	119
Figure 5.20 XRD analyses of the spent $La_{0.75}K_{0.25}CuO_3$, $La_{0.50}K_{0.50}CuO_3$, $La_{0.25}K_{0.75}CuO_3$ and $KCuO_3$ catalysts.	120
Figure 5.21 The FTIR spectroscopy analyses of the spent La _{0.75} K _{0.25} CuO ₃ , La _{0.50} K _{0.50} CuO ₃ , La _{0.25} K _{0.75} CuO ₃ and KCuO ₃ catalysts.	121
Figure 5.22 XPS Analysis of the spent (a) La _{0.75} K _{0.25} CuO ₃ , (b) La _{0.50} K _{0.50} CuO ₃ , (c) La _{0.25} K _{0.75} CuO ₃ and (d) KCuO ₃ catalysts.	122
Figure 5.23 SEM images of the spent (a) La _{0.75} K _{0.25} CuO ₃ , (b) La _{0.50} K _{0.50} CuO ₃ , (c) La _{0.25} K _{0.75} CuO ₃ , and KCuO ₃ catalysts under 3000 times of magnification.	123
Figure 5.24 SEM-EDX images of (a) $La_{0.75}K_{0.25}CuO_3$, (b) $La_{0.50}K_{0.50}CuO_3$, (c) $La_{0.25}K_{0.75}CuO_3$ and (d) KCuO ₃ catalysts.	124
Figure 5.25 C ₂ H ₅ OH and CO ₂ conversions for the best yttrium and potassium- promoted catalysts at 1:1 (C ₂ H ₅ OH:CO ₂) and 1023 K	126
Figure 5.26 H ₂ and CO Yield of the best catalysts for the best yttrium and potassium-promoted catalysts at 1:1 (C ₂ H ₅ OH:CO ₂) and 1023 K	127
Figure 5.27 CH ₄ yield for for the best yttrium and potassium-promoted catalysts at 1:1 (C ₂ H ₅ OH:CO ₂) and 1023 K	128
Figure 5.28 Product ratios for for the best yttrium and potassium-promoted catalysts at 1:1 (C ₂ H ₅ OH:CO ₂) and 1023 K	129

Figure 5.29 XRD analyses of the spent (a) $La_{0.75}Y_{0.25}CuO_3$ (b) $La_{0.75}K_{0.25}CuO_3$ catalysts	130	
Figure 5.30 SEM analysis of the spent (a) $La_{0.75}Y_{0.25}CuO_3$ (b) $La_{0.75}K_{0.25}CuO_3$ catalysts	131	
Figure 5.31 SEM-EDX of (a) $La_{0.75}Y_{0.25}CuO_3$ (b) $La_{0.75}K_{0.25}CuO_3$ catalysts	131	
Figure 5.32 XPS spectroscopy (a) full spectra scan (survey scan) (b) Carbon element of the spent $La_{0.75}Y_{0.25}CuO_3$ and $La_{0.75}K_{0.25}CuO_3$ catalysts	132	
Figure 6.1 Arrhenius plot of the power law model energy for the EDR reaction using equal pressure of feed on LaCuO ₃ catalyst	137	
Figure 6.2 Parity plots for the rates of consumption over $La_{0.75}Y_{0.25}CuO_3$ catalyst at the temperature of 998-1073 K on (a) C_2H_5OH , (b) CO_2 .	137	
Figure 6.3 The simplified steps of Langmuir-Hinshelwood based on a) a single- mechanism step of molecular adsorption of both reactants, b) single -site dissociative adsorption of both reactants and d) dual site mechanism considers that the both reactants adsorb favourably on two different sites (X1 and X ₂) available on the catalyst surface	139	
Figure 6.4 Parity plot of experiment versus predicted of C ₂ H ₅ OH consumption rate for La _{0.75} Y _{0.25} CuO ₃ catalyst using L-H model 1	142	
Figure 6.5 Parity plot of experimental versus predicted for rate of (a) C ₂ H ₅ OH consumption, (b) CO ₂ consumption, (c) H ₂ synthesis and (d) CO synthesis for La _{0.75} Y _{0.25} CuO ₃ catalyst using the L-H model 1.	143	
Figure C.1 Isothermal Adsorption of LaCuO ₃	178	
Figure C. 2 Isothermal Adsorption of CeCuO ₃	179	
Figure D.1 The calibration curve of syringe pump using C2H5OH.	180	
Figure D.2 The calibration curve of mass flow controller using CO2.	181	
Figure D.3 The calibration curve of mass flow controller using H2.	181	
Figure D.4 The calibration curve of mass flow controller using N2.	182	
Figure D.5 Calibration curve of GC-TCD analysis		

LIST OF SYMBOLS

A	Pre-exponential factor.
В	Half the maximum intensity (Full width half
	maximum)
b	Inert solids fraction of catalyst bed
С	The adsorbate constant
C_{Ab}	Gas phase concentration of component A
C_{AS}	Concentration of ethanol on the catalyst surface
C_D	Amorphous carbon percentage
C_p	Specific heat capacity of gases
C_{pg}	Specific heat capacity of feed gas mixture at constant
	pressure
C_{\propto}	Formation of carbon via hydrocarbon decomposition
C_{eta}	Formation of carbon via dissociation of CO
D	Dispersion
$D_{e\!f\!f}$	Effective diffusivity
D_g	Diffusivity
d_p	Average particle diameter
E_A	Activation energy
عبداعم	اونيۇرسىتى مليسيا Flow rate للطان
U h NIV	ERS Heat transfer coefficient AHANG
j _D	Colburn's mass transfer factor
k_c	Mass transfer coefficient
La	Size of crystallite
n_m	Number of molecules adsorbed
N	Avogadro's number
п	Reaction order
M_{ad}	Adsorbed molecular weight
Р	Pressure of gas
P_r	Prandtl number
P_s	Saturation pressure of adsorbed gas
R	Universal gas constant
R_t	Reactor tube radius

r	Rate of production
r _{exp}	Reaction rate
r_p	Actual radius
R_p	Catalyst particle radius
S_A	Total surface area of catalyst
S_C	Schmidt number
T_b	Boiling point
tads	Adsorbed layer thickness
U	Superficial gas velocity
V_a	Volume of gas adsorbed
W _{cat}	Weight of the catalyst
У	Mole fraction of component gases
λ	Wavelength
θ	Bragg angle
$ ho_b$	Bulk density of catalyst bed
$ ho_c$	Catalyst pellet density
$ ho_g$	Gas mixture density
σ_c	Constraction factor
μ_g	Viscosity of the gas mixture
سلطان عباصته	Catalyst pellet porosity
UNIVERSIT	Tortuosity YSIA PAHANG
A_{λ_p} -SUL	Thermal conductivity of catalyst pellet
З	Void fraction
ΔH	Heat of reaction
10	G'11 (

- ΔG Gibbs free energy
 - X Conversion
 - Y Yield

LIST OF ABBREVIATIONS

EDR	Ethanol Dry Reforming
ATR	Autothermal reforming
BET	Brunauer-Emmett-Teller
DME	Dimethyl ether
ESR	Ethanol steam reforming
EDX	Energy-dispersive X-ray
FTIR	Fourier-Transform Infrared
FTS	Fischer-Tropsch synthesis
MDR	Methane dry reforming
MT	Metric ton
MTBE	Methyl tert-butyl ether
GC	Gas chromatography
GHSV	Gas hourly space velocity
GTL	Gas to liquid
OD	Outer diameter
POX	Partial oxidation
SEM	Scanning electron microscopy
SR	Steam reforming
TCD	اونیور سیتے Thermal conductivity detector عبداللہ
TEM	UNIV Transmission electron microscopy HANG
TPR	A _ Temperature programmed reduction
TOS	Time on stream
TGA	Thermogravimetrics analysis
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
YSZ	Yttria-stabilized zirconia
WGS	Water gas shift reaction
SMR	Steam methane reforming
SWNT	Single walled-Nanotubes

LIST OF APPENDICES

APPENDIX A CALCULATION OF CATALYST PREPARATION	163
APPENDIX B TRANSPORT RESISTANCE CALCULATIONS	168
B.1 Resistance of External Mass Transfer	168
B.2 Internal (Intraparticle) Mass transfer Resistance	172
B.3 External Heat Transfer Resistance	173
B.4 Internal Heat Transfer Resistance	175
B.5 Effect of wall and Radial Heat Dispersion	176
APPENDIX C GRAPHS OF ISOTHERMAL ADOSRPTION FOR BET	
SURFACE ANALYSES.	178
C.1 Isothermal Adsorption of LaCuO ₃	178
C.2 Isothermal Adsorption of CeCuO ₃ MPSA	179
APPENDIX D CALIBRATION CURVE	180
D.1 Calibration Curve for Syringe Pump	180
D.2 Calibration Curve for Mass Flow Controller (MFC)	181
D.3 Calibration Curve of GC Analysis	

CHAPTER 1

INTRODUCTION

1.1 Overview

There is a growing interest in researching and developing alternatives to fossil fuels, driven by sustainability concerns related to their uncertain pricing, stock availability, and carbon credit (Lindsey, 2024). However, making a desperate choice between energy and the environment could potentially trigger a major economic crisis, especially if we are unprepared in terms of alternative resources or methods (Al Kez, Foley, Lowans, & Del Rio, 2024). The challenge lies in the fact that fossil fuels still account for about 90% of the world's energy supply. To mitigate the greenhouse effect and transition away from fossil fuel, suitable alternatives must be identified. These alternatives should not only address energy needs but also consider environmental impact. Finding a balance between energy security, economic stability, and environmental sustainability is crucial for our future. By investing in research, innovation, and responsible policies, we can work toward a cleaner and more sustainable energy landscape.

Syngas serves as an intermediate in various hydrocarbon synthesis reactions, including fuel production. It can be derived from both fossil and renewable resources. However, there is more attraction in producing syngas from renewable resources and greenhouse gases due to sustainability concerns. This shift is driven by global agreements such as the Paris agreement, which was signed by over 195 countries of the world in 2015 (Lokman, 2021). One promising renewable resource for syngas production is ethanol, which can be traditionally produced at a low cost through fermentation. Ethanol offers several advantages, including safety, ease of handling, storage, and transportation—qualities that surpass those of methane or methanol. However, there's a significant challenge: the reaction between the greenhouse gas carbon dioxide (CO₂) and ethanol is highly endothermic. The dry reforming reaction of ethanol (EDR) occurs at very high temperatures, typically starting from 550°C (Wei et al., 2020). Unfortunately, this extreme temperature range poses challenges for the catalysts used in EDR. These

catalysts are prone to deactivation due to sintering (agglomeration of particles) and carbon deposition resulting from undesired side reactions. In summary, while syngas production from renewable resources and greenhouse gases is attractive for sustainability reasons, addressing the endothermic nature of the EDR process and maintaining catalyst stability remain critical areas of research.

Noble metal-based catalysts can inhibit the formation of free carbon, but their prices are high and not suitable for mass use. Cobalt, nickel, and copper are common alternative metals for the reforming reaction catalysis owing to their comparable activity with the noble metal in terms of selectivity and yield (Dong Cao et al., 2018; Espitia-Sibaja, Muñoz, Moreno, & Molina, 2017). Nonetheless, the deactivation effect from sintering and carbon deposition is more severe on these less expensive metals. Mechanical strength and melting point can be an early indicator to the stability of the catalyst, which are cobalt and nickel. However, the stability is also contributed by the kind of support and method of the catalyst preparation. The structure of support is reportedly an essential factor to the activity and stability of these catalysts and thus no reports presented results of using solely copper, cobalt or nickel as the catalyst. Bahari, Fayaz, Ainirazali, Phuc, and Vo (2016); Bahari, Phuc, Abdullah, Alenazey, and Vo (2016) found that nickel and cobalt on alumina had high affinity to carbon and caused more carbon deposition in the EDR reaction at low temperatures. The conversion of reactants and selectivity of syngas are below 50% at above 900 K, but the conversion declined to 10% after 6 h due to sintering issue. Cu-based catalyst showed better result, which was 100% of ethanol conversion with 41-45% of hydrogen yield and carbon monoxide when the catalyst was supported by ceria, zirconia, (Cai et al., 2020; Dong Cao et al., 2018). This Cu-Ce-Zr oxide catalyst also showed better longevity based on the yields without a significant drop after 70 h on stream. Silica was tested by Bej, Bepari, Pradhan, and Neogi (2017) for supporting nickel and by T. Li, Li, Nginyo, Cai, and Yu (2023) for supporting cobalt. The test using Nisilica catalyst produced 100% of hydrogen yield and 34% of CO yield, while Co-silica catalyst use produced 68% and 58%, respectively. In terms of cost, copper price is half of nickel (Grace, 2023) and cobalt (Barrera, 2022) prices in the metal stock market making it a better option, deserving more attention. Other than these three metals, iron (Blanchard, Oudghiri-Hassani, Abatzoglou, Jankhah, & Gitzhofer, 2008), iridium (Hou, Lei, Zhang, Zhang, & Cai, 2015) and rhodium (Shulin Zhao, 2017) were also tested with

supports but their activity was not comparable to that of the Cu-based and Ni-based catalysts.

Lanthanum cost is two times the price of cerium (ISE, 2024) and was studied in the EDR reaction with nickel supported by alumina via impregnation method but the activity was not as high and sustained as using Cu-based catalysts (Bahari, Fayaz, et al., 2016). This rare earth could also form perovskites with nickel in methane dry reforming using citric the sol-gel method, which was the most preferable to prepare a strong catalyst (Dingshan Cao et al., 2023). Generally, a perovskite is mixed oxides (ABO₃) structure that is typically known with various A- and B- site ions. This structure can possess captivating redox properties to maximise dispersion of nano-scale metal particles in a reducing environment, thereby promoting better catalyst activity and inhibiting carbon deposition on the surface of the catalyst (Moogi et al., 2022), especially from transition metal elements. Hence, lanthanum has the potential to form an oxidation state and oxygen vacancies with copper based on what have been mixed in a preparation.

Production of CO can be increased by promoting more oxidative metals from alkaline metal like yttrium and potassium. Świrk, Motak, Grzybek, Rønning, and Costa (2019) found that 0.2 and 0.4 wt% loading of yttrium to the layered double hydroxide Ni/Al/Mg could convert 84% methane and 87% CO₂ and decreased H₂/CO in the methane dry reforming reaction. This selectivity of more CO was also reported in LaNiO₃ that was substituted with potassium in the carbon dioxide dehydrogenation reaction. Nevertheless, the addition may be less than 30 wt% to avoid issue with mechanical strength of the catalyst (Tsounis et al., 2020). This study investigates the preparation, characterization, kinetics and longevity of the A_{1-x}B_xCuO₃ where A will be lanthanum or cerium and B will be yttrium or potassium. The laboratory work will commence with zero x where A is selected from lanthanum and cerium that shows the best performance.

1.2 Problem Statement

The EDR reaction necessarily runs at high temperature, and this may deactivate catalysts, especially the alternatives to noble catalyst which are cobalt, nickel, and copper, due to sintering and carbon deposition. Many supports and promoters were used to increase stability and reduce free carbon formation such as zinc oxide (M. Wang, Li, Tian, Zhang, & Cai, 2024), alumina (Fayaz, He, Goel, Rintala, & Konttinen, 2023) and

silica (T. Li et al., 2023). The conversion of ethanol was generally 100% at 1023 K, but the longevity was only sustained for 1, 8 and 40 h using the feed flow rate of 14, 42 and 65 L.gcat⁻¹h⁻¹, respectively. Copper showed the best catalysis results with cerium and zirconium supports in the perovskite structure (Cai et al., 2020). Other than cerium, lanthanum is another rare earth that was studied extensively in other reforming reactions such as steam reforming of many organic compounds and dry reforming of methane because it is two times cheaper than cerium (ISE, 2024). Lanthanum was proven to reduce carbon deposition better (Bahari, Fayaz, et al., 2016) and the presence of carbon nanotube or nanofilament during the reaction within the perovskite structure was believed to be the reduction factor of carbon deposition (Luo et al., 2015). Lanthanum-promoted catalysts additionally showed excellent stability without significant deactivation in dry reforming of methane after 55 h (Fouzia Touahra, Chebout, Lerari, Halliche, & Bachari, 2019) and insignificant sintering, as shown by the absence of water side product from any water gas shift reaction (Dingshan Cao et al., 2023). The selection of reaction temperature studied previously ranged between 750 to 1100 K were crucial in getting high conversion, selectivity, and yield without jeopardizing the stability of the catalyst (M. Wang et al., 2024). Cu-based perovskites can be incorporated in ABO₃ structure with rare earth metal, such as lanthanum and cerium to have high oxygen mobility and capture CO₂. Promotion with alkaline or transition metals like potassium and yttrium, respectively may additionally improve carbon deposit reduction and selective towards high H₂/CO ratio. Carbon deposition decreased in the O₂-enhanced dry reforming of methane and the catalyst became more stable when 0.25 wt% was added to NiCo-NiAl₂O₄ nanocatalyst (Sajjadi, Haghighi, & Eshghi, 2019). CO₂ hydrogenation was believed to follow the dry reforming of methane when 0.4 wt% yttrium was added to a Ni-based layered catalyst (Swirk et al., 2019) while. All these promotions are new approaches in the EDR reaction and worth equal attention for achieving high selectivity, yield and longevity at a lower cost.

1.3 **Objectives of Research**

The objectives of this research are: -

1. To prepare, characterize and select trioxide perovskite catalyst from lanthanum, cerium and copper oxides and the subsequent complex perovskite promoted by yttrium and potassium that is more stable and has low carbon deposition.

- 2. To investigate the effect of feed ratios and reaction temperatures on product yields, H₂/CO ratios, and reactant conversions of the catalyst samples.
- 3. To evaluate longevity and the kinetics of the EDR reaction based on power law model and Langmuir-Hinshelwood models for the perovskite catalyst.

1.4 Scope of Study

The scopes of research based on the objectives of the study are as follows: -

Objective 1

- The catalyst sample was prepared by sol-gel method using citric acid in the molar ratio of 1:2 based on metal element and citric acid. The method was proposed by Abdel-Latif, Ismail, Bouzid, and Al-Hajry (2015) where the sol-gel was dried under 120°C for 24 h and subsequently calcined at 800°C for 5 h.
- The catalyst samples were characterized by using XRD, TPR, SEM, TEM, FTIR, XPS and BET methods. The details of equipment and method are presented in Methodology.

Objective 2

- The feed compositions were varied from 1:2.5 to 2.5:1 based on partial pressures of ethanol and CO₂ from 20 to 70 kPa at reaction temperature ranged between 923 and 1023 K. عالم المناطان عند المناطن عند المناطن عند المناطن ا
- 2. The high gas hourly space velocity, $GHSV = 42 L \text{ gcat}^{-1} \text{ h}^{-1}$ was used to eliminate the factor of mass transfer limitation in a fixed-bed reactor.
- 3. The samples were analysed by using gas chromatography equipment that was equipped with thermal conductivity detector.

Objective 3

1. Kinetics of the EDR reaction was modelled based on power law and Langmuir-Hinshelwood mechanism on the best perovskite catalyst.

1.5 Thesis organization

Thesis consists of 7 chapters as follows: -

Chapter 1 The overview, problem statement, objective, and scope of the study. The outline of the thesis also described in this chapter.

Chapter 2 The overview of global CO₂ emissions, syngas and ethanol as a renewable energy resource. the importance of reforming techniques in syngas production. The detail explanation basics of perovskite and the EDR techniques. Finally, the literature reviews on ethanol dry reforming, La, Ce, Cu, Y and K studied in the perovskite catalysts. The brief explanation about the coke formation, catalysts deactivation and sintering. In extension with kinetic study (i.e., Power law and Langmuir-Hinshelwood models).

Chapter 3 gives in detail of the materials used in this work followed by experimental methodology in which brief about the preparation of copper-based perovskites and promoted cu-based perovskites by using sol-gel method. The experimental setup of EDR was explained through the schematic diagram for conducting the experiments at various operating temperatures on a fixed bed reactor. The chapter ends with conditioning the reaction parameter to be free of mass and heat transfer limitation.

Chapter 4 The comparison study between LaCuO₃ and CeCuO₃ catalysts, the evaluation of catalytic activity by varying the reaction temperature, effect of reactant partial pressures, the fresh and spent characterization.

Chapter 5 Furtherly, promoted with Y and K on LaCuO₃ catalysts with effect of reaction temperatures and various promoter loading. Furtherly, Longevity tests of selective catalysts were illustrated in this chapter.

Chapter 6 In this reveals the information regarding the kinetic study (i.e., Langmuir-Hinshelwood model) and reaction mechanism (i.e., Power law model) of the copper based perovskites were used for EDR.

Chapter 7 contains the recommendations for further studies and general conclusions which are obtained in this research study.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

Syngas can be produced from renewable resources or waste and thus serve as an intermediate for alternative energy sources. This chapter provides a literature review on several aspects of dry reforming technology, which utilizes heterogeneous catalysts to produce syngas. The discussion evaluates the necessity of the present study to avoid redundancy and aims to develop necessary information to interpret research results. Additionally, the approaches of previous experiments are compared to design appropriate methods of the study.

The discussion of fossil fuel problems will be initially presented, briefly outlined the current scenario and stock trends. The use of syngas as an energy feedstock is subsequently discussed, including the techniques applied to produce the syngas. Ethanol is considered a potential feedstock for the syngas production, indirectly serving as an alternative to fossil fuels. In the 6th subchapter, the dry reforming of ethanol and carbon dioxide is discussed as a method to produce syngas. Next, catalysts for dry reforming are explored, with a focus on the perovskite catalyst. The discussion also covers catalyst promotion and deactivation. The following chapter delves into possible models that will be used to capture reaction data. This chapter is concluded with an explanation of the research gap from the critical review of the existing reports and the concept of experimental work in the subsequent chapter.

2.2 Pursuit of Clean Energy

Clean energy refers to renewable resource and environmentally friendly fuels (Babayomi, Dahoro, & Zhang, 2022). A 1.3% increase in energy consumption was reported in 2021, with 84% of that contributed by three fossil fuels: oil, natural gas, and coal (Tryggestad, 2022). As seen in Figure 2.1, most of the energy consumption is comes from oil (31.2%). The remaining global energy consumption is distributed among coal

(27.2%), natural gas (24.7%), hydropower (6.9%), renewables (5.7%) and nuclear power (4.3%). A similar trend is reflected in the BP statistics report for 2021, where 86% of world primary energy consumption is attributed to fossil fuels. Additionally, fossil fuels serve as feedstock for producing rubber, plastics, cloth and lubricants.



□ Oil □ Natural Gas □ Coal □ Nuclear energy □ Hydroelectric □ Renewables

Figure 2.1 Global primary energy consumption in 2021

Source: Tryggestad (2022)

The increment of non-renewable fuel consumption is also reflected in the rise of carbon dioxide emissions, as shown in Figure 2.2. Methane (CH4) and carbon dioxide (CO₂) constitute a major portion of greenhouse gases, which play a crucial role in climate change (Winter, Meys, Sternberg, & Bardow, 2022). The pursuit of clean energy and alternative feedstocks is essential to mitigate these carbon-credit components. Initiatives aimed at reducing carbon emissions are commonly discussed among developed countries. However, seeking clean fuels and syngas in developing nations presents additional challenges due to the unsystematic socioeconomics of their communities (Babayomi et al., 2022).



Figure 2.2 Global emission of CO_2 from fossil fuels until 2020

Source: Friedlingstein et al. (2022)

Renewable energy used as an energy source in the U. S. has steadily increased at about 50 % per year since 2000. In 2021, approximately 14 Quadrillion BTUs of renewable energy were utilized (Dunn et al., 2022). Strong energy policies drive green technology innovation for generating renewable energy, and further efforts are needed to ensure that these fuels are sustainable, clean, and safe. Various renewable energy resources are available, and their selection is influenced factors such availability and cost. Ethanol is one such resource, as it can be produced through the fermentation of sugar-contained biomass or food on a large scale, dating back to earlier times.

2.3 Ethanol Feedstock

Ethanol is a primary alcohol with two carbons. It serves as a potential fuel for fuels cells and vehicles due to its natural availability, renewability, and low toxicity, making it a viable alternative to hydrocarbons. Ethanol is typically produced in two routes: fermentation of sugars derived from various biomass resources such as corn, wheat, sugarcane etc. and hydration of ethylene. Notably, approximately 33,000 metric tons per day of solid biomass in Malaysia was generated from palm oil industries, which could potentially serve as valuable feedstock for ethanol production (Rashidi, Chai, & Yusup, 2022).

In industries, ethanol serves as a key raw material in pharmaceuticals, detergents, cosmetics, disinfectants, inks, odour agents, and coating additives, making a significant contribution to the food and beverage industries (Blanchard et al., 2008). Additionally, ethanol is used to produce organic chemicals and hydrocarbon-based products like ethyl esters, ethyl acetate, monomers, ethylene and ethyl amines (Takahara, Saito, Inaba, & Murata, 2005). As a substitute to gasoline, it boasts a high octane number of 108, which prevents engine knocking and provides excellent flammability (Aditiya et al., 2016). Despite its relatively low energy content, ethanol results in lower emission of toxic substances in exhaust gas due to high oxygen availability. Consequently, it contributes to reducing CO₂ emission by up to 80%, promoting a cleaner environment for the future (Krylova, Kozyukov, & Lapidus, 2008). Recent studies highlight that ethanol can be a practical alternative for fuel production through reforming technologies due to surplus availability, renewability, easy storage, less toxicity and high hydrogen content (Siang et al., 2020).

2.4 Syngas Production

Syngas aka synthesis gas, is composed of H₂ and CO. Most of the applications for syngas are depicted in a schematic diagram in Figure 2.3. Syngas is primarily used for generating electricity through combustion or electrochemical reaction in fuel cells. Additionally, it finds use in refineries to produce other chemicals, including fertilizer, fuels, wax, and paraffin, via the Fischer-Tropsch synthesis (FTS). Furthermore, syngas contributes to the production of petrochemicals such as dimethyl ether (DME) and methyl tert-butyl ether (MTBE) through various reactions. The FTS process involves three steps: syngas production via the reforming of natural gas, catalytic FTS reaction and cracking (Wood, Nwaoha, & Towler, 2012). Currently, several companies like Petronas, shell, Sosal and Chevron are actively working to establish the FTS plants around the globe.



Source: Hernández et al. (2017).

Syngas can be obtained from natural gas (Nichele, Signoretto, Menegazzo, Rossetti, & Cruciani, 2014) or derivatives from biomass decomposition or valorisation of waste with greenhouse gases (Law & Foo, 2023). Biomass decomposition generally involves gasification or reforming of organic wastes, oil products and biomass. The most studied synthesis route for clean syngas generation is dry reforming, which utilizes both greenhouse gases – methane and carbon dioxide (Usman & Daud, 2015). Other reactions involved in syngas production include steam reforming, partial oxidation and autothermal reforming. The following sections will provide brief explanation of these reaction routes and catalysts involved, using ethanol as the feedstock.

2.4.1 Steam Reforming

Reactions that are normally involved in the steam reforming of ethanol are shown in Equations (2.1). Ethanol steam reforming (ESR) usually took place at high temperatures i.e. 823 - 1073 K and high heat capacity of water requires great amount of energy to produce the syngas at those temperatures (Navarro Yerga et al., 2011). Nickel-based catalysts are favourable in steam reforming reaction because of its activity and selectivity of CO₂ and H₂ (Anil, Indraja, Singh, Appari, & Roy, 2022). However, water gas shift

reaction, as expressed in Equation (2.2), will consume carbon monoxide and increase H_2 /CO ratio. The syngas will turn to hydrogen product and carbon dioxide as expressed by Equation (2.3).

$$C_2H_5OH + H_2O \leftrightarrow 4 H_2 + 2 CO \quad \Delta H_{298 K}^{\circ} = + 347.4 \text{ kJ mol}^{-1}$$
 (2.1)

$$CO + H_2O \leftrightarrow H_2 + CO_2$$
 (2.2)

$$C_2H_5OH + 3 H_2O \leftrightarrow 6 H_2 + 2 CO_2 \qquad \Delta H^{\circ}_{298 K} = +207.8 \text{ kJ mol}^{-1}$$
 (2.3)

The other side reactions are usually decomposition, dehydration, dehydrogenation and coking (Furtado, Alonso, Cantão, & Fernandes-Machado, 2009). The main issue with catalyst deactivation is deposition of carbon from product of side reactions (Anil et al., 2022). Carbon encapsulated metal particles at temperatures lower than 500°C. The carbon might form filamentous coke at temperatures higher than 450°C via the Boudouard reaction. This reaction normally occurs on Ni, Co and Fe-based catalysts (Bolívar Caballero, Zaini, & Yang, 2022).

Syngas can be produced from the partial oxidation reaction of ethanol, as shown in Equation (2.4). Ni, Co, Ru, Rh and Pt were among noble and non-noble metals tested as the catalysts at various reaction conditions (Salge, Deluga, & Schmidt, 2005; Tóth et al., 2016). However, the partial oxidation of ethanol process was not attractive as other catalytic reforming processes due to its high cost and low selectivity. In this process, complete oxidation and decomposition occur simultaneously, resulting in the production carbon dioxide, water and free carbon (Z. Wang, Dai, & Wang, 2022).

$$C_2H_5OH + 0.5 O_2 \leftrightarrow 3 H_2 + 2 CO \quad \Delta H_{298K}^{\circ} = +14 \text{ kJ mol}^{-1}$$
 (2.4)

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2.4.3 Autothermal reforming

2.4.2 Partial Oxidation

Autothermal reforming (ATR) or oxidative steam reforming of ethanol combines steam reforming and partial oxidation in a reaction as expressed by Equation (2.5) (Ni, Leung, & Leung, 2007). Catalyst materials and the way they were prepared affected their activity and strength in synergizing energy during the reaction, while the selectivity of the hydrogen was high (Baruah, Dixit, Basarkar, Parikh, & Bhargav, 2015).

$$C_2H_5OH + 2H_2O + 0.5O_2 \leftrightarrow 5H_2 + 2CO_2 \qquad \Delta H_{298K}^{\circ} = -50 \text{ kJ mol}^{-1}$$
 (2.5)

Studies of ethanol ATR were reported using noble and non-noble metal-based catalysts such as Ir coated on CeO₂ by precipitation (Cai et al., 2020; L. Chen et al., 2010), Rh impregnated on Al₂O₃ (Gutierrez, Karinen, Airaksinen, Kaila, & Krause, 2011), Pt/CeO₂ incipient wetness impregnated on SiO₂ (Cifuentes, Hernández, Monsalve, & Cobo, 2016), Ni impregnated on CeO₂ (H.-H. Huang, Yu, Chuang, & Wang, 2014; Palma, Ruocco, Meloni, & Ricca, 2017), Cu emulsion technique with ZnO (Agrell, Boutonnet, & Fierro, 2003), Co incipient wetness impregnated on CNF (da Silva et al., 2011), Ni-Cu impregnated on Al₂O₃ (Furtado et al., 2009) and Rh-Ce impregnated on ZnO (Duan, Yuan, & Yu, 2011). Compared to partial oxidation and steam reforming processes, autothermal reforming offers several advantages, including relatively low reaction temperature which is 673-773 K, high H₂ production, and low capital and operating costs. However, it also has some disadvantages, such as the side product of CO_2 , greenhouse gas emission when the H_2/CO ratio was less than 2, and a high risk of explosion due to subsistence of O2 in the process complete combustion reaction (Bahari, Phuc, et al., 2016). IVERSITI MALAYSIA PAHANG -SULTAN ABDULLAH

The difficulty to optimize the reaction conditions and reduce carbon deposition leads to complete oxidation and steam reforming. Although energy consumption is minimal, H₂/CO ratio is high and not suitable for syngas production because low yield of carbon monoxide (Kugai, Subramani, Song, Engelhard, & Chin, 2006).

2.4.4 Dry Reforming

Dry reforming refers to the reaction of an organic chemical with CO_2 to produce H_2 and CO. The common organic chemical feedstocks used in the dry reforming reaction are methane (Ginsburg, Piña, El Solh, & De Lasa, 2005), glycerol (C.-H. Wang et al., 2011), butanol and ethanol (Fayaz et al., 2016) as shown in Equations (2.6), (2.7), (2.8) and (2.9), respectively.
$$CH_4 + CO_2 \leftrightarrow 2 H_2 + 2 CO$$
 (2.6)

 $C_{3}H_{8}O_{3} + CO_{2} \leftrightarrow 3 H_{2} + 4 CO + H_{2}O$ (2.7)

 $C_{4}H_{9}OH + 3 CO_{2} \leftrightarrow 5 H_{2} + 7 CO$ (2.8)

$$C_2H_5OH + CO_2 \leftrightarrow 3 H_2 + 3 CO$$
(2.9)

Various noble and non-noble metals supported by many structures were tested and the major hinderance to the dry reforming reaction methane, ethanol, butanol and glycerol were catalyst deactivation (Cai et al., 2020; Kim et al., 2020; Palo, Dagle, & Holladay, 2007).

The advantages and disadvantages of reforming reactions are summarized in Table 2.1. This comparison is based on syngas production, which include CO and not only hydrogen production. Reforming reactions that are involved with steam would have high hydrogen yield, thus the H₂/CO ratios higher than 2. Partial oxidation is also the same. Thus, they are not favourable for the syngas production even though the reaction temperature is low for autothermal reformation and partial oxidation. In terms of catalyst, all reactions had the same problem, which are deactivation of the catalyst through sintering due to high reaction temperatures and carbon deposition from undesired reactions that produce free carbon and polymeric carbon. Bolívar Caballero et al. (2022) stated that these two conditions are usually conflicting each where the free carbon will be more when the reaction temperature is low. Therefore, a compromising reaction temperature should be determined so that both negative effects can be minimized.

Reaction	Advantages	Disadvantages		
Steam	Low free carbon formation	High H ₂ /CO ratio and high		
Reforming		reaction temperature		
Autothermal	Low reaction temperature	Instable product distribution		
Reforming		between H ₂ , CO and CO ₂		
Partial	High yield of hydrogen and low	Low CO yield		
Oxidation	reaction temperature			
Dry	H_2/CO ratio < 2, thus favourable	High reaction temperature, prone		
Reforming	for Fischer-Tropsch Synthesis	to catalyst deactivation (more		
		carbon formation) and sintering		

Table 2.1 Advantages and disadvantages of reaction processes for syngas production

Source: Bolívar Caballero et al. (2022)

The primary limitation of the ethanol dry reforming (EDR) reaction lies in catalyst deactivation due to the formation of free carbon on the catalyst's surface, resulting in a graphite or filamentous structure. C.-H. Wang et al. (2011); F. Wang et al. (2009) reported that parallel reactions occurred simultaneously with the EDR reaction, including decomposition and dehydrogenation reactions (as shown in Equations (2.10) and (2.11)), leading to the formation of carbonaceous products such as CH₃CHO, CO, and CH₄.

$$C_{2}H_{5}OH \rightarrow CH_{3}CHO + H_{2} \quad \Delta H_{298 K}^{\circ} = 296.7 \text{ kJ mol}^{-1} \text{ AG}$$

$$C_{2}H_{5}OH \rightarrow CH_{4} + CO + H_{2} \quad \Delta H_{298 K}^{\circ} = 49.0 \text{ kJ mol}^{-1}$$
(2.10)
(2.11)

In addition, disassociation reaction undergoes internally based on Equations (2.12) and (2.13) forming H_2 and CO.

$$CH_{3}CHO \rightarrow CH_{4} + CO \quad \Delta H^{\circ}_{298 K} = -18.9 \text{ kJ mol}^{-1}$$

$$(2.12)$$

CH₃CHO + CO₂ → 2H₂ + 3 CO
$$\Delta H_{298 K}^{\circ}$$
 = -186.3 kJ mol⁻¹ (2.13)

Water gas shift and decomposition reaction likely occur to produce hydrogen, water and free carbon as shown in Equations (2.14) and 2.15).

$$\operatorname{CO} + \operatorname{H}_2\operatorname{O} \rightleftharpoons \operatorname{CO}_2 + \operatorname{H}_2 \quad \Delta H_{298\,K}^{\circ} = 41.2 \text{ kJ mol}^{-1}$$
 (2.14)

$$CH_3CH_2OH \rightarrow 2C + 2H_2 + H_2O$$
 $\Delta H_{298 K}^{\circ} = 75.0 \text{ kJ mol}^{-1}$ 2.15)

The free carbon can also be formed from carbon monoxide through decomposition as shown in Equations (2.16).

$$2 \text{ CO} \rightarrow \text{C} + \text{CO}_2 \ \Delta H^{\circ}_{298 K} = -171.0 \text{ kJ mol}^{-1}$$
 (2.16)

EDR reaction studies were conducted using several metal oxide catalysts under various conditions. From the thermodynamic analysis, the reaction is possible to yield 51% of each syngas product (Kale & Gaikwad, 2014a). Table 2.2 shows the summary of the EDR studies from 2005 to 2024. Comparisons of EDR results between the reports cannot be simply made because of different flow, feedstock ratio and reaction temperatures. Various range of the CO₂:ethanol ratios were used. Twelve reports, which are 4 - 7, 11 - 15, 17, 19 and 21, only employed the stoichiometric ratio of 1:1 whereas the others' ratios are either in the ranges of CO₂ excess (the highest ratio is 2.5:1) or ethanol excess (the highest ratio is 0.5/2). Nine of them could achieve 100% of ethanol conversion. All the reports in the table stated that ethanol is the limiting reactant, while carbon dioxide was the excess reactant and the EDR reaction underwent with catalysts.

The excess carbon dioxide portion employed for non-noble metal was used in the studies, indicating that cheap non-noble metals have the potential to be active catalysts for the EDR reaction. Earlier, iron was used as the catalyst in the form of stainless steel and carbon steel (Blanchard et al., 2008; De Oliveira-Vigier, Abatzoglou, & Gitzhofer, 2005). The advantage of using steel was its consistent activity in several runs after regeneration, removing carbon nanofilament using steam. However, the iron-based catalysts had low surface area and thus low yield of hydrogen and carbon monoxide. Nickel impregnated on supports like SBA-15, zirconia, alumina and perovskite was mostly studied due to its wide use in steam reforming processes. In the case of EDR, the yields of hydrogen and carbon monoxide were reported from 32 to 100% and from 14 to 40%, respectively, under the reaction temperatures of 872 to 1073 K. Eight reports stated wet impregnation as the preferred method to prepare the catalysts. Sintering was a common issue with nickel-based catalysts when the reaction was conducted at temperatures higher than 700°C, even though the ratio of carbon dioxide to ethanol was

low, spanning from 5 to 0.4. The flow rate of feed containing carbon dioxide, ethanol, and inert gas was mostly employed in continuous mode during a specific test period. Four of them used a gas hourly specific velocity (GHSV) of 42 L/gcat/h, while four others used 10 L/gcat/h. The highest conversion of ethanol was achieved by the works of Bahari, Fayaz, et al. (2016) using the 3%La/10%Ni/Al₂O₃ catalyst, which reached 45.5%.

The results of number 6, 11, 15 and 17 in Table 2.2 were from the studies employing copper-based catalysts and they are all reporting 100% of ethanol conversion. However, this was probably due to relatively low flow rate of feed, which was 10 L/gcat/h. If the Damköhler number, the dimensionless number for expressing the performance of a reactor, is calculated, the performance of the synthesis can be the same. The flow rate that was 4 times lower than of nickel-based catalyst results made time-on-stream (TOS) 9 times longer than that of the nickel-based catalysts using the same reaction temperatures and feed ratios. Nevertheless, these results indicate that copper could be an active catalyst like cobalt and nickel in catalysing the EDR reaction. Although copper has mechanical strength and melting point lower than nickel and cobalt, support it with cerium and zirconium in the perovskite structure might have made them same. Based on the affiliation of the authors, all the four papers are from the same group of research testing copper with cerium and zirconium promoter and supports.

Lanthanum is another favourable rare earth and it is two times cheaper than almost all variants of cerium product (ISE, 2024). From a topography of the SEM-EDX image, nickel could be dispersed to a few nanometres of crystal size on alumina support promoted with lanthana. Thus, the longevity of La-Ni/alumina was evidenced in 8 h on stream, which was better than cerium-promoted catalyst using the same catalyst preparation method (Bahari, Fayaz, et al., 2016). The ethanol conversion using that Lapromoted catalyst was 44% using 42 L/gcat/h of GHSV, which was close to the theoretical value based on the thermodynamic and simulation study conducted by López Ortiz, Pallares Sámano, Meléndez Zaragoza, and Collins-Martínez (2015) using calcium oxide, which has the same alkalinity to lanthana (Greenwood & Earnshaw, 1997). Nevertheless, a comparison of both favourite rare earth metals are probably needed in other catalyst studies using different preparation methods since the active non-noble metal like copper not only relies on the material but the structure of a catalyst support (M. Wang et al., 2024).

				Reaction condition	ons		Results	
No	Catalyst	Preparation	CO2:C2H5	T(K)/ TOS (h)	GHSV		H ₂ , CO and CH ₄	References
		methods	ОН		$(Lg_{cat}-^{1}h^{-1})$	Conversions	yields/selectivity	
1.	SS316	NA	1:3	773-873 /8	40,000	$C_2H_5OH =$	$Y_{H2} = 2.5-98\%;$	(De Oliveira-
						57-86%	$Y_{CO} = NA$	Vigier et al.,
								2005)
2.	Carbon steel	NA	1:3	823/4	2.3	C ₂ H ₅ OH=	$Y_{H2} = 53.5\%; Y_{CO}$	(Blanchard et
						100%; CO ₂ =	= 30%	al., 2008)
						26%		
3.	Ni/Al ₂ O ₃	Wet	1:5	873 1073/205/	NA	$C_2H_5OH =$	NA	(Hu & Lu,
		Impregnation				96.4 - 98.9		2009)
						%; CO ₂ =		
		الله	طان عبد	با قهعُ السا	تے ملبس	21.1 %		
4.	5%Ni/SBA-15	Wet		823-1073/24	15594	$CO_2 = 13\%$	$Y_{H2} = 40\%; Y_{CO} =$	(Xusheng Wu,
		Impregnation					40%	2009)
5.	Ni/Y ₂ O ₃ -ZrO ₂	Wet	- 7 .1 U	873-1073/6	NA	$C_2H_5OH =$	NA	(Bellido,
		Impregnation				80-100%;		Tanabe, &
						$CO_2 = 61\%$		Assaf, 2009)

Table 2.2 Synopsis of earlier studies in the EDR reactions.

Table 2.2 Continued

				Reaction condition	ons		Results	
No	Catalyst	Preparation methods	CO ₂ :C ₂ H ₅	T(K)/ TOS (h)	GHSV	Gamming	H ₂ , CO and CH ₄	References
			OH		(Lg _{cat} -'h'')	Conversions	yields/selectivity	
6.	$Cu/Ce_{0.8}Zr_{0.2}O_2$	Co	1:1	1073/90	10	$C_2H_5OH =$	$Y_{H2}=45\%$	(Y. Cao, Zhu,
		precipitation				100%	$Y_{CO} = 40\%$	Qiu, Pang, & Ji,
								2012)
7.	2% Ir/CeO ₂	Deposition –	1:1	723-973/72	4.5	$C_2H_5OH =$	$Y_{H2} = 43\%; Y_{CO} =$	(Hou et al.,
		precipitation				90-100%;	48%	2015)
8.	3%Со	Wet	2.5:1-1:2.5	923-973/ 8	42	$C_2H_5OH =$	$Y_{H2} = 24.5\% Y_{CO}$	(Bahari, Fayaz,
	10%Ni/Al ₂ O _{3,}	Impregnation		IIMDS		44%; CO ₂ =	= 14%	et al., 2016)
	3%Се-			UMI-S/		34.5%		
	10%Ni/Al ₂ O ₃							
	and 3%La-	N. J.						
	10%Ni/Al ₂ O ₂	الله	طان عبد	يا فهغ السا	تى مليس	اونيۆرسىي		
0	N:0/S:0	Cal and	V05-BS		VSIA		V = 1000/	(Dei et el
9.	N10/S10 ₂ -	Sol-gel	0.5:2	1123/10	NA	$C_2H_5OH = C_2H_5OH$	$Y_{H2} = 100\%$	(Bej et al.,
	Al_2O_3	method	-5UI	LIAN A	RDU	96%; CO ₂ =		2017)
						76%		

Table 2.2 Continued

				Reaction condition	ons		Results	
No	Catalyst	Preparation	CO2:C2H5	T(K)/ TOS (h)	GHSV	~ .	H ₂ , CO and CH ₄	References
		methous	ОН		(Lg _{cat} - ¹ h ⁻¹)	Conversions	yields/selectivity	
10.	Rh/CeO ₂	Deposition –	2.5:1 -	973/65	NA	$C_2H_5OH =$	NA	(Shulin Zhao,
		precipitation	1:2.5			100%; CO ₂		2017)
						= 65%		
11.	Cu/Ce _{0.8} Zr _{0.2} O ₂	Facile co-	1:1	723–1073/90	10	$C_2H_5OH =$	$Y_{H2} = 41\%$	(Dong Cao et
		precipitation				100%	$Y_{CO} = 40 - 36\%$	al., 2017)
							$Y_{CH4} = 17 - 21\%$	
12.	NiO/SiO ₂	Sol-gel	1:2 - 2:1	723–1123/10	2.34	$C_2H_5OH =$	$Y_{H2} = 100\%$	(Bej et al.,
				Unit O		90-98%	$Y_{CO}=34\%$	2017)
						$CO_2 = 71-$		
				t . ti 5 . 5 1 .		77%		
13.	Rh/CeO ₂	Incipient	1:1	773/28	NA 🥥	$C_2H_5OH =$	$Y_{H2} = 40\%$	(Samsudeen,
		Wetness	IVERS	ITI MALA	YSIA F	50%; CO ₂ =	$Y_{CO} = 45\%$	Ahmed, Yahya,
		impregnation	-SUI	LTAN A	BDU	12%		Ahmed, &
								Anis, 2018)
14.	Ir/Ce _{0.75} Zr _{0.25} O ₂	Со	1:1	1073/90	10	$C_2H_5OH =$	$Y_{H2} = 49\%$	(Qu et al., 2018)
		precipitation				100%;	$Y_{CO} = 35\%$	

			Reaction conditions				Results	
No	Catalyst	Preparation	CO2:C2H5	T(K)/ TOS	GHSV		H ₂ , CO and CH ₄	References
		methods	OH	(h)	$(Lg_{cat}-^{1}h^{-1})$	Conversions	yields/selectivity	
15.	Cu/CeO ₂ -ZrO ₂	Co-	1:1	873-1073/90	10	CH ₃ OH =	$S_{\rm H2} = 65\text{-}40\%$	(Dong Cao et
		precipitation				100%	$S_{CO} = 15-47\%$	al., 2018)
							$S_{CH4} = 5\text{-}26\%$	
16.	Ni/KIT-6	Facile	1:2 - 2:1	673-973/40	40	$C_2H_5OH =$	$Y_{H2} = 46-51\%$	(Wei et al.,
		methanol-	Higher ratio			90-93%	$Y_{CO} = 27-45\%$	2020)
		assisted co-	higher X			$CO_2 = 0-21\%$	$Y_{CH4} = 20-16\%$	
		impregnation		UMPS	Δ			
17.	Cu-Ce _{0.8} Zr _{0.2} O ₂	Microwave-	1:1	723-1023/50	14, 24 and	$C_2H_5OH =$	$S_{\rm H2} = 36\text{-}38\%$	(Cai et al.,
		assisted co-			29	40-100%	$S_{CO}=31\text{-}34\%$	2020)
		precipitation	in the		to		$S_{CH4} = 21-27\%$	
18.	5 wt%	Impregnation	1:2-1:3	873-	NA	$C_2H_5OH =$	$Y_{H2} = 20-65\%$	(Arapova et
	Ni/Ce _{0.75} Zr _{0.25-}	and	IVERSI	1023/0.167	YSIA F	PAHANG	$Y_{CO2} = 25-80\%$	al., 2021)
	x(Nb,Ti)xO2-δ	solvothermal	SUL	TAN A	BDU	LLAH	$Y_{CH4} = 1-0.3\%$	

Table 2.2 Continued

]	Reaction conditions			Results	
No	Catalyst	Preparation	CO2:C2H5	T(K)/ TOS	GHSV		H ₂ , CO and CH ₄	References
		metnods	ОН	(h)	(Lg _{cat} - ¹ h ⁻¹)	Conversions	yields/selectivity	
19.	Co@SiO ₂	Stöber method	1:1	773-1023/40	65	$C_2H_5OH =$	$S_{H2}=50\%$	(T. Li et al.,
						100%	$S_{CO}=50\%$	2023)
						$CO_2 = 32-$		
						23%		
20.	15%Co/Al ₂ O ₃	Wet	1:3:1(O ₂)	773-973/8	42	$C_2H_5OH =$	$Y_{H2} = 16-68\%$	(Fayaz et al.,
		impregnation				24-94%	$Y_{CO} = 14-58\%$	2023)
						$CO_2 = 17-$		
						53%		
21.	Co(Ni)/ZnO	Co-	1.1	773-973	14	$C_2H_5OH =$	$H_2 = 75 - 35\%$	(M. Wang et
		precipitation	لطان عبا	با فهع الس	تي مليسب	100%, CO ₂ = 26-75%	CO = 43 - 55%	al., 2024)
		UN	IVERSI	TI MALA	YSIA F	AHANG		
		AL	SUL	TAN A	ABDU	LLAH		

2.5 Perovskite

Mineral perovskite (CaTiO₃) was first invented in the year 1839 by Gustav Rose (mineralogist and German chemist), named by Russian dignitary "Lev Alexeievinch Perovsky". Perovskites are used for many compounds produced through synthetic and natural routes, and they typically have the structure of ABX₃ (Badini, Saracco, Serra, & Specchia, 1998). The synthetic perovskites were formulated by V.M. Goldschmidt, who developed the principal of tolerance factor (Bhalla, Guo, & Roy, 2000). The perovskite structure exhibits great flexibility in metal oxide composition, especially with low-cost ones. It consists of a three-dimensional array of corner-shared octahedra, separated by layers of cations. Charges within the framework allow for subtle distortions, easing bond strains and competing within stoichiometric structures (Bilal & Jackson, 2013). Perovskites exhibit various properties that influences the structure, including factors like symmetrical elemental arrangement, band energy levels, and bond overlaps. Proper understanding and prediction of the structure are necessary for designing new and practical catalysts and materials.

The ABX₃ structure of perovskite combines metallic elements (denoted by A and B) with non-metals (denoted by X), usually oxygen. It has a specific atomic arrangement and forms a cube made up of three individual chemical elements (A, B and X) present in a ratio of 1:1:3 (Abdullah, Jawaid, Khalil, Zaidon, & Hadiyane, 2012). The A cations lie at the centre of the cube, consisting of two kinds of metals, while the B cations occupy the eight corners of the structure. The X anions are placed at the midpoints of the cubes, attached to 12 edges.

In Figure 2.4, the mineral perovskite is a unit cell or basic building block consisting of a single cube, CaTiO₃. This structure forms at higher temperatures and reflects the ideal arrangement (J. Zhu, Vanommen, Knoester, & Lefferts, 2005). The A position, occupied by calcium, is larger than the B position, which contains titanium and oxygen connected to all 12 edges from X sites. The crystal often grows into the shape of a cube or octahedron, reflecting the symmetry of the atomic structure. In most perovskite structures, atomic arrangements are disturbed because the centre position of A cation is too small relative to the B cations at the corners of the cube (Labhsetwar, Biniwale, Kumar, Rayalu, & Devotta, 2006). Consequently, this affects the X atoms, sometimes

causing them to move out of the position B. Crystallographers typically describe the unit cell as a cluster of polyhedral.



Figure 2.4 Basic perovskite structure of CaTiO₃ Source: Labhsetwar et al. (2006)

The estimation of suitable and combination of cations are calculated by using the tolerance factor t as observed in Equation (2.17) where r_A and r_B are the ionic radii of A and B site cations, respectively, and r_0 is the radius of the O^{2-} .

$$t = \frac{(r_{A+r_B})}{\sqrt{2}(r_{A+r_O})} \tag{2.17}$$

if t = 1, it indicates the formation of an ideal cubic structure having the size of cation A larger than that of B as indicated by LaCuO₃ and CeCuO₃. When the t lies in between 0.8 to 1 formation of stable perovskites can be suggested. If t lies above 1 and below 0.8, it represents the cation A is too big or small to fit into the BX₆ octahedron and leads to formation of substitute structures as shown in Table 2.5

Goldshmidt tolerance	Structure	Example
factor (t)		
0.9-1.0	Cubic	LaCuO ₃ , CeCuO ₃
0.71-0.9	Orthorhombic	GdFeO ₃ , CaTiO ₃
	rhombohedral	
<0.71	Ilmenite	FeTiO ₃ , KNbO ₃
>1	Hexagonal or tetragonal	BaNiO ₃

Table 2.3 Goldshmidt tolerance factor on various perovskite structures with examples

Source: J.-Y. Liu, Lee, Wang, Yeh, and Wang (2010)

The octahedral factor (μ) can be calculated by Equation (2.18)

$$\mu = \frac{r_B}{r_X} \tag{2.18}$$

as the ratio between ionic radii of B and X. The octahedral factor should lie within the range of 0.44-0.72 for B and X to form a stable BX₆ octahedron (Yi et al., 2019). The Goldschmidt tolerance factor plays a key role in identifying suitable perovskite materials that can accommodate the ABX₃ structure and develop catalysts with specific properties (Szuromi & Grocholski, 2017). Stable perovskites can be achieved by combining distant A/B cations and X anions in a particular composition (L. Wang, Fang, Feng, Wan, & Guan, 2016).

2.5.1 Structure of Perovskite

The A position is normally occupied by rare earth metals (La, Ce, Pr) and base metals (Cs, Sr, Ba and Ca). The ionic radius for A, r_A , is usually 0.90 Å, which is larger than that of the B position. The B position is reserved for transition metals (Co, Fe, Cu, Ni, Mn, Cr, Al) and the ionic radius of B, $r_B = 0.51$ Å. In the ideal cubic structure unit cell, the atomic sites for A and B positions are (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, respectively. The oxygen atoms occupy the $\left(\frac{1}{2}, \frac{1}{2}, 0\right)$ positions (Ciambelli et al., 2001). The A and B ions fit within the frame of dodecahedra and Octahedra in 3d, 4d and 5d transition metals. Oxygen atoms are represented as red spheres in Figure 2.5. Many metal ions exhibit different valence positions for A and B (Civera, Negro, Specchia, Saracco, & Specchia, 2005). Desirable properties can vary with proper formulation; in particular, catalytic properties depend on the nature of A and B ions and heir valance states. Therefore, as depicted in Figure 2.5, the A site represents the stability of the perovskite phase, while the B site determines catalytic activity. Substitution at the A site with ions having lower vacancies or change in the oxidation state of the transition metal cation help maintain the electro-neutrality of the compound. When the oxidation state of B cation increases at relatively low temperature, the enhanced availability of oxygen favours oxidation activity and catalytic performance in oxidation reaction (Zhong, Bonakdarpour, Zhang, Gao, & Dahn, 1997).



Figure 2.5 Perovskite structural frame positions of atoms.

Source: Zhong et al. (1997)

More oxygen vacancies can be observed at high temperatures. The oxidation activity of perovskites has been attributed to their ionic conductivity, oxygen mobility within their lattice, reducibility, and oxygen sorption properties. The released oxygen species can be divided into two categories depends on temperature:

- 1. Lower temperature superficial species: These are weakly chemisorbed on the surface of the perovskite and desorb in the 300-600 °C range. They are related to surface oxygen vacancies (Patel & Patel, 2013).
- 2. Higher temperature oxygen interfacial species: There are less easy to desorb and are therefore more bound to the perovskite structure. They desorb above 600 °C and are related to the bulk nature of the catalyst (Patel & Patel, 2013).

اونيۇرسىيتى مليسيا قھڭ السلطان عبدالله 2.5.2 Classification of Perovskites ALAYSIA PAHANG

Perovskite is classified according to its structures and the root of radii of the periodic metallic ions, as illustrated in Figure 2.6. The characteristic of the perovskite structure may change due to existence of large compound groups with dissimilar cations in the B position (AB_xB_{1-x}O₃), different cations in the A position (A_xA_{1-x}BO₃), or substitution in both cation positions (A_xA_{1-x}B_xB_{1-x}O₃). The A and B cations can have valences of 2^+ , 4^+ and 3^+ . Consequently, oxide phases can be divided into two types: ternary oxides and newer complex compound. Ternary oxide perovskite structures are based on oxidation states such as $A^{3+}B^{3+}O_3$, $A^{2+}B^{4+}O_3$, $A^{1+}B^{5+}O_3$, or cation deficient species (Galasso, 2013). The new complex compounds, such as AB'_xB''_yO₃, where B' and B'' represent two different oxidation states (Bhalla et al., 2000), satisfy the condition x + y = 1.



Figure 2.6 Classification of perovskite structures

Source: Kuzmanovski, Dimitrovska-Lazova, and Aleksovska (2007)

The buckling of (AO₃)⁴⁻ layers in perovskite structures occurred due to the distortion or displacement of the oxygen anion array, which was caused by variations in valences at the A cation position (Pengfei, Pengcheng, Shijie, Bo, & Yao, 2017). Perovskite materials exhibited characteristic chemical nature such as non-stoichiometric of anions or cations, mixed valence electronic structures, distortion of cation configurations, and mixed valence. The preparation of multicomponent perovskites through partial substitution of cations in A and B positions led to various complex types with unique properties, including dielectric and optical properties, ferroelectricity, superconductivity, piezoelectricity, multiferroicity, Colossal magneto-resistance (CMR) and catalytic activity (Min, Kim, Oh, Regan, & Logan, 2005).

2.5.3 Perovskite Catalysts in Reforming Reaction.

The perovskite catalysis studies in various reforming processes are summarized in Table 2.4. All the perovskite catalysts had either nickel, cobalt or copper as the main active sites of the catalyst, but all except paper 8 remarkably had lanthanum. Lanthana was favourable to enhance the dispersion of nickel and increase yield and selectivity of desired products. The surface area was also superior the catalyst was modified with lanthanum (Guo et al., 2024). While there are many runs and data in the literature, the

most optimum results highlighted by the authors will only be focused on the discussion here. Papers 1, 2 and 3 were published in 2008, 2008 and 2015 respectively. The authors investigated the use of LaCuO₃ or La₂CuO₄ in reforming reactions, including methane dry reforming. These catalysts were prepared using the precipitation method. Remarkably, 100% conversion of methane was achieved with feed ratios of methane to water between 1:1 and 2:3. The reaction temperatures varied from as low as 673 K to 873 K. However, at low temperatures, carbon formation and filament structures became problematic. Hence, temperatures higher than 873 K are advisable to conduct dry reforming reactions.

The other perovskites such as papers 2, 6, 7, 10, 11, 12 and 13 are newer complex with three or four different metals in oxidation state. The 3rd and 4th metal promoted by the authors included nickel, cobalt, ferum, calcium, strontium, aluminium, and potassium. Methods involving the precipitation of salt solutions of these metals in desired ratios were used to form gel-like catalyst precursors or precipitates. The highest longevity was observed in the result reported for La_{0.8}Sr_{0.2}Ni_{0.8}Cu_{0.2}O₃, which lasted for 24 h. The subsequent promotion of those metals further improved the reduction of carbon deposit on the perovskite catalysts (Morales, Laguna-Bercero, & Jiménez-Piqué, 2023)

Dry reforming reactions were catalysed by the perovskite catalyst between 548 K and 973 K, while steam reforming reactions were only operated at temperatures up to 923 K. Besides the free carbon formation, the slightly higher reaction temperatures in the dry reforming reactions were to increase carbon dioxide conversions. Therefore, the preferable range of the EDR reaction may be between 873 K to 973 K. Temperatures higher than 973 K may be used to check stability of the catalyst and compare with other reforming catalysts.

Four papers, numbered 6, 7, 8, 10 reported the reduction temperatures lower than the reaction temperatures, while the others reported the opposite. This discrepancy is likely due to the nature of oxide state of the metal in the catalyst. Pre-reaction reduction only removed unstable metal oxides without necessarily activating the metals. Unfortunately, no clear pattern emerges to differentiate these differences, especially between steam reforming and dry reforming reactions. Nevertheless, those who used higher reaction temperatures achieved significant 100% conversion of the key reactants.

The perovskite-type oxide catalysts LaNiO₃ and La_{1-x}Ce_xNiO₃ were prepared using the Pechini method and used as catalysts for carbon dioxide reforming to form synthesis gas. The methane and CO_2 conversions stand at 66% and 51%, at 600°C. Cerium provided lattice oxygen vacancies, which activated C-H bonds, and increased H_2 selectivity (Su, Pan, & Chang, 2014). Good catalytic performance was expected in the presence of cerium, which can attract and release adsorbed oxygen on the oxygen vacancies (Junjiang Zhu, Yanxi Zhao, Duihai Tang, Zhen Zhao, & Sónia A. C. Carabineiro, 2016). The activity and stability of potassium-copper perovskite catalysts substituted with SrKTiCuO3 are higher than those impregnated K-Cu/SrTiO3 due to strong interaction between copper and the perovskite support. Alkali metals like potassium can improve catalyst activity by increasing surface mobility (López-Suárez, Bueno-López, Illán-Gómez, & Trawczynski, 2014). Six papers, numbered 7, 8, 9, 11, 12 and 13, reported the use of the sol-gel method. The conversions of reactant were considerable high and comparable with other perovskite catalysts that were prepared using other methods. This method of preparation was preferably preferred due to better metal dispersion compared to other methods (Guo et al., 2024).

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No	Catalyst	Reforming	Preparation	Reaction	Reduction	Reaction	Conversions and	References
			Method	Variables	Temperature	Temperature	Selectivity	
					(K)	(K)		
1.	La ₂ CuO ₄	Methanol	Co-precipitation	$MeOH:H_2O =$	723	673	% $X_{MeoH} = 100\%;$	(L. Gao, Sun,
		steam	onto single-	1:1.3			$S_{CO2} = 100\%; H_2$	& Kawi,
		reforming	walled carbon	Flow rate: 0.04			Prod. = 2.11	2008)
			nanotube	ml/min				
			template					
2.	LaCo _{0.7-}	Methane dry	Conv. Citrate	H ₂ /CO/He: 8/4/3	723	548	$X_{CH4} = 40\%; S_{CH4} =$	(Tien-Thao,
	Cu _{0.3} O ₃	reforming					$46\%; P_{CH4} = 65\%.$	Alamdari, &
								Kaliaguine,
			لان عبدالله	با فهع السلط	بتی ملیس	او نبؤ ر س		2008)
3.	La ₂ CuO ₄	Methanol	Hydrothermal	$MeOH:H_2O = 1:1$	673	473	% $X_{MeoH} = 100\%;$	(J. Yang et
		steam	reaction with	Flow rate: 0.05			$S_{CO2}=95\%$	al., 2013)
		reforming	fermented	ml/min	DUU			
			bacteria					
			cellulose					

Table 2.4 Synopsis on the perovskite catalysts involved in reforming processes of ethanol, methanol and glycerol.

Table 2.4 Continued

No	Catalyst	Reforming	Preparation	Reaction	Reduction	Reaction	Conversions and	References
			Method	Variables	Temperature	Temperature	Selectivity	
					(K)	(K)		
4.	LaCuO ₃	Methanol	Solid state	CH ₃ OH/H ₂ O=2/3	873	673	% $X_{MeoH} = 100\%;$	(Y. - H.
		steam	reaction				$S_{CO2} = 98\%; S_{CO} =$	Huang,
		reforming					2.5%	Wang, Tsai,
								& Kameoka,
								2014)
5.	LaNiO ₃ /	Methane dry	Pechini method	CH ₄ /CO ₂ : 1/1	1123	873	$X_{CH4} = 94\%, X_{CO2} =$	(Su et al.,
	CeNiO ₃	reforming					92%, $S_{CO} = 33\%$ &	2014)
							$S_{H2}=57\%$	
6.	LaNi _{0.9} Cu _{0.1}	Glycerol	Co-Precipitation	Glycerol/H ₂ O =	773	823	$X_{GC} = 70\%; \ S_{H2} =$	(Ramesh,
	O ₃	steam		1/3	، ي ،	- J.J., J'	$68\%; S_{CO} = 28\%;$	Yang, Jung,
		reforming	UNIVERS	SITI MALA		AHANG		& Moon,
			AL-SU	LTAN A	BDUI	LAH		2015)
7.	La _{1-x} Ca _x Al ₁₋	Ethanol	Citrate sol-gel	Water/Ethanol =	773	873	$X_{ethanol} = 100\%; S_{H2}$	(Agüero et
	yNiyO3	steam	method	5:1			= 80% $S_{\rm CO}\!=10\%$;	al., 2015)
		reforming						

Table 2.4 Continued

No	Catalyst	Reforming	Preparation	Reaction	Reduction	Reaction	Conversions and	References
			Method	Variables	Temperature	Temperature	Selectivity	
					(K)	(K)		
8.	NiTiO ₃	Steam	Citrate sol-gel	Water/Ethanol =	773	873	$X_{ethanol} = 80\%; S_{H2} =$	(Ruiz-
		reforming	method	3:1;			70% $S_{CO} = 50\%$;	Preciado,
		and		Oxygen/Ethanol:			$S_{CO2} = 20\%$;	Kassiba,
		oxidative		3:1				Gibaud, &
		steam						Morales-
		reforming		UMPSA				Acevedo,
								2015)
9.	LaCuO ₃	Dry	Citrate Sol-Gel	CH4:CO2:Ar	923	823	$X_{CO2} = 15\%; X_{CH4}$	(F. Touahra
		reforming of methane	method	20:20:60 ;	يتي مليس	اونيۇرس	$= 10\%; H_2/CO =$ 0.99 ·	et al., 2016)
		methane	UNIVER	SITI MALA	YSIA PA	HANG	,	
			AL-SU	LTAN A	BDUL	.LAH		

Table 2.4 Continued

No	Catalyst	Reforming	Preparation	Reaction	Reduction	Reaction	Conversions and	References
			Method	Variables	Temperature	Temperature	Selectivity	
					(K)	(K)		
10.	La ₁₋	Selective	One step citrate	Water/Ethanol:	823	923	$X_{ethanol} = 100\%; S_{H2}$	(Junjiang
	_x K _x Fe _{0.7} Ni _{0.}	ethanol	complexation	3:1			$= 60\% S_{CO} = 8\%$;	Zhu, Yanxi
	$_{3}O_{3} x=0,$	oxidation	method				$S_{CO2} = 18.5\%$; S_{CH4}	Zhao, Duihai
	0.05, 0.1;							Tang, Zhen
								Zhao, &
				UMPS				Sónia A.C.
								Carabineiro,
								2016)
11.	LaCoO ₃ and	Dry	Sol-Gel method	CH ₄ /CO ₂ /Ar:	973	673-973	X _{CH4} =15-57%;	(Fouzia
	LaCu _{0.55} Co	reforming		20/20/60; F.R: 20	ييني متيله	او بيو ر م	X _{CO2} =18-61%;	Touahra et
	0.45O3	methane	UNIVERS	ML/min;	YSIA PA	AHANG	TOS = 55 h	al., 2019)
			AL-SU	LTAN A	BDUI	LAH		

Table 2.4 Continued

No	Catalyst	Reforming	Preparation	Reaction	Reduction	Reaction	Conversions and	References
			Method	Variables	Temperature	Temperature	Selectivity	
					(K)	(K)		
12.	La _{0.6} Sr _{0.4} Co	SR and ATR	Citrate sol-gel	$H_2O/CH_3OH =$	923	473 - 873	$X_{CH3OH} = 0 - 100\%$	(Morales et
	Оз-б	of methanol	method	1.3, 2 and 4			$S_{H2} = 60 - 80\%$	al., 2023)
				$O_2/H_2O/CH_3OH =$			$S_{CO2}=4-50\%$	
				0.1/1.3/1,				
				0.2/1.3/1 and				
				0.3:1.3:1				
13.	LaABNiO ₃	n-dodecane	Citrate sol-gel	15 mL/gcat/h	923	973	$X_{C12} = 50-70\%$	(Guo et al.,
	A and B:	steam	method with	$H_2O:C_{12}H_{26} = 24$				2024)
	Ce, Pr, Sm,	reforming	ethylene glycol	با قععُ السلط	ىتى ملىسا	او ئىۋ ر س		
	Tb							
			UNIVER	JIII MALA		MANG		
			AL-SU	ILTAN A	BDUI	LAH		

2.6 Promotion to Perovskite Catalyst

Catalysts are usually promoted with other metals to provide additional active sites for chemical reactions and control selectivity. Reaction intermediates may be stabilized by the metal promoters. The surface area and dispersion of the active metal contribute for stability, adsorption, and activity of reactants on the catalyst surface may be enhanced. Electronic properties of the catalyst can change with the presence of new metal promoters, enhancing overall performance. Ultimately, the reactivity and cost are considered when selecting catalyst metals after evaluating all the benefits mentioned above (Bartholomew, 2001).

Promoting alkali metals could reduce acidic gases and increase hydrogen to reforming reactions. Potassium, in particular, improved catalyst stability and activity for steam reforming of ethanol. Additionally, coking problems were significantly minimized since they are usually associated with acid cite (Lin Zhao, 2016). Table 2.5 presents the catalyst studies using potassium promoter. For instance, potassium promotion on perovskite catalysts was studied such as La_{1-x}K_xCoO₃ (0 < x < 0.3) perovskites prepared by the solgel method. These catalysts exhibited 100% selectivity towards the methanation of CO₂ at various reaction temperatures. Tuning the selectivity (i.e., the ratio of CH₄ to CO products) can be beneficial for downstream hydrocarbon reforming while valorising waste CO₂ (Tsounis et al., 2020).

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The intrinsic ability of Ni to disperse easily over various supports makes it a more viable active phase for steam reforming catalysts. The optimal reaction conditions are at 650-900°C, 1 bar, and 15 wt% Ni in the catalysts for high glycerol conversion. Ni/LaNi_{0.9}Cu_{0.1}O₃ synthesized using perovskite-type supports had shown high conversion and sufficient hydrogen selectivity at low temperatures. Hydrotalcites-like catalysts demonstrated higher catalytic stability due to their high thermal stability and low coke formation (Saeidabad et al., 2020). K-promoted bimetallic NiCo-NiAl₂O₄ nano-catalysts with various loadings of potassium were fabricated by a hybrid sol-gel plasma method. Despite the adverse impact of K such as lower activity and coverage of defective site, it enhanced reducibility and improved the rate of carbon gasification, leading to the improved stability and reduced coke deposition. The small average particle size, tuneable morphology, larger surface area and optimum amount of appended K contributed to superior performance (Seyed Mehdi Sajjadi, 2019).

No.	Catalyst	Reactions	Preparation method	Catalytic Conditions	Catalytic activity	Reference
1.	$La_{1-x}K_{x}Fe_{0.3}Ni_{0.3}O_{3}$ (x=	Steam	Citrate sol-gel	Red: 5%vol H ₂ -Ar 700°C,1h	Х _{с2н50н} : 100%	
	0,0.05,0.1)	reforming		Rec: H ₂ O/CO ₂ : 1/3; WHSV: 60,000 ml/ gcat h	S _{H2} : 60%	(Lin Zhao, 2016)
2.	Pd/Al ₂ O ₃	Dry	Co-impregnation	Red: H ₂ -500°C/2h	$X_{CO2} = 93\%$	(Shia & Zhang,
	K-Pd/Al ₂ O ₃	reforming		Rec.: CH4/CO2/He: 1:1:2		2012)
	Y-Pd/Al ₂ O ₃			700°C/8h		
				$GHSV = 24,000 h^{-1}$		
3	La _{1-x} K _x NiO ₃	CO ₂	Citrate sol-gel	Flow of $H_2 = 25 \text{ mL/min}$	$X_{CO2} = 0 - 100\%$	(Tsounis et al.,
		hydrogenati	تح السلطان	بورسينى 150-450°C/2h	$\mathbf{S}_{\mathrm{CO}} = 100 - 0\%$	2020)
		^{on} UNIV	ERSITI M	ALAYSIA ["] PAHAN	IG	
		AL-9	SULTAI	N ABDULLA	H	
4.	K-NiCo-NiAl ₂ O ₃	Oxidative	Hybrid Sol-gel	Red: 750°C/3h	$Y_{H2} = 91.2\%$	(Seyed Mehdi
		dry	plasma	Rec.: 550-850°C/48h		Sajjadi, 2019)
		reforming		CH ₄ /CO ₂ /O ₂ : 1:1:0.08		
				$GHSV = 24 l/g_{cat}h$		

Table 2.5 Synopsis of K-promoted perovskite catalysts

Table 2.5 Continued

No.	Catalyst	Reactions	Preparation	Catalytic Conditions	Catalytic activity	Reference
			method			
5.	K-Ni/Al ₂ O ₃	Dry	Impregnation	Red: 50% $H_2/N_2 - 973 \text{ K/2h}$	$X_{CH4} = 83.6\%$	(A. Nandini,
		reforming	technique	Rec.: 1073 K/6h; CH ₄ /CO ₂ :1:1	$X_{CO2} = 80.2\%$	2005)
					$Y_{H2} = 79.9\%$	
					$Y_{CO} = 76.5\%$	
6.	K doped LaNiO ₃	Water gas	Citrate sol-gel	Red: H ₂ (20 ml/min) at 600°C	$X_{CO}=90\%$	(Maneerung,
		shift	method	lh		Hidajat, & Kawi,
				Rec: 350-550 °C 50 ml/min;		2017)
				1		
7.	K-Co-Zn-Al ₂ O ₃					
		Steam	Citrate sol-gel	Red: H ₂ , 400°C, 1h	$X_{C2H5OH} = 98\%$	(Bogna Banach,
		reforming	method ERSITI M	Rec.: H ₂ O/CO ₂ : 12:1; 700°C;	$X_{CO2} = 76\%$	2015)
		AL-	SULTA	N ABDULLA	H	

No.	Catalyst	Reactions	Preparation	Catalytic Conditions	Catalytic	References
			Method		activity	
1.	Y-SBA15	Dry	Sol-Gel	Red:H ₂ -700°C/0.5h	$X_{CH4} = 68\%$	(Baitao Li, 2013)
		reforming	method	Rec.: 750°C/6h; CH4:CO ₂ : 1:1GHSV =	$X_{CO2} = 56\%$	
				15,000 h ⁻¹		
2.	Y_2O_3	Methane	Co-	CH_4/CO_2 : 1/1; GHSV = 24000 mL/g _{Cat} h	$X_{CH4} = 92\%;$	(B. Li, Su, Wang, & Wang,
	promoted	dry	Precipitation	700	$X_{CO2} = 90\%;$	2016)
	Co-	reforming		800	$Y_{CO} = 79\%;$	
	Ni/Al ₂ O ₃			altet di Sasta di site	$H_{2}/CO = 1.2;$	
3.	Ni-	Steam	Wet	Red: H ₂ /Ar - 800°C/2h	$X_{CH4} = 92\%$	(F. Chen et al., 2020)
	Cu/Yttria-	Reforming	Impregnation	Rec.: 650°C/20h ALAYSIA PAH	$S_{H2}=30\%$	
	Stabilized		AL-S	SULTAN ABDULI	_AH	
	Zirconia					
	(YSZ)					

Table 2.6. Synopsis of study on Y-promoted perovskites

No.	Catalyst	Reactions	Preparation	Catalytic Conditions	Catalytic	References	
			Method		activity		
4.	Ni-Al ₂ O ₃ -	Steam	Sol-Gel	Red: H ₂ -923K/2h	$X_{C2H5OH} =$	(Guadalupe Yonatan	
	Y_2O_3	reforming	method	Rec.: 873K, H ₂ O/C ₂ H ₅ OH: 3	100%	Ramı'rez-Hernandez,	
					$Y_{H2}=5\%$	2016)	
5.	Sr _{1-x} Y _x TiO ₃	Dry	Impregnation	Red: 10%H ₂ /Ar -900°C/2h	$X_{CH4} = 97.8\%$	(Kim et al., 2020)	
		reforming	method	Rec.: 900°C;	$X_{CO2} = 99.2\%$		
				$CH_4/CO_2 - 1$			
	UMPSA						
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	UNIVERSITI MALAYSIA PAHANG						
	AL-SULTAN ABDULLAH						

Table 2.6 shows a summary of Y-promoted catalysts. As the yttrium content in the catalysts support increased, nickel started to reduce at lower temperatures, resulting in higher hydrogen production. NH₃-TPD analysis revealed that yttrium presence decreased the total acidity of alumina while simultaneously lowering the strength of acid sites. When studying the spent catalysts, it was observed that the yttrium-containing catalysts were less prone to carbon deposits compared to nickel-supported pure alumina (Ramı'rez-Hernandez, Viveros-Garcı, a, & Galindo-Esquivel, 2016). The bimetallic Ni-Cu/YSZ catalyst demonstrated enhanced reducibility and stability during reaction studies. In ESR, Ni was mainly responsible for C-C bond cleavage, while copper played a role in the WGS. YSZ had a limited role in reducing coke formation as the catalyst support, despite its high surface oxygen mobility. However, the presence of coke led to serious deactivation of the Ni/YSZ monometallic catalyst. Among the catalysts studied, Cu₁Ni₉/YSZ exhibited superior performance and stability, with negligible activity loss during a 20-h ESR reaction at 450°C and 650°C, respectively(F. Chen et al., 2020).

A series of mesoporous yttrium (Y)-containing SBA-15 was synthesized using solgel method with various Y/Si molar ratios, and these materials were evaluated for methane dry reforming. The presence of yttrium in the framework of SBA-15 in Ni catalysts effectively enhanced the formation of the small-sized Ni metallic particles and significantly promoted the reduction of NiO. This enhancement was attributed to the oxygen vacancies on the surfaces of the yttrium containing SBA-15 supports and the high mobility of surface oxygen species. Ni-Y/Si (0.04) performed high activity due to its well-ordered mesoporous structure, large pore diameter and small metallic metal size (B. Li & Zhang, 2013). Additionally, Ni/Al/Mg layered double hydroxides (LDHs) modified with low loadings of yttrium (0.2 and 0.4 wt%) were used in dry reforming of methane at 700 °C. The lower yttrium loading led to decreased reducibility of Ni and basic sites in the catalysts. However, doping with 0.4 wt% of Y improves catalytic activity, resulting in higher CH4 (84%) and CO₂ (87%) respectively. The increase in CO₂ conversion and a decrease of H₂/CO ratio indicates that the side reaction occurs during dry reforming of methane (Świrk et al., 2019).

The promising catalytic activity material, yttria-doped strontium titanium oxide traces of ruthenium (Sr_{0.92}Y_{0.08}Ti_{0.98}Ru_{0.02}O₃), was synthesized using the impregnation method for use in the dry reforming of methane reaction. Ru doping was varied, and it was observed that the oxygen vacancy formation energy, calculated by density functional theory, led to a high activity for the surface oxygen. The surface oxygen's ability to donate electrons to the catalysts was facilitated the dissociation and decomposition of CH_4 and CO_2 . As a result, this catalyst exhibited high conversion efficiency, good syngas selectivity, stability, and minimal coke formation (Kim et al., 2020).

2.7 Catalyst Deactivation

The loss or decrease in the activity of a catalyst can be due to poisoning, coke formation, and sintering. Argyle and Bartholomew (2015) explained the six intrinsic mechanisms of catalyst deactivation, as shown in Table 2.7. Catalyst crushing may occur due to aggressive stirring or vibration. The mechanism can destroy the structure of the catalyst support, leading to a decrease in active sites on the catalyst. Vapour-vapour, vapour-solid and solid-solid reactions for number two and three involve impurities or by-products interacting with the catalyst at different phases, which ultimately reduced the active sites of the catalysts.

No	Mechanism	Category	Brief description
1	طان عبدالله UNIVERS AL-SUI	Mechanical معليا فهغ السل ITI MALAY	By the mechanical-induced crushing of catalyst particles affects the catalytic loss due to the abrasion and internal surface area.
2	Vapour-solid and solid-solid reactions.	Chemical	Reaction of vapour to support or promoter with catalytic phase infers to inactive.
3	Vapour formation	Chemical	Reaction of has with the catalyst phase to produce volatile compounds.
4	Sintering (thermal degradation)	Thermal	Reaction happens between the active phase and support.
5	Coking (Fouling)	Mechanical	Physical deposition of species from the fluid phase on both surface and pores of the catalyst.

Table 2.7	Deactivation	n of catalyst
		2

No	Mechanism	Category	Brief description
6	Poisoning	Chemical	Strong chemisorptions of species on
			catalytic sites which resulted from
			block sites for catalytic reaction.

Table 2.7 Continued

Source: (Argyle & Bartholomew, 2015)

Coking refers to the chemisorption and physisorption of by-product carbon from polymerization and decomposition reactions onto active sites or pores of a catalyst. In a dry reforming of methane, filamentous carbon could be formed, as shown in Figure 2.7. The ethylene polymerization, Boudouard decomposition reaction, and methane decomposition typically occurred as described by Equations 2.19), (2.20) and (2.20), respectively (Zawadzki, Bellido, Lucrédio, & Assaf, 2014). This carbon deposition can be reversed by using steam if the absorption is purely physical, but the CO₂ utilization will decline in the case of the dry reforming reaction. Thus, addition of hydrogen can help alleviate catalyst deactivation caused by coking (J. Zhang et al., 2020).

$$C_2H_5OH \rightarrow C_2H_5 \rightarrow Polymerization \rightarrow Coke$$
 2.19)

ونيورسيتي مليسيا قهع السلطان عبدالله	(2.20)
	(2.21)

$$\mathbf{AL-SULTAN \ ABDULLAH}$$
(2.21)



Figure 2.7 coke formation on a supported metal catalyst (Ochoa, Bilbao, Gayubo, & Castaño, 2020): (i) carbon chemisorption or physisorption blocking the access to reactants; (ii) metal particle encapsulation; (iii) pore plugging; (iv) degradation of catalyst structure by carbon filament. (v) FESEM analysis revealed coke filament on the catalyst after methane dry reforming.

Source: Zambrano, Soler, Herguido, and Menéndez (2019).

Sintering is a phenomenon where the catalyst's crystalline size increases, reducing the surface area of active site and weakening the interaction between the catalyst and the support. It usually occurs at higher temperatures (> 427° C) and hypothetically involves two mechanisms: atomic migration through adsorption on smaller metal particles (adatoms) to larger particles, known as Ostwald ripening and small particle migration on the outer surface of the support, as illustrated in Figure 2.8. The latter mechanism is more likely due to the relatively greater exposure of the support (Moulijn & Babich, 2011). In atomic migration, atoms move on the surface of the support and become encapsulated by larger crystallites, separating them from the metal atoms. In crystallite migration, the entire crystallite moves on the support surface, driven by collision and coalescence.



Figure 2.8 Theoretical models of crystallite growth due to sintering: (A) Ostwald ripening; (B) small particle migration.

Source: Ochoa et al. (2020)

Poisoning rate depends on the concentration of catalyst poison and conditions of the chemisorption. The chemisorption reaction route is normally complex involving multiple catalytic reactions that block active sites and suppressing surface for reactant-catalyst contact (Bartholomew, 2001). Some of instances are summarized in Table 2.8. For the EDR reactions, the catalyst poisoning may be due to impurities in the feedstock, such as H_2S (Fabrik, Salama, & Ibrahim, 2023). Additionally, Co-based catalyst can be poisoned by the presence of oxygen (Wittich, Krämer, Bottke, & Schunk, 2020).

Catalyst	Process Process	Poisons
Fe, Ru	Ammonia synthesis	O_2 , S, CO, C_2H_2 , H_2O
Ni	Steam reforming of methane,	H_2S , As
	Naphtha	
Ni, Pt, Pd	Hydrogenation, dehydrogenation	Compounds of P, S As,
		Hg, Zn, halides, Pb, NH ₃ .
Silica-alumina,	Cracking	Organic-bases,
Zeolites		Hydrocarbon heavy
		metal
Noble metals on	Hydrocracking	S, P, Se, Te, NH ₃
Zeolites		
VO_2	Oxidation selective catalytic	As, K, Na, Fe from fly
	reduction	ash

او نیو رسیدی ملب Table 2.8 Catalyst poisons in typical processes

Table 2.8	Continued
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Catalyst	Process	Poisons
Pt, Pd	Oxidation of CO and hydrocarbons	Fe, P, Pb, Zn, SO ₂
Ag	Ethylene oxidation to ethylene oxide	C_2H_2
Co and MoS	Hydrotreatment of residue	Asphaltenes, N
		Compounds, Ni, V

Source: (Bartholomew, 2001)

2.8 Reaction mechanism and kinetic study of ethanol dry reforming

Kinetic model is determined based on a proposed mechanism of reactions. If a catalyst is involved, the rate determining step typically involves temporary binding to form complex intermediates between reactants or products and active site of the catalyst. Once the kinetic model significantly fits the data from experiments, rate laws can be derived. The rate law derivation also includes the mole balance of the reactor, considering the type and mode of operation of the reactor used in the experiment. Additionally, statistical experimental design ensures the number of conditions and replication necessary to ensure result repeatability. Lastly, the experiment must be free from mass transfer or mixing hindrance (H. S. Fogler, 2013).

An ideal reaction is free from mass transfer limitations, and its rate-determining step depends solely on concentration of the reactant. This behaviour is describe by the power law model. Initially, this model is postulated, and many gaseous reactions follow it. Other modified models of rate law consider various rate determining steps. This review will also discuss the model that considers mechanism of absorbed reactants to form intermediates, which is called the Langmuir Hinshelwood model (Ohtani, 2011).

2.8.1 Power Law Model

The power law model is expressed using a power equation that involves the activation energy (Ea), the order of reaction (m and n) and the rate constant (k). The relationship is shown in Equation (2.22). Additionally, there is a rate constant equation that includes the pre-exponential factor (A), as demonstrated in Equation (2.23). In gaseous reactions, concentrations are expressed in partial pressures, which can be converted to concentration by using the gas law.

$$r = k \left(P_{CO_2}^m P_{C_{2H_5}OH}^n \right)$$
(2.22)

$$k = Aexp\left(\frac{-E_a}{RT}\right) \tag{2.23}$$

where,

$$r =$$
 rate of consumption of reactants formation rate (mole/g⁻¹ s⁻¹) P_{CO_2} $= CO_2$ partial pressure (kPa) $P_{C_2H_{5OH}}$ $= C_2H_5OH$ partial pressure (kPa)

The power law kinetic model is well-known for estimating the activation and order of reaction of reforming processes involving methane, ethanol, and glycerol. In a study of ethanol steam reforming, a Ni-based catalyst was investigated at temperatures ranging from 673 K to 863 K using a stainless-steel tubular reactor. The activation energy was obtained 51 kJ mol⁻¹ by Akpan, Akande, Aboudheir, Ibrahim, and Idem (2007). Another the kinetic study focused on methane dry reforming over La_{2-x}Sr_xNiO₄, conducted at temperatures between 723 K and 1073 K, revealing an activation energy of 41.2 kJ mol⁻¹ (Ch Pichas, P Pomonis, D Petrakis, & A Ladavos, 2010). Additionally, the glycerol hydrogenolysis reaction on a Cu/SiO₂ catalyst occurred at temperatures of 453 K to 513 K, with the catalyst weight and hydrogen pressure specified as 0.05-0.35g and 2-8MPa, respectively. The activation energy for this reaction was determined to be 96.8 kJ mol⁻¹ (Cernea et al., 2013).

Kinetic study of the EDR reaction is scarce as compared to methane dry reforming (J. Zhang et al., 2020). Nakajima et al. (2023) used power law model in their kinetic study of methane dry reforming using Ni/Si-MCM-41 catalyst and they found 90% fitness of the reaction data to the irreversible model, with the activation energy of 77.7 kJ mol⁻¹. A kinetic study of the EDR reaction was particularly carried out under atmospheric pressure at the temperatures ranging from 773 K to 873 K over NiO/SiO₂-Al₂O₃, yielding an activation energy of 97.87 kJ mol⁻¹ (Bej et al., 2017).

2.8.2 Langmuir-Hinshelwood Model

Langmuir-Hinshelwood kinetic model is used to identify single or double catalytic reaction sites. Two reactants A and B are adsorbed first on the surface then chemisorbed and finally the product (P) will be desorbed from the surface as shown in Figure 2.9.



Figure 2.9 Langmuir – Hinshelwood reaction mechanism (A) and (B) are reactants; (P) is product

Source: (Rousseau et al., 2009).

The adsorption mechanisms like associative adsorption and dissociative adsorption of the single site as follows **SITI MALAYSIA PAHANG**

$k_{rxn}P_AP_B$	(2	2.24)
$(1 + K_A P_A + K_B K_B)^2$		

$$\frac{k_{rxn}P_A\sqrt{P_B}}{\left(1 + K_AP_A + \sqrt{K_BP_B}\right)^2} \tag{2.25}$$

$$\frac{k_{rxn}\sqrt{P_A P_B}}{\left(1 + \sqrt{K_A P_A} + K_B P_B\right)^2} \tag{2.26}$$

$$\frac{k_{rxn}\sqrt{P_A P_B}}{\left(1 + \sqrt{K_A P_A} + \sqrt{K_B P_B}\right)^2}$$
(2.27)

Where,

 k_{rxn} = Reaction rate constant

 $P_{A,B}$ = Reactant partial pressure (kPa)

 $K_{A,B}$ = Reactant adsorption constant (kPa⁻¹)

The Langmuir Hinshelwood mechanism, single site displays the reactant adsorption on the same site but in case of dual sites the reactant adsorption on the catalyst might happen on the different sites. The adsorption depends on associative or dissociative of the sites (G. Liu et al., 2015). The Ni-based catalyst was on ESR for the production of H₂ at the reaction temperature 673-863 K and the kinetic model of activation energy is about 35.2 - 57.8 kJ mol⁻¹ (Akpan et al., 2007). The MDR reaction carried out over Co-Ni/Al₂O₃ catalyst with different promoters such as Pr, Sm and Ce at the reaction temperature from 923-1023 K in a fixed-bed reactor and found the activation energy values 46.6 kJ mol⁻¹ of dual sites (Say Yei Foo, Cheng, Nguyen, & Adesina, 2011). (J. Zhang et al., 2020) conducted a microkinetic study on the EDR reaction using the Rhbased catalyst and an integrated analysis-reaction system. Initial decomposition of ethanol and the later C-O bond formation are crucial steps on the reaction free energy landscape.

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2.9 Concluding remarks

Syngas is an important immediate in many chemical processes and currently produced from non-renewable feedstocks. The EDR reaction is studied, among others that produce syngas, to seek the potential of consuming renewable feedstock and greenhouse gases. The high reaction temperature causes deactivation to many reforming catalysts due to sintering and carbon deposition. Non-noble metals are comparable to noble metal in the reforming activity but prone to these deactivation problems. Perovskite structure has the potential to be a strong catalyst support to the transition metal, particularly copper, and co-factor to the oxidation reaction of free carbon. The oxidation of carbon to eliminate the carbon deposition and production of CO can be further improved by promoting yttrium and potassium to the perovskite structure.

The reaction conversion, selectivity and yield reflect the activity of the catalyst. Hence these parameters will be the indicators to the catalyst activity. Reaction temperature and feed ratio are two essential variables in controlling the reaction rate and become the factors of a rate law equation. Reaction temperature from 923 to1023 K and feed molar ratios of CO₂:ethanol from 2.5:1 to 1:2.5 are preferable operating parameters to be studied as what have been previously employed by many authors. The pressure of the EDR reaction seemed not too critical and will be subject to equipment setups. The study of reaction kinetics must be based on the free mass transfer limitation where the activity is only under the influence of reaction rate rather than mixing or diffusion. The reaction kinetics will be commenced based on the power law model and mechanism. Langmuir-Hinshelwood model will also be used to examine the involvement of limiting step in the reaction.


CHAPTER 3

METHODOLOGY

3.1 Overview

This chapter describes in detail about the materials, equipment, catalyst preparation techniques and Ethanol Dry Reforming (EDR) evaluation procedures. Explanations are given on various catalyst characterization techniques such as Hydrogen Temperature Programmed Reduction (TPR), X-Ray Diffraction measurement (XRD), Brunauer-Emmett-Teller (BET), Scanning Electron Microscopy – Energy Dispersive X-Ray Analyser (SEM-EDX), X-ray photoelectron spectroscopy (XPS) and Transmission Electron Microscope (TEM) measurements are also provided in this chapter below.

Figure 3.1 illustrates the steps taken to achieve the objectives of the study, beginning with the preparation of a catalyst based on $A_{1,x}B_xCuO_3$ where A is lanthanum or cerium and B is yttrium or potassium that was prepared based on mole fraction between A and B, which are 1-x and x, respectively. In the first objective, copper-based perovskites were synthesized using lanthanum and cerium precursors via the sol-gel method. The resulting calcined catalysts underwent characterization using XRD, TPR, XPS, TEM, and SEM-EDX techniques. Reaction tests were also conducted to determine the optimal composition for achieving good catalytic activity and stability. The preferred rare earth element for the copper-based perovskite was identified and would be used in subsequent procedures for the second objective. Potassium (K) and yttrium (Y) were added to the best composition, varying x from 0 to 1 with increments of 0.25, in the copper-based perovskite. The same characterization and reaction test procedures were followed. In the third objective, the resulting catalyst composition with the best catalytic activity and stability for both promoters was determined. The best catalyst composition was then used to determine the kinetic model of the EDR reaction.



Figure 3.1 The flowchart of steps in methodology in accordance with the objectives

3.2 Materials

The list of chemicals employed in the study including their applications and purity. Lanthanum and cerium (III) nitrate hexahydrate and Copper (II) nitrate trihydrate were used as catalyst precursor. Yttrium and Potassium hexahydrate were used as promoter precursors. The chemicals were purchased from Merck (KGaA, Darmstadt, Germany) and Sigma-Aldrich (St. Louis, Missouri) applied for catalysts preparation. All catalysts were prepared by using distilled water from water distillation unit (Aquamatic, Hamilton, England).

Chemicals	Formula	Concentration	Supplier	Application
		Purity (%)		
Copper (II)	Cu(NO ₃) ₂ .3H ₂ O	99.9	Merck	Active metal
nitrate trihydrate				
Lanthanum (III)	La(NO ₃) ₃ .6H ₂ O	99.9	Sigma	Precursor
nitrate			Aldrich	
hexahydrate	U	MPSA		
Cerium (III)	Ce(NO ₃) ₃ .6H ₂ O	99.9	Merck	Precursor
nitrate	مع السلطان عد	ىتى مارسىا ق	اه ندهٔ ر سه	
hexahydrate			AHANG	
Potassium nitrate	KNO ₃ .6H ₂ O	99.9 BDU	Merck	Precursor
hexa hydrate				
Yttrium (III)	Y(NO ₃) ₃ .6H ₂ O	99.9	Merck	Precursor
nitrate				
hexahydrate				
Citric Acid	$C_6H_8O_7$	99.5	Sigma	Support
			Aldrich	
Ethanol	C ₂ H ₅ OH	99.9	VWR	Reactant
			Chemicals	
Drierite	CaSO ₄	99.9	W.A	Moisture
			Hammond	removal

Table 3.1 List of materials used for catalyst preparation and experiment

List of the gases used in this work shown in Table 3.2 with respective their purities and the applications. All the air products cylinders were supplied from Singapore. During the catalyst preparation the compressed air is used for the calcination and drying. The key reactant for EDR was carbon dioxide and ethanol while nitrogen was used as a diluent.

Gases	Concentration of purity	Function
	(%)	
Hydrogen (H ₂)	99.9	Catalyst reduction
Nitrogen (N ₂)	99.9	Carrier gas or diluents (Reactor)
Carbon dioxide (CO ₂)	99.5	Reactant
Helium (He)	99.9	Carrier gas (GC)

Table 3.2. List of gases for GC analyses

3.3 Catalyst Preparation Method

The copper-based perovskites (LaCuO₃ and CeCuO₃) were prepared for the first objective by using the citrate sol-gel method as proposed by Stege, Cadús, and Barbero (2011) since this method is favourable to produce perovskite for additional oxidation catalysis of carbon deposit. The steps in preparing the catalyst samples are illustrated in Figure 3.2. Composition of promoted metals follow A_{1-x}B_xCuO₃ where x, the molar fraction between A and B, varies from 0 to 1. The detail mass for the 5-g catalyst sample from this composition variation is presented in Table 3.3. For LaCuO₃ (where x = 0), lanthanum (III) nitrate hexahydrate and copper (II) nitrate trihydrate were initially mixed into 1:1 ratio of metal elements in distilled water and the mixture was kept under stirring for 20 minutes. Then, citric acid was added to the aqueous solution within the molar ratio of 1:2 between the total metal ions to citric acid for 5 hours at 80°C. If sponge-like solid formed, it would be dried at 120°C for 24 hours. Otherwise, the step was repeated with different preparation conditions. The resulted sludge was next calcined in a muffle furnace at 800°C for 5 hours. The calcined samples were kept in a desiccator to void contact with moisture. The other compositions followed the same method.



Figure 3.2 The steps in preparing catalysts by the sol-gel method.

Catalyst	Cu(NO3)3.	La(NO3)3.	Ce(NO3)3.		Y(NO3)3.	C.H.O.
	3H ₂ O	6H2O	6H2O	(g)	3H ₂ O	(a)
	(g)	(g)	(g)	(g)	(g)	(g)
LaCuO ₃	5.90	8.64	-	-	-	15.29
CeCuO ₃	5.90	-	8.23	-	-	15.29
La _{0.75} Y _{0.25} CuO ₃	2.30	2.59	-	-	0.76	6.14
$La_{0.50}Y_{0.50}CuO_{3}$	2.30	1.73	-	-	1.53	6.14
La _{0.25} Y _{0.75} CuO ₃	2.66	0.86	-	-	2.29	6.53
YCuO ₃	2.66	- UN	IPSA -	-	3.44	6.91
La _{0.75} K _{0.25} CuO ₃	2.3	2.5	-	0.2	-	6.10
La _{0.50} K _{0.50} CuO ₃	2.6	1.9	-	0.4	-	6.9
La _{0.25} K _{0.75} CuO ₃	2.9 2.9	لهع السلطان	ي مل ي سيا ق	اونيو0.7سيتم	-	7.6
KCuO ₃	3.8	RSITI MA	LAYSIA	PAH.3ANG	-	9.9
	AL-S	ULTAN	ABD	JLLAH		

Table 3.3 Amount of the chemicals used for the 5 g of catalyst preparation.

3.4 Catalyst Characterisation Methods

The catalyst samples were analyzed using the following methods. Crystallinity, reduction temperature, surface morphology and element topography, functional groups, oxidation state of elements, carbon presence and surface area are key characteristics of a catalyst that enable in-depth understanding of catalytic reaction mechanism.

3.4.1 X-ray Diffraction Analysis

The crystal structures of LaCuO₃ and CeCuO₃ catalysts were investigated using the X-ray diffraction (XRD) to identify the phases in the crystalline material and infer to give information on unit cell dimensions, study the crystal structure, atomic spacing. The basic principle of XRD as shown in Figure 3.3. It is based on constructive interference of monochromatic X-rays and a crystalline sample. The crystal size is calculated by Bragg's equation shown in Equation (3.1).



Figure 3.3 Bragg's law for XRD measurement

The XRD analyses were carried by using Rigaku Miniflex II system with wavelength, $\lambda = 1.5418$ Å at 30 kV and 15 mA. The diffraction patterns were recorded as 20 from 3° to 80° with 1° min⁻¹ scan speed and a step size of 0.02°.

3.4.2 Temperature-Programmed Reduction

The temperature-programmed reduction (TPR) was used to examine the surface chemistry of metal oxides by using flowing hydrogen mixed with nitrogen under various temperatures including the reaction temperature. The Micrometrics AutoChem II-2920 chemisorption system was employed. Approximately, 0.1 g of catalyst was placed in a quartz U-tube and sandwiched by quartz wool. After a pre-treatment at 373 K for 30 min in flowing He gas of 50 ml min⁻¹, specimen was heated with a constant rate of 10 K min⁻¹ from 373 to 1173 K under 50 ml min⁻¹ flow of 10%H₂/Ar and held at the final temperature for 30 min.

3.4.3 Scanning Electron Microscopy Energy Dispersive X-ray

Scanning electron microscopy (SEM) branded as Carl Zeiss AG-EVO® 50 series instrument was employed using high-energy electrons to generate a variety of signals at the surface of solid specimens including X-ray (EDX). SEM was used to identify the surface morphology (texture), crystalline structure and orientation of materials. EDX function was used to determine surface chemical topography and composition. The images of fresh and spent catalysts were characterized by using the smartSEM software. About 0.1g of the samples was pressed under vacuum condition to remove moisture before it was subsequently inserted into the sample holder of the SEM instrument. Then, the images of fresh and catalyst specimens were scanned by varying the magnification until suitable images were analysed.

3.4.4 Transmission Electron Microscopy

Transmission electron microscopy (TEM) employs high-energy beam of electrons to get more information on crystal structure such as dislocation and grain boundaries. Potassium and yttrium doped LaCuO₃ were examine on the instrument FEI Titan G2 80-300 inclusive the with imaging filter GIF TRIDIEM from Gatam Inc., and $4k \times 4k$ resolution CCD camera with the model US4000. Before placing the synthesized catalyst on to the sample holder of TEM instrument, the fresh and spent samples were withdrawn

 \leq 0.1g and were kept in the sample presser in presence of vacuum conditions to remove moisture on the surface. The catalyst was mixed with ethanol to reduce aggregation. From the resultant slurry mixture, a drop was placed on a copper grid which the hollow space filled with carbon. Finally, the dried sample was used for characterization.

3.4.5 Fourier Transform Infrared Spectroscopy

Fourier transform infrared analysis work was used to identify the functional groups that absorbed light and excited at different frequencies. The electromagnet wave was radiated within the infrared region that has a longer wavelength and a lower frequency than visible light. About 0.1 g catalyst samples were loaded onto the sampling port and scanned by using Nicolet iS5 FTIR spectrometer, Waltham, USA.

3.4.6 X-ray Photoelectron Spectroscopy

The X-ray photoelectron spectroscopy of the model JEOL JPS-9200 was used to get information about surface and nature of the chemical bond exists between the elements. The XPS equipment could detect all elements except hydrogen and helium. Using a standard Al K α source with an X-ray power of 300 W, analyser passed energy of 10 eV and energy resolution less than 0.65 V on the sample. To correct all XPS spectra, the binding energy of C1s was kept at 284.6 eV.

اونيۇرسىيتى مليسىيا قھى السلطان عبدالله 3.4.7 Raman Spectroscopy II MALAYSIA PAHANG AL-SULTAN ABDULLAH

Raman spectroscopy was used to identify the molecular vibration of the prepared catalyst. It is most widely used technique for studying chemical bonding and intramolecular bonds. The spent and fresh catalysts were carried out on a Thermo Fisher Scientific (DXR Raman Microscope) and it had a laser beam emission wavelength of 532 nm.

3.4.8 Brunauer-Emmett-Teller

Brunauer-Emmett-Teller (BET) was used to analyse the sample surface area by means of adsorption of multilayer to determine total pore volume and average pore diameter. The sample characterization was carried out on the Micrometrics ASAP-2020 apparatus by conducting N₂ adsorption-desorption isotherms at 77 K and the data was interpreted by using the Micrometrics ASAP 2020 V.3.04 software. Earlier to the

analysis, the specimen was thermally pre-treated for 1 h by flowing N_2 at 573 K to remove the moisture and adsorbed impurities on the catalyst surface.

3.5 Ethanol Dry Reforming Reaction

The EDR reaction was carried out in a quartz tubular fixed-bed reactor with the dimensions (L = 17 inches, Outer diameter, O.D = 3/8 inches) at the reaction temperatures ranged from 923 to1023 K and various molar feed ratios of C₂H₅OH:CO₂ from 1:2.5 to 2.5:1 under atmospheric pressure. About 0.1 g of catalyst was sandwiched by quartz wool in the middle of quartz tube reactor placed vertically in a split tubular furnace. Before the reaction, H₂ reduction was carried out in situ from room temperature to 973 K with a heating rate of 10 K min⁻¹ in a flowing 50% H₂/N₂ mixture (60 ml/min). The high gas hourly space velocity, GHSV = 42 L gcat⁻¹ h⁻¹ and particle size of the catalyst within 125-160 µm for each run were employed to ensure the negligibility of internal and external transport. The schematic diagram of the reactor system is shown in Figure 3.4.



Figure 3.4 Schematic diagram of the EDR reactor setup

Ethanol was fed to the fixed-bed reactor from the top by using a KellyMed KL-602 model Syringe pump. The flow rates of gaseous CO_2 , H_2 and N_2 carrier gas were regulated by Alicat mass flow controllers. The outlet gas products of reactor were collected in gas sampling bag (Tedlar bag) and the gas sample was then analysed using Agilent 6890 GC Gas Chromatograph series, which was equipped with thermal

conductivity detector (TCD). Before the gaseous product entered gas chromatography, it passed through the cold trap and Drierite to collect the liquid of unconverted ethanol and remove the moisture, respectively. The bubble flow meter was used in this research for measuring the flow rate of inlet and outlet gases in each reaction.

The mass flow controllers and syringe pump were calibrated by using N_2 , CO_2 and liquid ethanol to the EDR system, respectively. Five (5) points were measured for each calibration and results of calibration obtained from linear plot of signal versus actual flow rate. A GC sampling was performed twice to minimize human errors. Besides, initial, middle, and final setting of parameters were repeated to ensure reproducible results of the reaction study.

3.5.1 Gas Chromatography

The concentrations of gaseous components were measured by using Agilent 6890 Series GC and thermal conductivity detector. The gas flowed through HP Plot Q ($30 \text{ m} \times 0.53 \text{ mm} \times 40 \text{ }\mu\text{m}$) capillary column in helium carrier gas inside oven under constant temperature of 353 K and 393 K. The results were compared with calibration curves to estimate the accurate elemental compositions and retention time. The calibration curves were derived from the 4-5 runs of the standard gases at different pressures. The standard gases with composition and retention time information are shown Table 3.4. The calibration curves can be seen from the previous author who used the same equipment in the same laboratory (Osazuwa, 2017).

Compound	Composition (%)	Retention time (min)
CO ₂	19.98	10.07
H_2	25.06	5.39
CH4	5.05	7.29
СО	24.89	13.73

Table 3.4 Standard gas information

3.5.2 Ethanol Dry Reforming Reaction Parameters

The reaction species of EDR were calculated based on mole balance. The ethanol liquid $(X_{C_2H_5OH})$ and carbon dioxide (X_{CO_2}) conversions are shown in Equations (3.2) and (3.3).

$$X_{C_{2}H_{5}OH}(\%) = \frac{F_{C_{2}H_{5}OH}^{In} - F_{C_{2}H_{5}OH}^{Out}}{F_{C_{2}H_{5}OH}^{In}} \times 100\%$$
(3.2)

$$X_{CO_2}(\%) = \frac{F_{CO_2}^{ln} - F_{CO_2}^{Out}}{F_{CO_2}^{ln}} \times 100\%$$
(3.3)

where $F_{C_2H_5OH}^{In}$, $F_{C_2H_5OH}^{Out}$, $F_{CO_2}^{In}$ and $F_{CO_2}^{Out}$ denote flow rates of ethanol feed, unconverted ethanol, carbon dioxide feed and unconverted carbon dioxide, respectively. The instantaneous selectivity of a reaction species (*S_i*) and overall yield (*Y*_{H2}, *Y*_{CO} and *Y*_{CH4}) calculations are shown in the Equations (3.4), (3.5), (3.6) and (3.7).

$$S_{i}(\%) = \frac{r_{i}}{\sum_{i=H_{2},CO,CH_{4}} r_{i}} \times 100\%$$
 (3.4)

$$Y_{H_2}(\%) = \frac{2F_{H_2}^{Out}}{6F_{C_2H_3OH}^{In}} \times 100\% \qquad (3.5)$$

$$Y_{CO}(\%) = \frac{F_{CO}^{Out} - S}{F_{CO}^{In} + 2F_{C_2H_5OH}^{In}} \times 100\% \qquad (3.6)$$

$$Y_{CH_4}(\%) = \frac{F_{CH_4}^{Out}}{F_{CO_2}^{In} + 2F_{C_2H_5OH}^{In}} \times 100\%$$
(3.7)

3.6 Preliminary Works

The results from preliminary works before EDR experiments such as blank test and determination of mass and heat transport limitations are discussed in this chapter. The rate limiting conditions for EDR was desirable so that all the subsequent results obtained from the EDR experiments would be valid.

3.6.1 Blank Test Results

The blank test was conducted in the empty reactor that would be used for the EDR reaction at 973 K. A gaseous flow containing reactants with a CO₂:C₂H₅OH feed ratio of 1 was fed into the reactor for 8 h under atmospheric pressure. To achieve the total flow rate of 70 ml/min, N₂ gas was added as a carrier gas. The results of GC analysis detected the existence of H₂ and CO peaks, indicating that ethanol decomposition is inevitable under EDR reaction conditions. However, both CO₂ and C₂H₅OH conversions acquired from the blank test had relatively low values of 15.08% and 9.72%, respectively. Indeed, C₂H₅OH and CO₂ conversions obtained from EDR reaction with the presence of catalyst are substantially higher that these values (as discussed later in Chapter 4 & 5). Therefore, the improvement of catalytic activity by using Cu-based perovskite catalysts in EDR reaction was attributed to the physicochemical properties and efficient contribution of utilized catalysts.

3.6.2 Transport Resistance Estimations

The heterogeneous catalytic reaction is conventionally arranged in seven sequential steps including the interaction between reactants and the surface of catalyst (Fogler, 2010). The seven steps are described below and illustrated in Figure 3.5:

- 1. Mass transfer of reactants from bulk fluid to the external catalyst surfaces.
- 2. The transport of gaseous reactants by diffusion process via the pores into the particles
- 3. The reactants adsorption onto the internal surface of the catalyst.
- 4. Reaction on the internal catalyst surface.
- 5. Desorption of products from the surface.
- 6. Transport of products via the pores to the external catalyst surface
- 7. Mass transfer of products from the external surface to the bulk fluid.



Figure 3.5 Individual steps of a heterogeneous catalytic reaction. Source (Mitchell, 2007)

As seen in Figure 3.5, the chemical reaction kinetics was illustrated by steps 3, 4 and 5. However, steps 1 and 7 represent the external transport estimation. Steps 2 and 6 are related to the internal transport processes. The EDR process operated away from transport-limited area to reduce the influence of both mass and heat transfer resistance in kinetics study. Four main transport resistances were selected and eradicated from the EDR reaction. The parameters and properties in the EDR reaction system considered for estimation of the transport resistances are shown in Table 3.5. The calculations are illustrated in Appendix B.

Parameters	Value	References
А	$4.90 \times 10^{-5} m^2$	Reactor tube property
C_{Ab}	$4.90 \times 10^{-5} \text{ mol cm}^{-3}$	Experimental condition
С _{р-С2Н5ОН}	$3.06 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$	(Perry & Green, 2008)
C _{p-CO2}	1.22×10 ³ J kg ⁻¹ K ⁻¹	
C _{p-N2}	$1.16 \times 10^3 \text{J kg}^{-1} \text{K}^{-1}$	
h_{w}	30 J m ⁻¹ s ⁻¹ K ⁻¹	
R	8.314 J mol ⁻¹ K ⁻¹	
$\lambda_{\rm C2H5OH}$	$0.13 \text{ Jm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$	

Table 3.5 properties employed in the calculation of transport resistance

Table 3.5 Continued

Parameters	Value	References
λ _{CO2}	0.07 J m ⁻¹ s ⁻¹ K ⁻¹	
λ_{N2}	0.07 J m ⁻¹ s ⁻¹ K ⁻¹	
λ_{m}	8 J m ⁻¹ s ⁻¹ K ⁻¹	
μс2н5он	2.59×10 ⁻⁵ kg m ⁻¹ s ⁻¹	
$\mu_{\rm CO2}$	3.92×10 ⁻⁵ kg m ⁻¹ s ⁻¹	
μ_{N2}	4.08×10 ⁻⁵ kg m ⁻¹ s ⁻¹	
D_{eff}	1.21×10 ⁻⁵ m ⁻² s ⁻¹	Calculation
D_g	$1.13 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$	Calculation
d _p	1.95×10 ⁻⁴ m	Experimental condition
d_t	7.9×10 ⁻³ m	Reactor tube property
EA	$1.13 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$	Experimental condition
$-\Delta H_r$	302.10 kJ mol ⁻¹	Experimental condition
-r _{exp}	$3.46 \times 10^{-5} \text{ mol gcat}^{-1} \text{ s}^{-1}$	Experimental condition
R _p	9.75×10 ⁵ m	Experimental condition
Т	973 K	Experimental condition
V	70 ml m ⁻¹	Experimental condition
3	0.8	(Adhikari, Fernando, &
لان عبدالله	سيتي مليسيا قهغ السلط	Haryanto, 2008)
ρ _e INIVER	SITI M 3.35 g cm ⁻³ A PA	Experimental condition
ρ _b L-SU	0.67 g cm^{-3}	LAH $(1-\varepsilon)\rho_{c}$
$ ho_{ m g}$	0.435 kg m ⁻³	Calculation
σ_{c}	0.8	(H. S. Fogler, 2005)
τ	3.0	(H. S. Fogler, 2005)
ω_p	0.4	(H. S. Fogler, 2005)

3.6.2.1 External Mass Transfer Resistance

External mass transfer refers to the molecular diffusion from one phase to another phase. The criterion about the absence of external mass transport resistance can be expressed in Equation (3.8) (Mears, 1971; Oh, Baron, Sloan, & Hegedus, 1979)

$$\frac{(-r_{exp})\rho_b R_p n}{K_c C_{Ab}} < 0.15$$
(3.8)

Where,

n = reaction order

 R_p = catalyst particle radius (m)

 $k_c = mass transfer coefficient (cm s⁻¹)$

 ρ_b = bulk density of catalyst bed (g cm⁻³)

 C_{Ab} = bulk gas phase concentration of ethanol in (mol cm⁻³)

 $(-r_{exp})$ = reaction rate (mol g_{cat}^{-1} s⁻¹) (the main point of reaction rate gained from the experimental data for calculation)

The mass transfer coefficient (k_c) can be calculated from Equation (3.9) (Upadhyay, 1977).



The details of calculation for Equation (3.8) are detailed in Appendix B. From Equation (3.8), the calculated amount of the Mears criterion in this study is about 1.22×10^{-4} , which is lower than 0.15 suggesting that the external mass transfer resistance was negligible for the EDR reaction.

3.6.2.2 Internal Mass Transfer Resistance

The internal mass transfer resistance can be obtained from the diffusion of reactants and products via the catalyst pores. The Weisz-Prater criterion was employed to get negligible pore diffusion resistance (Fogler, 2006) as shown in Equation (3.10);

$$\frac{(-r_{exp})\rho_b R_p^2}{D_{eff} C_{As}} < 1 \tag{3.10}$$

where

 ρ_c = catalyst pellet density (g cm³)

 D_{eff} = effective diffusivity of CO₂ into a mixture of C₂H₅OH and N₂ (m²s⁻¹)

 C_{Ab} = Concentration of C_2H_5OH on the surface of catalyst (mol cm⁻³)

The C₂H₅OH concentration on the surface of catalyst (C_{Ab}) was equated to C₂H₅OH concentration in the bulk gas-phase (C_{As}). The effective diffusivity was computed using Equation (3.11) as below;

$$\mathbf{D}_{\rm eff} = \frac{D_g \omega_{p \, \sigma_c}}{\tau} \tag{3.11}$$

Where

 τ = tortuosity

 ω_p = porosity of catalyst pellet

 σ_c = construction factor

 D_g = diffusivity of CO₂ into a mixture of C₂H₅OH and N₂ (m²s⁻¹)

The detailed calculation for Equation (4.3) is shown in Appendix B. the value of Weisz-Prater criterion in this study was about 2.23×10^{-3} indicating the negligible of internal mass transfer resistance for EDR reaction.

3.6.2.3 External Heat Transfer Resistance

The external heat resistance contained the temperature difference between the surface of the catalyst and the bulk gas phase. According to the previous study, the external heat transport resistance in reactor may be negligible and Mears criterion was computed by using Equation (3.12) (Fogler, 2006).

$$\frac{(-\Delta H_r)(-r_{exp})R_p^2 \rho_b E_A}{hRT_b^2} < 0.15$$
(3.12)

Where

 $E_A = activation energy (J mol⁻¹)$

 $-\Delta H_r$ = reaction heat for EDR (J mol⁻¹)

R = ideal gas constant (J mol⁻¹ K^{-1})

 T_b = reactant gas bulk temperature (K)

h = heat transfer coefficient between catalyst and gas mixture (J $m^{-2}s^{-1}K^{-1}$).

The relation of the heat transfer coefficient, mass transfer and heat of j-factor was proposed by Colburn-Chilton (Perry & Green, 2008) as follows;

$$j_{D} = j_{H} = \frac{hPr^{\frac{2}{3}}}{C_{pg\rho_{g}U}}$$
(3.13)

where

 P_r = Prandtl number

 $j_{\rm H}$ = heat factor of j-factor ($j_{\rm H} = j_{\rm D}$)

U = superficial gas velocity (m s⁻¹)

 ρ_g = gas mixture density (kg m⁻³)

 C_{pg} = specific heat capacity of feed gas mixture at const pressure (J kg⁻¹K⁻¹)

From Equation (3.13), the left-hand side value was obtained at about 3.60×10^{-5} , which is also less than 0.15. Therefore, the effect of external heat transfer resistance was negligible for the conditions of the EDR reaction.

3.6.2.4 Intraparticle Heat Transfer Resistance

The intraparticle heat transfer is the thermal energy transport from an external surface of catalyst to the pores of its particles. However, smaller particle size may lead to a significant drop in pressure across the catalyst bed (S. Y. Foo, 2012) Therefore, the range of particle size important part for limitation of internal heat transports influence. The internal heat transfer resistance may be estimated when the reaction rate and experimental conditions of EDR reaction are fixed with the Anderson criterion in Equation (3.14).

$$\frac{|(-\Delta H_r)|(-r_{exp})\rho_b E_A R_p^2}{\lambda_p R T_s^2} < 0.75$$
(3.14)

where

 λ_p = catalyst pellet thermal conductivity (J m⁻² s⁻¹ K⁻¹) $T_b = T_s$ = reactant gas bulk temperature (K)

The calculation details for internal heat transfer resistance are illustrated in Appendix B. The bulk temperature of gas phase (T_b) was considered to be equal to the surface of the catalyst. Wilhelm, Simbeck, Karp, and Dickenson (2001) suggested that the thermal conductivity of the catalyst pellet (λ_p) can be estimated via the thermal conductivity of the catalyst material (λ_m) as given in Equation (3.15);

$$\log \left(\lambda_{\rm p} \times 10^5\right) = 0.859 + 3.12 \left(\frac{\lambda_m}{\omega_p}\right) \tag{3.15}$$

Where λ_m = thermal conductivity of the catalyst material (J m⁻¹ s⁻¹ K⁻¹). The calculated left-hand side value of Equation (4.7) was about 8.40×10⁻²⁹, which is lower than 0.75. This suggests the negligible resistance to intraparticle heat transfer to the EDR reaction.

3.6.2.5 Effects of Wall and Radial Heat Dispersion

Dixon (1997) proposed that the effect of wall heat transfer is negligible when the ratio of reactor tube diameter (dt) to the diameter of the catalyst particle (dp) is more than 4. In the EDR reaction, the ratio of dt/dp was about 40.5. Thus, the wall effect was insignificant. However, a high ratio of dt/dp, concentration gradients and radial temperature become important (Dixon, 1997). Therefore, the effect of radial heat dispersion was determined via the Mears criterion in Equation (3.16).

$$\left(\frac{E_a}{RT_w}\right) \left(\frac{\left|\left(-\Delta H_r\right)\right|\left(-r_{exp}\right)\rho_b R_p^2\left[\frac{(1-\varepsilon)}{(1-b)}\right]}{4\lambda_p T_w}\right) \left(\frac{1}{8} + \frac{B_p}{Bi_w R_t}\right) < 0.05$$
where

$$T_w = T_b = \text{tube wall temperature (K)}$$

$$R_t = \text{radius of reactor tube (m)}$$

$$b = \text{inert solids fraction of the catalyst bed}$$

$$\varepsilon = \text{void fraction in the catalyst bed}$$
(3.16)

Wall biot number (Bi_w) may be calculated using Equation (3.17).

$$\operatorname{Bi}_{w} = \frac{h_{w}d_{p}}{\lambda_{p}}$$
(3.17)

where

 d_p = diameter of the catalyst particle (m)

 h_w = reactor tube wall heat transfer coefficient (quartz tube)

$$\lambda_p$$
 = thermal conductivity of the catalyst pellet (J m⁻² s⁻¹ K⁻¹)

As the result, the calculated left-hand side of Equation (3.16) was about 2.23×10^{-8} , which was very far from 0.05. Significantly, the EDR reaction was in negligible radial heat dispersion effects based on Mear's criterion.

3.6.3 Thermodynamics Analysis

Thermodynamics of the EDR reaction was analysed to describe its feasibilities and any side reactions while varying reaction temperature using chemEq Version 1.0 software. As seen in Figure 3.6, the change of Gibbs free energy in ethanol dry reforming whilst the summarized results are described in Table 3.6. Based on thermodynamic features in that figure and Table 3.6, the minimum operating temperature of EDR should be more than 596 K. Furthermore, reactions that are significant during the process include ethanol decomposition, ethanol dehydrogenation, methane dry reforming, methane decomposition and acetaldehyde since these reactions could affect the production of syngas and product selectivity.



Figure 3.6 Change of Gibbs free energy for all EDR reactions at various temperatures

Table 3.6 Summar	y of thermody	ynamics of th	ne EDR reaction

Reaction No.	Reaction	Temperature	ΔG
		(K)	(kJmol ⁻¹)
	Ethanol dry reforming		
R1	$C_2H_5OH + CO_2 \rightarrow 3H_2 + 3CO$	>596	(-)

Table 3.6 Continued	
---------------------	--

Reaction No	o. Reaction	Temperature	ΔG
		(K)	(kJmol ⁻¹)
	Ethanol dehydrogenation		
R2	$\rm C_2H_5OH \rightarrow CH_3CHO + H_2$	>688	(-)
	Ethanol decomposition reaction		
R3	$\mathrm{C_{2}H_{5}OH} \rightarrow \mathrm{CH_{4}+CO+H_{2}}$	>214	(-)
	Acetaldehyde reaction		
R4	$\rm CH_3CHO \rightarrow \rm CO + \rm CH_4$	>149	(-)
R5	$\rm CH_3CHO + \rm CO_2 \rightarrow \rm 3CO + \rm 2H_2$	>574	(-)
	Methanation reaction		
R6	$4\mathrm{H}_2 + \mathrm{CO}_2 \rightarrow \mathrm{CH}_4 + 2\mathrm{H}_2\mathrm{O}$	>865	(+)
R7	$3H_2 + CO \rightarrow CH_4 + H_2O$	>893	(+)
	Dry reforming of methane		
R8	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	>914	(-)
	Decomposition of methane		
R9	$CH_4 \rightarrow C + 2H_2$	>820	(-)
	Water-gas shift reaction		
R10	$CO + H_2O \rightarrow CO_2 + H_2$	>1077	(+)
	Boudouard reaction		
R11	$CO \rightarrow 0.5C + 0.5CO_2$	>971	(+)

Source: (W. Wang & Wang, 2009).

3.7 Concluding Remarks

The EDR reaction requires catalyst that enables running the reaction under moderate temperatures. The catalyst samples were prepared using the citric sol-gel method. The composition of metals is in according with the exact ratio for the perovskite structure. The reduced catalysts and used catalysts were analysed by using BET surface and porosity, XRD, TPR, SEM-EDX, XPS and FTIR techniques. The conditions of free mass transfer limitation were ensured before the reaction tests. The EDR reaction test was run for the ACuO₃ catalyst where A is lanthanum and cerium. From the reaction test, the catalyst showing the highest conversion, selectivity, and yield of desired products at

various reaction temperatures and feed ratio will be preferred. After the post-reaction characterization, the preferred composition of the catalysts was used to prepare the catalysts with yttrium or potassium precursors for B metal in the $A_{1-x}B_xCuO_3$ catalyst. The same procedure was followed for the catalyst characterization. The optimal portions of metal in the Cu-based perovskite would be tested for longevity.

The low conversion of the reactants in a blank test without catalysts at 973 K and atmospheric pressure for 8 h proved the importance of the prepared catalyst in the EDR reaction. Based on the equations under the Weisz-Praters and Mears criteria, the conditions, and properties of the reactant for the reaction tests were under free internal and external mass transfer limitation. The intraparticle and external heat transfer resistance were also not significant to the setup of the reactor. The thermodynamic analysis showed that the reaction temperature should be higher than 596 K to achieve the spontaneity. The conditions would be employed in the study of the reaction catalysis study.

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CHAPTER 4

TRIOXIDE PEROVSKITE OF COPPER AND LANTHANUM OR CERIUM: CATALYST CHARACTERIZATION AND ETHANOL DRY REFORMING REACTION STUDY

4.1 Overview

This chapter discusses relationship between characteristics of the rare earth elements copper-based perovskite (LaCuO₃ and CeCuO₃) catalysts prepared in this study and mechanism of the ethanol dry reforming (EDR) reaction. The EDR reaction tests were carried out at various reaction temperatures from 973 to 1073 K and partial pressure of C_2H_5OH and CO_2 from 20 to 50 kPa. The reaction data is regressed using Sigmaplot 10 by fitting appropriate models that are commonly used in reaction study. The explanation of trendlines will be based on the equation of the models.

4.2 Catalyst Characterization

اونيۇرسىتى مايسيا في Surface Area and Pore Size

The surface areas of the freshly reduced catalysts were measured according to the BET method and the results are presented in Table 4.1. The surface area of the LaCuO₃ catalyst is higher than Lanthana-based perovskite like the catalyst that was prepared by J. Yang et al. (2013) and ceria-based catalyst in this study. The catalysts exhibited type V adsorption isotherm, and can be seen in Appendix C, according to the IUPAC classification indicating that they were all mesoporous catalysts.

Table 4.1 BET Analysis Results

Catalyst	Surface area (m ² /g)	Pore Size (nm)
LaCuO ₃	59.52	17.09
CeCuO ₃	1.8	10.09

4.2.2 X-ray diffraction of LaCuO₃ and CeCuO₃ catalyst

The X-ray diffraction (XRD) spectra of LaCuO₃ and CeCuO₃ reduced catalysts are exhibited in Figure 4.1. The Joint Committee on Powder Diffraction Standards (JCPDS) database was used as the reference for interpreting the XRD spectra of the catalyst specimens. From the XRD analysis of LaCuO₃ in Figure 4.1, the diffraction lines registered orthorhombic (JCPDS#82-2142) structure with high crystallinity and well-defined. These peaks could be attributed to metal oxides Cu₂O (JCPDS 34-1354) which formed when substituting metal ions did not fully diffuse into La₂O₃ during the formation of LaCuO₃ prepared via high-temperature calcination. Its characteristic peaks, $2\theta = 23.68$, 31.87, 33.11, 40.37, 47.29, 53.10, 58.15, 58.75 and 67.52 strongly indicated the presence of perovskite structure, which are more than LaCoO₃ rhombohedral structure reported by Luo et al. (2015) in their benzene oxidation study. All the intense XRD peaks in the diffractogram of CeCuO₃ sample between the scanning ranges from 20 - 70 indicate high crystallinity (JCPDS#81-0792) in the form of cubic structure. They are at $2\theta = 28.6$, 33.1, 35.7, 39.2, 47.5, 56.4, 59.1, and 69.4 for the (111), (110), (002), (202), (311), (211) and (200) planes, respectively.

UMPSA



Figure 4.1 XRD patterns of reduced (a) LaCuO₃ (b) CeCuO₃ catalysts.

Using the Debye–Scherrer equation, the average crystallite size was calculated by taking half width at half maximum (HWHM) of the most intense peak. This was done by the Rigaku Miniflex II software. Table 4.2 and Table 4.3 show the detected crystals of the catalysts and their respective sizes. The identity of perovskite was clearly seen in LaCuO₃, which is La₂CuO₄ but not in CeCuO₃. No crystal of combination between cerium and copper was in the result. The lanthanum-promoted perovskite crystal size even bigger after the reaction. All metal oxide crystals were missing and copper metal appeared after the reaction but not lanthanum and cerium metals both naturally exist in double hexagonal close-packed structure and face-centred-cubic structure, respectively (Luo et al., 2015).

LaCuO3 Catalys	st Cryst	allite Size (nm)
Crystal	Fresh	Spent
La ₂ CuO ₄	1.27	2.97
La ₂ O ₃	5.17	-
Cu ₂ O	UMPSA	-
Cu	-	4.10

Table 4.2 Crystallite size of the LaCuO₃ catalyst.

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Table 4.3 Crystallite size of the CeCuO₃ catalyst.

CeCuO3 Catalyst	Crysta	llite Size (nm)
Crystal	Fresh	Spent
CeO ₂	3.74	-
Cu ₂ O	3.10	-
Cu	-	4.70

4.2.3 Temperature Programmed reduction

The TPR profile was used to study the presence of metal oxide in the catalysts that can be reduced by hydrogen flowing under elevating temperatures. Two reduction temperatures were particularly observed from both catalysts, as seen in Figure 4.2. Initial peak (P1) occurs at 260°C corresponding to H₂ consumption 0.71 mmol/g_{cat} for the LaCuO₃ catalyst. At lower temperatures, partial reduction of La₂CuO₄ to a delafossiatetype phase of LaCuO_{2+x} consisting of monovalent Cu or Cu²⁺, as shown in Equation (4.1), was viable (Sarno, Luisetto, Zurlo, Licoccia, & Di Bartolomeo, 2018). This can be observed from the previous XRD analysis in Figure 4.1 for the spent catalyst at a reduction temperature of 750°C (Leontiou, Ladavos, Giannakas, Bakas, & Pomonis, 2007). The initial peak was also associated with the reduction of Cu²⁺ to Cu⁺, leading to the formation of Cu₂O as expressed by Equation (4.2). The second peak (P2) of reduction temperature was improperly formed, ramping up around 212°C and reaching a climax at 427°C before declining towards 527°C. This peak corresponds to the 0.24 mmol/gcat of H₂ consumption, likely attributed to the reduction of copper in the metallic state as given by Equations (4.3) and (4.4) (Yuan et al., 2011).

$$2La_{2}CuO_{4} + H_{2} \rightarrow 2LaCuO_{2+x} + La_{2}O_{3} + H_{2}O \quad T=230-320^{\circ}C$$
(4.1)

$$2La_2CuO_4 + H_2 \rightarrow Cu_2O + 2La_2O_3 + H_2O T = 230-320^{\circ}C$$
(4.2)

$$Cu_2O + H_2 \rightarrow 2Cu^0 + H_2O T = 420-550°C$$
 (4.3)

$$2LaCuO_{2+x} + (2x+1)H_2 \rightarrow 2Cu^0 + (2x+1)H_2O + La_2O_3 T = 420-550^{\circ}C$$
(4.4)

The TPR profile for CeCuO₃ likely shows two overlapped peaks of the reduction temperature as well, occurring at 480 °C and 506 °C. Approximately 0.34 mmol/g_{cat} and 0.48 mmol/g_{cat} of H₂ consumption were measured for P1 and P2, respectively. P1 and P2 represent from the respective α and β -reduction of cerium from Ce³⁺ to Ce²⁺ based on Equation (4.5) (Luo et al., 2015). Besides perovskites, impurities such as Cu, CuO and rare earth oxides were present. However, the reduction of CuO was expected first due to its more favourable standard Gibbs free energy (98.9 kJ/mol for CuO reduction compared to 24.4 kJ/mol for CeO₂ reduction) at this temperature. This observation aligns with the diffractogram peaks corresponding to CuO and CeO₂ detected from previous XRD analysis result shown in Figure 4.1. Additionally, Figure 4.2 reveals the pure crystalline phase of metallic copper alongside CeCuO₃, supporting the second reduction peaks associated with the surface reduction of a metal oxid(Luo et al., 2015)e (Maluf & Assaf, 2009).



Figure 4.2 TPR characterisation of (a) LaCuO₃ (b) CeCuO₃ catalysts.

4.2.4 Fourier Transform Infrared Spectroscopy

According to the FTIR analysis in Figure 4.3, LaCuO₃ spectra show strong and welldefined absorption bands. The band centred in the interval of 400-700 cm⁻¹ corresponds to the metal-oxygen bonds such as La-O. The band at around 846 nm demonstrates the presence of the Cu-O bonds in the perovskite structure [30]. The bands observed in the 1000–1500 cm⁻¹ regions are associated to the carbonate and C-H groups generated due to the chemisorption of CO₂ in ambient. The broad band around 3400-3500 cm⁻¹ indicates O-H stretching of adsorbed water molecules. Unfortunately, there is no peak could be observed for CeCuO₃. This might be due to the broken bonding of lanthana, copper oxide and carbonaceous material on the catalyst like what had happened to titania when cerium was promoted too much for HCHO oxidation reaction (Zheng et al., 2024).



Figure 4.3 FT-IR of LaCuO₃ and CeCuO₃ freshly reduced catalysts

4.2.5 Raman spectroscopy

Raman spectroscopy analysis was carried out on fresh catalysts of LaCuO₃ and CeCuO₃ to investigate phase changes and type of deposited carbons on catalyst surface after the EDR reaction. Figure 4.4 shows Raman spectra for fresh catalysts. Three peaks detected at Raman shift of 295Cm⁻¹ (P1) for both catalysts were due to the oscillation of Cu-O bond in Cu₂O phase corroborated by XRD results. However, the characteristic peaks of 279, 325 and 385 cm⁻¹ belonging to La₂O₃ phase were not identified on Lapromoted catalyst. It could be due to the fine dispersion of La₂O₃ particles on support surface with small crystallite size. Furtherly, the characteristics peaks of CeO₂ were clearly identified at 292 (P1), 464 (P2), 1130 (P3) cm⁻¹ respectively. These clearly distinctive peaks indicate that the rare earth metal oxide did not disperse well on others due to the presence of carbon deposition on the freshly reduced catalyst (Wijaya et al., 2022).



Figure 4.4 Raman spectroscopy of Fresh LaCuO₃ and CeCuO₃ catalysts

4.3 Ethanol Dry Reforming Reaction

Effects of reaction temperature and feed ratio to the conversion of the reactants were discussed separately for both lanthanum and cerium-based perovskites.

4.3.1 Effect of Reaction Temperature

The activity of LaCuO₃ and CeCuO₃ catalysts was investigated by varying the reaction temperatures from 725 to 800 °C (998 – 1073 K). Although the reaction was run continuously, fresh catalyst was used for each reaction temperature. Pressure of reactants at constant 20 kPa was exerted while they were continuously fed to the reactor and ethanol was preferred as the key reactant for conversion calculation at steady state. The main reaction in Equation (4.6) was the basis of the conversion calculation. The GC results indicate that the reaction achieved the steady state approximately 30 min after the reactor temperature reached the desired values.

$$C_2H_5OH + CO_2 \rightarrow 3H_2 + 3CO \tag{4.6}$$

Figure 4.5 exhibits the conversion for both catalysts, which increased exponentially by the reaction temperature. The conversions of CO_2 and C_2H_5OH are 15% and 75%, respectively, at the reaction temperature of 998 K, indicating that the latter increased due

to both catalysts as compared to the blank test (as discussed earlier in Section 3.6.1). Using regression with the exponential rise equation (with R² of 99.9% and 94.2% fitness, respectively), we found that LaCuO₃ and CeCuO₃ catalytic EDRs could hypothetically achieve complete conversion at 980 and 1113 K. LaCuO₃ catalyst was relatively active, showing higher CO₂ conversions than CeCuO₃ catalyst in the EDR. These results were identical to report that are presented in Table 2.2 such as M. Wang et al. (2024), T. Li et al. (2023) and Cai et al. (2020). These conversion differences at the same reaction temperatures also indirectly indicate that the LaCuO₃-catalysed reaction has lower activation energy. The high activity of the LaCuO₃ catalyst is coincident with the finding of metal oxide species in the FTIR analysis such as La-O and Cu-O, and their low reduction temperatures in the TPR analysis. BET surface of LaCuO₃ catalyst was 3 time higher as discussed earlier in the previous subchapters. This would also be the factor the high activity. Thus, lanthana and copper oxide might have played their important role in catalysing the EDR reaction and this was also reported by Bahari et al. (2017) while studying La-impregnated nickel/alumina and Cai et al. (2020) in their Cu-based perovskite study.



Figure 4.5 Effect of reaction temperatures of LaCuO₃ and CeCuO₃ from 998-1073 K; $P_{C2H5OH} = P_{CO2} = 20 \text{ kPa}.$

Side reactions might have also occurred because the H_2/CO ratio was greater than unity, which differs from the stoichiometry of the EDR reaction in Equation (5.5). As

illustrated in Figure 4.6, both catalysts produced H_2/CO ratios ranging from 1.7 to 1.0 through linear declination until 1073 K. At 1000 K, the ethanol decomposition reaction that produces free carbon can be proposed as shown in Equation (4.7), which probably justified why carbon deposit was high at low reaction temperatures (Kale & Gaikwad, 2014a)

$$C_2H_5OH \rightarrow C + CO + H_2 \tag{4.7}$$

Kale and Gaikwad (2014b) reported similarly this decrease, albeit with a different trend – exponential decay. A high ratio of H_2/CO is favourable as feedstock for Fischer-Tropsch synthesis. The ethanol dehydrogenation reaction likely caused the high ratio at the low temperatures, but analysis of the unconverted ethanol and other hydroxyl compounds could not be done due to the limitation of the GC column and TCD detector to separate and detect alcohol molecules. Consequently, the details of side reactions could not be proposed. Nevertheless, those reactions probably began to disappear at 1040 K, which corresponds to the midpoint of the sigmoid trendline as expressed in Equation 4.8)

$$Y_{ij} = Y_0 + \frac{A_S}{1 + \exp\left(\frac{T_0 - T}{B_S}\right)}$$
(4.8)

where, Y denotes yield, i and j are species and catalyst, respectively. A_S, B_S, Y₀ and T₀ are constants from regression, as summarized in **PAHANG**

Catalyst	Species	As	Bs	Y0	To	R ²
La _s CuO ₃	H ₂	10.875	7.830	43.680	1042.088	1.0
	CO	8.206	10.809	39.433	1046.890	1.0
CeCuO ₃	H_2	32.902	18.473	23.193	1046.956	1.0
	CO	20.729	21.407	21.272	1038.040	1.0

Table 4.4 Parameters of sigmoid equation for yields

in the four yield plots. The increment of CO yield toward high temperature for LaCuO₃ catalyst exceeded that of H₂, both following sigmoid trends. Additionally, the yields of both products from EDR using the LaCuO₃ catalyst were higher than those using the CeCuO₃ catalyst.



Figure 4.6 Effect of reaction temperature w.r to H_2 & CO yield and H_2 /CO ratio of LaCuO₃ and CeCuO₃ catalyst from 998 to 1073 K, $P_{CO2} = P_{C2H5OH} = 20$ kPa.

Methane yield increased over reaction temperature for both catalysts where LaCuO₃ catalyst performed better but it was unlike the thermodynamics analysis (B. Kumar et al., 2016) where, methane concentration was high at the reaction temperatures below than 998 K. This difference was probably due to the different catalyst used in their study, which were other than copper-based ones. The increment revealed methane selectivity of the catalyst, and the increment significantly followed either sigmoid or peak trend as shown in Figure 4.7. On the CeCuO₃ catalyst, the same trend appeared at lower methane yield. The increment of methane at high temperatures for the EDR reaction was also reported by Dong Cao et al. (2017) using the Cu/Ce_{0.8}Zr_{0.2}O₂ perovskite catalyst which was prepared by using a co-precipitated method. Ethanol decomposition and successive methane dry reforming as shown by Equation (4.9) were probably responsible reactions for this result.

$$C_2H_5OH \rightarrow CH_4 + CO + H_2 \rightarrow 3CO + 3H_2$$

$$(4.9)$$

The decrease of CH₄ was likely due to the increase of rate constant of methane decomposition reaction at higher temperature. This indicates that decomposition reaction of methane has high activation energy and sensitivity to high temperature.



Figure 4.7 The effect of reaction temperature to CH₄ yield using the LaCuO₃ and CeCuO₃ catalysts under the reactant pressures, $P_{CO2} = P_{C2H5OH} = 20$ kPa.

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The catalytic EDR reactions were run for various ratios of ethanol-CO₂ based on pressures. Figure 4.8 shows the decrease of carbon dioxide conversion for both catalysts where the sigmoid equation was the best model to fit the data, strongly implying low CO₂ conversion at the ratios higher than 2.5. CO₂ conversion was high at the low ratios. The extrapolation using the fitted model suggests the CO₂ conversion could be close to 95% or the reduction of CO₂. Steep decreases are clearly seen from 80% to 20% for both catalysts before plateauing out at 20% after the ratio of 1.0 even though carbon dioxide was the limiting reactant after this ratio for the EDR reaction. Reactions other than the EDR that did not consume CO₂ seemed to be dominant after the stoichiometric ratio.



Figure 4.8 Effect of feed ratio on the CO₂ conversion by LaCuO₃ and CeCuO₃ catalysts.

From the reaction temperature tests, the ratios of H_2/CO and the stoichiometric ratio of reactants at 1023 K are 1.47 and 1.38 for LaCuO₃ and CeCuO₃ catalytic EDR reactions, respectively. As shown by Figure 4.9, these ratios were initially high up to 2.2 and 2.0 for the reactant ratio of 0.5 indicating that carbon monoxide was produced lesser than the stoichiometric ratio as also shown by the CO yield at the reactant ratio lower than unity. Hydrogen yield was high at low H₂/CO ratio, which is in disagreement with thermodynamic analysis proposed by Kale and Gaikwad (2014b) for the carbon steel catalyst. Unlike H₂ yield, the increment of CO yield was clearly low at the condition of excess carbon dioxide despite the conversion of carbon dioxide was high as previously seen at Figure 4.9. Maximum yields were exhibited by the EDR using both catalysts where the CO yields are 30.5% and 29% at 0.87 and 0.9 reactant ratios for LaCuO3 and $CeCuO_3$, respectively. Other side reactions that produced carboxyl compound greater than C1 (Dong Cao et al., 2018), unfortunately could not be detected by the GC-TCD, might have occurred consuming both ethanol and carbon dioxide. However, those compounds were not the objective of this study, and the flame ionization detector can therefore be advisable for the GC analysis.



Figure 4.9 Effect of feed ratio with regard to H₂ & CO yields and H₂/CO ratio of LaCuO₃ and CeCuO₃ catalysts.

Figure 4.10 shows the yield of methane in response with pressure ratios of reactant feeds. Methane yield increased under the fitness of the rational equation for a peak trendline,

$$Y_{CH_4} = \frac{A_p + B_p \Theta}{1 + C_p \Theta + D_p \Theta^2}$$
(4.10)

where A_P , B_P , C_P , and D_P are constants, and Θ is ethanol-CO₂ ratio when the high ethanol-CO₂ ratio increased. Interestingly, maximum methane yields were produced at the same ratio of 1.85 for both catalysts based on the peak equation regression. This implies that ethanol decomposition reaction might become predominant at that ratio regardless of what catalyst was used. Nevertheless, LaCuO₃ is more superior to CeCuO₃ catalyst in producing methane. The downturn after the optimum ratio in the methane yield was probably due to the formation of carbon as also exhibited previously in Figure 4.7. This result was however opposite to the thermodynamic analysis proposed by Kale and Gaikwad (2014b) as well.



Figure 4.10 effect of molar ratio w.r to CH₄ yield of LaCuO₃ and CeCuO₃ catalysts.

4.3.3 Effect of ethanol partial pressure

The catalytic performances of LaCuO₃ and CeCuO₃ catalysts where P_{CO_2} was kept constant at 20 kPa during the entire reaction and $P_{C_2H_5OH}$ were played between 20 to 50 kPa at 1023 K. Both ethanol and carbon dioxide conversions decreased with their increasing pressures. P_{C2H5OH} and the P_{C2H5OH} maximum conversions were observed at the lowest pressure, which is 20 kPa as seen in Figure 4.11. The space time of the reactor increased when the feed pressure was decreased (H. S. Fogler, 2020) and this was the cause to the opposite response of ethanol. Interestingly, De Oliveira-Vigier et al. (2005) also found a similar trend for the conversions of C₂H₅OH and CO₂ vs. P_{C2H5OH} and the optimal C₂H₅OH/CO₂ ratio was at 20 kPa. Nevertheless, the pressure could not be decreased further due to mass transfer limitation issue and high drop where the process would be in the reaction factor anymore (H. S. Fogler, 2020). The decline in both reactant conversions at high P_{C2H5OH} was probably due to the CO₂ adsorption on the catalyst surface. Additionally, as seen Figure 4.12, the CH₄/CO ratios increased from 0.50 to 0.75 with rising P_{C2H5OH} further confirming the reduction of EDR reaction and increase of H₂/CO ratio indicates more ethanol dehydrogenation occurred.


Figure 4.11 Effect of ethanol partial pressure of C_2H_5OH on ethanol and carbon dioxide conversions at $P_{CO2} = 20$ kPa at 1023 K.



Figure 4.12 Effect of ethanol partial pressure of H_2/CO and CH_4/CO ratios at $P_{CO2} = 20$ kPa at 1023 K.

4.3.4 Effect of CO₂ partial pressure

The CO₂ partial pressure was varied from 20 to 50 kPa at 1023 K for LaCuO₃ and CeCuO₃ catalyst whilst ethanol partial pressure was controlled at 20 kPa. As seen in Figure 4.13, the conversions of both C_2H_5OH and CO_2 increased significantly from 80% to 93.5% and 22% to 73.3%, respectively, with the increase of CO₂ partial pressure.

 C_2H_5OH conversion was always higher than the conversion of CO_2 and not equal molar like the EDR reaction stoichiometry as expressed previously in Equation (2.9). Thus, side reactions consuming ethanol can be suspected. Methane and free carbon might be formed from the ethanol dehydrogenation and decomposition reactions like what have been discussed earlier for Figure 4.12 and the reactions can be expressed as Equations (2.11) and 2.15), respectively. Nonetheless, the difference or gap between X_{C2H50H} and X_{C02} curves decreased with the increment of P_{CO2} suggesting that EDR reaction became dominant at high CO₂ partial pressure. Similarly, Hu and Lu (2009) had observed an enhancement of nickel-based alumina activity with the rising CO₂ partial pressure to the EDR reaction. The presence of excess CO_2 concentration improved the rate of CH_4 dry reforming that further converted CH₄ intermediate product to syngas mixture and thus increasing both ethanol and carbon dioxide conversions. The rate increment of H_2 and CO formation reactions was observed with the increase of P_{CO2}. Additionally, Jankhah, Abatzoglou, and Gitzhofer (2008) found that EDR was thermodynamically favoured with high ratio of CO₂:C₂H₅OH in their thermodynamic study. Figure 4.14 also shows the effect of P_{CO2} on H_2/CO ratio at $P_{C2H5OH} = 20$ kPa and T = 1023 K. The highest H_2/CO ratio was obtained at P_{CO2} = 50 kPa. The ratios of H₂/CO within the range from 1.3 to 2.3 are preferred for Fischer-Tropsch synthesis. The effect of CO₂ partial pressure on product yield is depicted on Figure 4.15. H_2 yield, Y_{H2} exhibited a considerable increase of more than 2 times with rising P_{CO2} whilst a linear enhancement of CO yield with P_{CO2} was

observed.

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Figure 4.13 Effect of CO₂ partial pressure of C_2H_5OH and CO₂ conversions at $P_{ethanol} = 20$ kPa at 1023 K.



Figure 4.14 Effect of CO_2 partial pressure of H_2 and CO Yields at $P_{C2H5OH} = 20$ kPa at 1023 K.





4.4 **Post-Reaction Characterization**

4.4.1 Surface Area and Pore Size

Figure 4.3 shows the result from BET analysis method on the spent catalyst. Despite the surface area of LaCuO₃ is almost 5 times greater than CeCuO₃ catalyst, it is 28.7 m²/g, decreasing 50% after the EDR reaction. The presence of carbon nanofiber blocking the pores might be the reason (Luo et al., 2015). Both catalysts show type V adsorption isotherm, which can be seen in Appendix C, indicating that they were all mesoporous catalysts according to the IUPAC classification.

Table 4.5 BET Analysis Results A BDULLAH

Catalyst	Surface area (m ² /g)	Pore Size (nm)
LaCuO ₃	28.7	14.66
CeCuO ₃	6.3	6.08

4.4.2 X-Ray Diffraction

The peaks dropped after the reaction, as shown in Figure 4.16 for the spent catalyst. Simultaneously, the Cu phase (JCPDS#80-1917) was also identified with small peaks at $2\theta = 43.90^{\circ}$, 50.20° and 75.20°. Interestingly, the intensity of these peaks is higher after the EDR reaction (specifically La₂CuO₄). Additionally, a carbon peak at $2\theta = 27.01^{\circ}$ was observed on the spent catalyst, indicating that copper oxide was reduced during the reaction and carbon was deposited. The intensity of the perovskite peaks for CeCuO₃ was

high on the freshly reduced catalyst (JCPDS#81-0792), appearing with diffraction peaks at $2\theta = 29.40^{\circ}$, 33.90°. However, these peaks also dropped after the reaction. Using the Scherrer equation, the mean crystallite size of La₂CuO₄ (appeared at 23° and 43°) and CeO₂ were calculated to be 12.7 nm and 37.4 nm, respectively. La₂CuO₄ is perovskite structure for the lanthanum-promoted catalyst. Furthermore, diffraction peaks attributed to Cu₂O confirmed the reduction of Cu²⁺ to Cu¹⁺ under our experimental conditions. Interestingly, the presence of the non-stoichiometric delafossite-type oxide LaCuO_{2+x} is proposed, suggesting the existence of both Cu⁺ and Cu²⁺.



Figure 4.16 XRD of LaCuO3 and CeCuO3 spent catalysts

4.4.3 Fourier Transform Infrared Spectroscopy

Figure 4.17 shows the analysis result of FTIR on the catalysts after being used in the EDR reaction with equal reactant pressure at 1023 K. The analyses were conducted in the wavenumber range from 500 to 3500 cm⁻¹ to identify the metal bonds and functional groups. Similar wavenumbers of functional groups were registered by the spectrogram for both catalysts: LaCuO₃ and CeCuO₃. The freshly reduced CeCuO₃ catalyst did not exhibit peaks like the one after the reaction. The appearance of functional groups following the EDR reaction was likely due to reactions that altered the metal oxidation state. Adsorption bonds in the range of 500 to 750 cm⁻¹ were observed, corresponding to metal oxides (M-O) such as Ce-O, La-O and Cu-O at 510, 520 and 600 cm⁻¹, respectively

(Khoshbin, Haghighi, & Technology, 2014). Peaks associated with C-O and C-H groups appeared at 1380 and 1560 cm⁻¹. Additionally, bands related to hydroxyl groups were detected at 1630 and 3450 cm⁻¹, indicating the presence of interlayer water molecules and water on the catalyst surface due to reaction products (Dong Cao et al., 2017). Although both catalysts exhibited identical peak positions, the transmittance percentages for C-O, C-H, water, and hydroxyl groups were higher in the spent LaCuO₃ catalyst. These groups likely serves as intermediates in the dehydrogenation reaction, producing methane and hydrogen (Kourtelesis, Panagiotopoulou, & Verykios, 2015).



Figure 4.17 FTIR spectrums of (a) LaCuO₃ and (b) CeCuO₃ spent catalysts.

4.4.4 Scanning and Transmission Electron Microscopy

The surface morphology and elemental analysis of the LaCuO₃ and CeCuO₃ catalysts are shown Figure 4.18. The physical view of the SEM images for 1.8 k magnification and TEM images at 22 k magnification clearly revealed the surface structure of both catalysts. In Figure 4.18(a), the LaCuO₃ catalyst particle exhibited many pores and a rough surface, while the CeCuO₃ particle in Figure 4.18(b) shows a different morphology. This difference justifies the lower BET surface area of CeCuO₃ compared to LaCuO₃. Additionally, carbon deposits on the CeCuO₃ catalyst were more than double those on the LaCuO₃ catalyst suggesting that carbon might have covered the copper and oxygen elements. Notably, no copper element was lost during the sol-gel method due to the absence of washing. Therefore, coking was likely the factor that deactivated this ceriumbased perovskite catalyst, resulting in the copper element being covered on the particle surface after the reaction. Nanofibers of La₂CuO₄ were also observed in Figure 4.18(c), consistent with the previous report by E.-h. Yang et al. (2015). On the CeCuO₃ catalyst, Nanofibers were apparently present as well in Figure 4.18(d) along with agglomerated structure of carbon with higher density. The carbon nanofiber appeared denser in Labased compared to Ce-based catalyst where XRD and EDX show otherwise. This was probably due to amorphous nature of the carbon nanofiber in La-based catalyst that could be detected by the XRD analysis, and it was not coating on the catalyst surface like what happened to cerium-based catalyst.

a			Summar	Summary results			
	A SAST	SAN PARA	Element	Weight 9	% Weight %	σ Atomic %	
1.10	1. 1. 1.		Carbon	20.883	0.391	50.952	
500		ACH CAS	Oxygen	17.188	0.305	31.483	
Part 1	A ANT	5 6 6 C V	Copper	20.103	0.389	9.272	
	Spectrum 1	A THE COUNT	Lanthanum	33.274	0.370	7.020	
the state	The Area		Gold	8.553	0.289	1.273	
the f	States M	Ser Car					
19		- Los Land					
	in- Par		PSA /				
St.	- A. I.	A CONTRACT OF					
	A A A A A A A A A A A A A A A A A A A	45 2 1					
40	Dum						
	عبدالله	هع السلطان	مليسيا ٥	رسيتى	او نيۇ		
b)	A STREET	S & LT L ROAD	Summar	y results	ANG		
(M			Element	Weight %	Weight % σ	Atomic %	
			Carbon	45.968	0.484	82.016	
all the	1.00		Oxygen	7.631	0.302	10.221	
	Spectrum 3	- And	Copper	4.929	0.325	1.662	
	A CAR	1 P 2	Cerium	35.975	0.454	5.502	
	A second	Strange -	Gold	5.497	0.286	0.598	
4	G Wards						
1 2	Con Card Street	and the second					
The second	1 . 1945 - 1 ()						
	- CARLER AN ALCO						

40µm



Figure 4.18 SEM-EDX images for (a) LaCuO₃ and (b) CeCuO₃ catalysts and TEM images for (c) LaCuO₃ and (d) CeCuO₃ catalysts after the EDR reaction.

4.4.5 X-ray photoelectron spectroscopy

The elemental compositions of lanthanum, cerium, and copper in the perovskite catalysts were analysed by using XPS, particularly to identify the energy state of their orbitals. Figure 4.19 shows the spectrogram of the lanthanum-promoted catalyst and the cerium-promoted catalyst in Figure 4.19(a) and (b) respectively, before (after being reduced by using hydrogen) and after the EDR reaction. Two copper oxidation states were present in both catalysts: $Cu2p_1$ and $Cu2p_3$, corresponding to Cu^+ and Cu^{2+} ions, at binding energies of 932.4 and 952.5 eV, respectively. Notably, these copper peaks in the lanthanum-promoted catalyst exhibited greater intensity compared to those in the ceriumpromoted catalyst, implying better activity potentials (Ivanova et al., 2020). Additionally, Cu2p₁ peak in the spent La-promoted catalyst was smaller than the reduced one, suggesting the reduction of that copper oxide species after the EDR reaction. Furthermore, a different copper oxidation state at binding energy of 77 eV that was interpretated as Cu3p₃ and appeared in the La-promoted catalyst but not in the Cepromoted catalyst, before and after the EDR reaction. Cu^0 (metal), Cu^+ and Cu^{2+} typically correspond to this spectrum and was previously reported before by Khalakhan, Vorokhta, Xie, Piliai, and Matolínová (2021) when copper was prepared with platinum.

The La3d core level was characterized by two single-phase spectra in the reduced and spent La-promoted catalysts, which are La3d_{5/2} and La3d₃ at binding energies of 837.5 and 834.3 eV (Smirnova, Yakovkina, & Borisov, 2015). These binding energies

correspond to La³⁺ oxidation state at multiple energy levels. The La3d intensity did not significantly differ after the EDR reaction, indicating the robust structure of the catalyst.

Moving on to cerium, Ce3p appeared in the XPS spectra for Ce³⁺ with similar pattern but at lower intensities, giving three lobed envelopes at 880-890 and 900-910 eV. The Ce3d_{5/2} and Ce3d_{3/2} were labelled as v and u, respectively. The doublets (v₁, u₁) correspond to the Ce³⁺ species, while the doublet (v₀, u₀), (v₂, u₂) and (v₃, u₃) represent the Ce⁴⁺ species. The low intensity suggests that there was less free orbital energy of electrons, likely due to metallic state rather than ionic bonding of cerium. This observation aligns with the low O1s peak observed at a binding energy of 530 eV for the cerium-promoted catalyst. (Sato et al., 2013). In summary, oxygen was adsorbed on the lattice of both catalysts and on the surface, serving as an intermediate for oxidizing cation or atoms with a high affinity to electrons.

C1s corresponds to a carbon film thickness of less than 0.2 nm at a binding energy of 284 eV (Sunding et al., 2011) in both catalysts. Interestingly, the lanthanum-promoted catalyst exhibited a smaller peak than the cerium-promoted one after the EDR reaction. The presence of cerium-promoted results even before the EDR reaction could be attributed to carbon from citric acid used during the catalyst preparation. This might explain why cerium-promoted catalyst performed worse in the EDR reaction.





Figure 4.19 XPS characterisation of (a) LaCuO₃ and (b) CeCuO₃ catalysts

4.4.6 Raman spectroscopy

The Raman spectra of spent LaCuO₃ and CeCuO₃ catalysts after 50 h of the EDR reaction consists of two major large intensity peaks with the Raman shifts at 1335.8 and 1574.1 related to D- and G- bands, respectively, as shown in Figure 4.20. In general, the D-band peaks occurred due to the defects in sp3 bonding which leads to the formation of amorphous carbon or carbon fibres on the surface catalyst. The G-band was formed because of defects in sp2 bonding in presence of carbon materials such as graphite. da Silva et al. (2011) explained that the presence of D- and G- bands indicates the observation of heterogeneity on the carbon surfaces includes carbon nano filament and graphitic carbon formed during the EDR Reforming reaction. Zawadzki et al. (2014) also confirmed that the formation of crystalline or graphite and filamentous carbon were due to methane decomposition and ethanol dehydration. Therefore, the ID/IG ratio calculated for the LaCuO₃ and CeCuO₃ spent catalysts stands was 2.3 indicating the formation of amorphous carbon on the surface of catalyst. The percentage of amorphous carbon (CD) deposition were calculated resulting 46% of all peaks in the spectrogram. These two parameters strongly authenticate the filamentous carbon on the catalyst surfaces. The actual amorphous carbon contents, which were determined using its composition in EDX result shown Figure 4.18, are 9.6% and 21.16% in LaCuO₃ and CeCuO₃, respectively.



Figure 4.20 Raman spectroscopy of LaCuO₃ and CeCuO₃ spent catalysts

4.5 Concluding Remarks

The Cu-based perovskite catalysts were prepared with lanthanum or cerium. Surface area and pore size analyses by using vacuum BET method revealed 30 and 2 times higher, respectively at LaCuO₃ as compared to CeCuO₃. More perovskite crystals in LaCuO₃ were identified from the XRD analysis. The TPR results of this catalyst showed relatively low reduction temperatures as well. The highest ethanol conversion was 90% using LaCuO₃ under 1.5 of CO₂ excess condition. Carbon on the surface of LaCuO₃ was 4 times than that of CeCuO₃. The superior characteristic of the LaCuO₃ catalyst sample was probably the main cause of its activity. There were carbon nanofilaments appeared on all catalysts' surface after the EDR reaction as shown by SEM, TEM, XPS and Raman spectroscopy results.

CHAPTER 5

EFFECT OF YTTRIUM AND POTASSIUM PROMOTION ONTO LaCuO₃ PEROVSKITE CATALYST

5.1 Overview

This chapter discusses the results of catalyst characterization and EDR reaction after the best catalyst from the first objective, which is LaCuO₃, was promoted with yttrium and potassium. The discussion of each metal promotion loading is presented separately beginning with the effect of yttrium promotion. Finally, result of longevity test on the best potassium and yttrium promoted perovskite catalyst was discussed to delineate catalyst deactivation and carbon formation.

5.2 Effect of Yttrium Promotion

For Cu-based catalysts, many researchers found that the surface area and dispersion of Cu play a crucial role in determining their catalyst performance. While some studies suggest a linear relationship between activity and Cu surface area (Jinghu Zhu et al., 2023). Others reported that catalytic activity increased with increasing Cu surface area and/or dispersion, but the relationship was not linear (Zhigalina et al., 2024). To address this, proper promoters can be used. Among the studied promoters, yttrium oxide (Y_2O_3) stands out as a promising candidate. The introduction of Y_2O_3 into Cu-based catalysts significantly enhances the specific surface area of Cu.

In our previous work, the influence of several modifiers (Mn, La, Ce, Zr and Y) on the properties of Cu/ZnO/Al₂O₃ catalysts was investigated and it was found that the Y₂O₃modified catalyst exhibited the highest CO₂ conversion with maximum surface area and dispersion of Cu compared with that modified by other additives. However, a comprehensive study on the influence of Y₂O₃ on methanol synthesis catalysts is – to the best of our knowledge – still lacking. By the considering the above discussion Yttrium promoted on LaCuO₃ catalysts are studied by varying its metal load (0-1%) with gap 0.25% under Ethanol Dry Reforming (Li Zhang, Xue, & Zhang, 2024).

5.2.1 X-Ray Diffraction

The XRD patterns reveal the overall crystal structure of the synthesized La_2O_3 . The diffraction peaks seen at (100), (002), (101), (102), (110), (200), (112), and (201) reflection planes correspond to the pure hexagonal phase with lattice constants of a = b =0.3973 nm, and c = 0.6129 nm (JCPDS card No. 83-1348). The well-defined, strong, and sharp diffraction peaks of the nanoparticles confirmed the high crystallinity of La₂O₃ in nanoscale. The broader nature of the XRD peaks indicates the nanostructures of the La₂O₃. As the calcination temperature is at 900 °C, this confirms that as La₂O₃ particles continue to be nanoparticles, the diffraction peaks become stronger and sharper revealing the higher degree of crystallinity of the nanoparticles. La2CuO4 crystal was again spotted at 24° and 42° (JCPDS#82-2142), which is the perovskite structure. The crystal structures of the Y₂O₃-promoted samples were different. It is observed from the XRD patterns that the diffraction peaks of $(2 \ 1 \ 1)$, $(2 \ 2 \ 2)$, $(4 \ 0 \ 0)$, $(4 \ 4 \ 0)$ and $(6 \ 2 \ 2)$ for Y_2O_3 crystals are clearly distinguishable, and all of them can be perfectly indexed to the cubic phase (according to JCPDS 25-1200), indicating that the crystal structures of these Y₂O₃promoted samples are similar despite of their different morphologies shown in Figure 5.11 and Figure 5.12. The CuO peaks are identified at 36.10° and 38.78° with respective (h k l) values are (-111) and (200). The size of each crystallite for all catalyst is summarized in Table 5.1. To further investigate the texture properties of the catalysts, XRD analysis of the reduced catalysts was conducted and shown in Figure 5.1.

Catalysts	Crystals	Crystallite Size	
		(nm)	
YCuO ₃	CuO	2.66	
	Y_2O_3	2.85	
	Cu	-	
$La_{0.25}Y_{0.75}CuO_3$	La ₂ CuO ₄	1.27	
	La ₂ O ₃	1.84	
	CuO	2.85	
	Y ₂ O ₃	1.72	
	Cu	-	

Table 5.1 Size of Crystallites for Each Catalyst



Table 5.1 Continued

Figure 5.1 X-ray diffraction spectrums of fresh La_{0.75}Y_{0.25}CuO₃, La_{0.50}Y_{0.50}CuO₃, La_{0.25}Y_{0.75}CuO₃ and YCuO₃ Catalysts

5.2.2 Fourier Transform Infrared Spectroscopy

The FT-IR spectra of the fresh catalysts $La_{0.75}Y_{0.25}CuO_3$, $La_{0.50}Y_{0.50}CuO_3$, $La_{0.25}Y_{0.75}CuO_3$ and $YCuO_3$ in the wavenumber range 400–4000 cm⁻¹ for the identification of metals such as La_2O_3 , Y_2O_3 and CuO calcined at 900 °C are presented

in Figure 5.2. The major broad band is observed at 2348 cm⁻¹ confirms the presence of O–H stretching vibrations associated with absorbed moisture on the surface of the samples. Additionally, the peaks at 2165 cm⁻¹, as well as the sharp bands at 1941 cm⁻¹, originated from the asymmetric and symmetric stretching of C-H and COO– functional groups, respectively. Minor broad bands at 1450, 937 and 549 cm⁻¹ are associated with Cu-O, Y-O and La–O stretching vibrations. The presence of these La–O stretching and bending vibration bands confirms the existence of La₂O₃ phases in the nanoparticle samples.



Figure 5.2 FTIR spectrums of fresh $La_{0.75}Y_{0.25}CuO_3$, $La_{0.50}Y_{0.50}CuO_3$, $La_{0.25}Y_{0.75}CuO_3$ and YCuO₃ Catalysts.

5.2.3 Hydrogen Temperature Programmed Reduction

The TPR profiles of the fresh catalysts $La_{0.75}Y_{0.25}CuO_3$, $La_{0.50}Y_{0.50}CuO_3$, $La_{0.25}Y_{0.75}CuO_3$ and YCuO_3 are shown in Figure 5.3. For all samples, a broad reduction peak accompanied by shoulders was observed in the temperature range of 230–623 K. The quantitative TPR results include the onset reduction temperature, which corresponded to the temperature of peak maxima. Specifically, the lowest temperature peak (P1) is attributed to the reduction of La_2CuO_4 in dispersed CuO as explained in Section 4.2.3 based on Equation (4.1). The peak appearing at high temperature (P2) is ascribed to the reduction of Cu^{2+} to Cu^+ , as expressed by Equation (4.2). Finally, the third peak at the highest temperature (P3) was observed as Y_2O_3 loading increased, likely due to the reduction of highly dispersed Cu₂O to Cu according to Equation (4.3).

Two effects can be observed from the promotion of yttrium. First, the intensity of the peak of P1 and P2 decreased and broadened as yttrium loading increased (Świrk et al., 2019). This change implies that more dispersed and stronger copper oxide bonding existed in the structure. Furthermore, the addition of yttrium slightly increased the P3 temperature (Świrk et al., 2019). These results revealed that suitable amounts of Y_2O_3 could enhance the reactivity of the surface Cu²⁺ species.



Figure 5.3 TPR of fresh $La_{0.75}Y_{0.25}CuO_3$, $La_{0.50}Y_{0.50}CuO_3$, $La_{0.25}Y_{0.75}CuO_3$ and $YCuO_3$ Catalysts.

5.2.4 Ethanol Dry Reforming

The EDR catalytic activity of LaCuO₃ catalyst and La_{1-x}Y_xCuO₃ (25% \leq x \leq 100%) catalysts was assessed at 1023 K under atmospheric pressure using stoichiometric C₂H₅OH:CO₂ ratio of 1:1 ($P_{C_2H_5OH} = 20$ kPa, $P_{CO_2} = 20$ kPa) at the gas hour space velocity (GHSV) of 42 L g_{cat}^{-1} h⁻¹. The temperature of 1023 K was fixed based on the previous findings from the heat transfer limitation analysis in Subchapter 3.6, in which the highest ethanol conversion via decomposition reactions could occur with minimum undesired side reactions such as the Boudouard reaction. Figure 5.4 shows reactant conversions for the yttrium-promoted catalysts after 8-h on stream. The error bar analysis

of 5% on the graph revealed a significant drop of 10% ethanol conversion for the $La_{0.75}Y_{0.25}CuO_3$ catalyst after 8 h of TOS. Another significant drop was shown by the $La_{0.25}Y_{0.75}CuO_3$ catalyst. Reduction of perovskite structure and metal oxide exhibited in the XRD results before (Figure 5.1) and after (Figure 5.8) the EDR reaction might indicate sintering and became the cause of the activity decrease. This was not conforming the sintering resistance shown by the yttrium-promoted, nickel-based catalyst that was prepared by the impregnation method (Świrk et al., 2019). Fluctuation conversions were additionally observed when the ratio of yttrium higher than 0.25. The CO₂ conversions significantly dropped greater than that of ethanol for all catalysts after 8 h of TOS.

The catalytic activity results revealed that the C_2H_5OH conversions were always greater than the CO₂ conversions for all the catalyst, confirming there was no water gas shift occurred. In addition, the H_2/CO ratio was less than 1, indicating the reduction of CH_4 dry reforming reaction occurred (see Figure 5.4). Furthermore, the H₂ yield was consistently higher than the CH₄ yield for all the catalysts, as displayed in Figure 5.5. The C₂H₅OH and CO₂ conversions for the La_{0.75}Y_{0.25}CuO₃ catalyst were 87.9% and 36.4%, respectively, which are about 10% higher than the same results using the LaCuO₃ catalyst. However, at higher yttrium content (x > 0.25) both parameters linearly dropped. Additionally, the H_2 yields exhibits the same dropping trend, as shown in Figure 5.5. However, the methane yield showed otherwise. Initial CH₄ yield was approximately 5 to 12%, increased for about 13 - 15% after 8 h. As a result, the H₂/CO ratio decreased but the CH₄/CO ratio increased, as depicted in Figure 5.6. This scenario is same as the results reported by (M. Wang et al., 2024) whereby the desired reaction of the EDR, Equation (2.9), was likely in parallel with two reactions: the reverse reaction of water gas shift as given by Equation (2.14) and methane formation from ethanol decomposition reaction shown by Equation (2.11).

All these mean that this behaviour was possibly due to the strong shrinkage or collapse of the high surface area LaCuO₃ support, which strongly affected the dispersion or accessibility of active metal surface sites. Additionally, the C_2H_5OH and CO_2 conversions were stable during the 8-h span, except for 0.25%-yttrium catalyst, which showed a slight decline of about 5.6% and 3.1% in the corresponding C_2H_5OH and CO_2 conversions. This behaviour might be due to the formation of partially dehydrogenated

carbon (CHx) species on the surface of the catalyst, blocking the active metal sites and reduced its activity with time-on-stream (Świrk et al., 2019).



Figure 5.4 Time on stream of the reactant conversions for the yttrium-promoted perovskite catalysts at $P_{C_2H_5OH} = P_{CO_2} = 20$ kPa and 1023K.



Figure 5.5 Time on stream of (a) H₂ and (b) CO₂ Yields for the yttrium-promoted perovskite catalysts at $P_{C_2H_5OH} = P_{CO_2} = 20$ kPa and 1023K

Figure 5.6 exhibits the product ratios from the EDR reaction tests for all the yttriumpromoted perovskite catalysts for 8 h on the test stream. The error bar results show greater uncertainty in the H₂/CO ratio compared to the CH₄/CO ratio, probably due to the inconsistency of the EDR reaction caused by the carbon formation (Qiu et al., 2024). This was perhaps supported by the reduction of metal oxides in the post-reaction XRD results illustrated in Figure 5.8 and high carbon content in the EDX result for used catalyst in Figure 5.12. The syngas product ratio declined while methane to carbon monoxide ratio increased, indicating the domination ethanol decomposition reaction as expressed previously in Equation (2.11) at longer time. The greater CO₂ conversion decrease compared to ethanol conversion decrease as depicted in Figure 5.4 may also be the evidence of the domination (Dingshan Cao et al., 2023).



Figure 5.6 Time on stream of product ratios the yttrium-promoted pervoskite catalysts at $P_{C_2H_5OH} = P_{CO_2} = 20$ kPa and 1023 K

Figure 5.7 shows the catalytic activity analysis for different yttrium loadings. The $La_{0.75}Y_{0.25}CuO_3$ result exhibits the highest ethanol and CO₂ conversion, with 87.98 % and 27.02 %, respectively (as shown in Figure 5.7(a)). The enhancement in catalytic performance upon the addition of Y₂O₃ on LaCuO₃ might be attributed to the increase in Cu dispersion like what had resulted in the Ni-based catalyst for the same reaction (Świrk et al., 2019). However, the catalytic activity decreased with an increase in yttrium

composition due to reduced reactant consumption and methane increase, leading to the formation of carbonaceous species on the catalysts (Dong Cao et al., 2018). Similarly, it was seen with the H₂, CO and CH₄ yield and H₂ and CO selectivity shown in Figure 5.7(b) and (c). The highest H₂/CO ratio was obtained at x = 0.75 and H₂/CO ratio was greater than the stoichiometric ratio of 1:1 regardless of P_{CO2} reasonably due to the parallel ethanol dehydrogenation reaction during EDR reaction. Interestingly, the ratio of H₂/CO varied from 1.3-2.3 preferred for downstream Fischer-Tropsch synthesis (Finocchio, Rossetti, & Ramis, 2013) shown in Figure 5.7(d).



Figure 5.7 The EDR activity: (a) reactant conversions, (b) product selectivities, (c) product yields and (d) product ratios at $P_{C2H5OH} = P_{CO2} = 20$ kPa and 1023 K.

5.3 Yttrium-Promoted LaCuO₃ after the EDR Reaction

5.3.1 X-ray Diffraction

The XRD spectrum of spent La_{0.75}Y_{0.25}CuO₃, La_{0.50}Y_{0.50}CuO₃, La_{0.25}Y_{0.75}CuO₃ and YCuO₃ catalysts are shown Figure 5.8, Metal oxides that were previously seen in the XRD results turned into metals. The lanthanum peaks are identified at $2\theta = 28.04^{\circ}$, 55.86°

using the standard JCPDS #04-0856 and Y_2O_3 peaks are identified at $2\theta = 20.66^\circ$, 29.30°, 34.2°, 36.12°, 48.72° and 57.86° using the standard JCPDS card #89-5591, indicating a cubic phase in the structure. The metallic Cu peaks are indicated at $2\theta = 43.48^\circ$, 50.56° and 74.28° with the JCPDS card 003-1018. J. Gao, Hou, Lou, and Zheng (2011) explained that at lower metal loadings of the catalyst, temperatures above 498 K resulted in three kinds of copper species. These results suggest that the reduction of CuO to metallic Cu proceeded through an intermediate Cu₂O phase, which was very unstable and quickly reduced to metallic Cu under H₂ atmosphere. Therefore, the highest intensity peak obtained in the La_{0.75}Y_{0.25}CuO₃ spectrum are metallic Cu with the crystalline size of 45.9 nm using the Sherrer equation and a similar peak size was observed. The crystal appeared in the crystallite size results is Cu, which are 3.27, 4.59, 5.66 and 5.24 nm in YCuO₃, La_{0.25}Y_{0.75}CuO₃, La_{0.5}Y_{0.5}CuO₃, and La_{0.75}Y_{0.25}CuO₃, respectively.



Figure 5.8 XRD analyses of the spent La_{0.75}Y_{0.25}CuO₃, La_{0.50}Y_{0.50}CuO₃, La_{0.25}Y_{0.75}CuO₃ and YCuO₃ catalysts.

5.3.2 Fourier-Transform Infrared Spectroscopy

The FTIR transmittance spectra for the spent yttrium-promoted catalysts are shown in Figure 5.9 in the same wavelength range. The band at around 800 cm⁻¹ is attributed to stretching vibrations of Cu-O, Y-O and La-O bonds (in agreement with the XRD results). The band intensity is higher in yttria-promoted catalysts. In the region around 1600 cm⁻¹, the band is associated with the angular deformation of adsorbed water molecules. The broad and intense band at wavelengths of 2500-3000 cm⁻¹ refers to the stretching vibrations of the hydroxyl groups. This band was also higher with yttria addition. The presence of OH groups is related to the capacity for the removal of coke deposited on the catalytic performance and resistance to coke formation in the case of the catalysts with yttria inserted. The intensity of Lanthanum peaks are clearly observed the reduction with the increasing the yttrium loading.



Figure 5.9 FTIR analyses of the spent La_{0.75}Y_{0.25}CuO₃, La_{0.50}Y_{0.50}CuO₃, La_{0.25}Y_{0.75}CuO₃ and YCuO₃ catalysts.

5.3.3 X-Ray Photoemission Spectroscopy (XPS)

XPS analysis was performed to determine the surface chemical states and compositions of the $La_{0.75}Y_{0.25}CuO_3$, $La_{0.50}Y_{0.50}CuO_3$, $La_{0.25}Y_{0.75}CuO_3$ and YCuO₃ catalysts. As shown in Figure 5.10(a), the spectra consisted of two peaks at 932.5 and 952.5 eV which were mainly attributed to Cu 2p3/2 and Cu 2p1/2 peaks of Cu⁰, respectively. The absence of satellite peaks around 942 and 962 eV suggested that the Cu²⁺ species were completely reduced after being exposed to 573 K. The identification of Cu⁺ species by ex situ measurements is not always unambiguous proof that they were present on the surface of the catalyst under the reaction conditions, because it was hard to completely prevent the sample from exposure to air during the separation of the used

catalyst from quartz sand. Similar results have been reported for various Cu/ZnO-based catalysts (Lei Zhang et al., 2015).

Figure 5.10(b) shows that the binding energy of $Y3d_{5/2}$ for all these four spent catalysts is around 156.2 eV, which is comparable to that of Y $3d_{5/2}$ for pure Y₂O₃. All of these results indicate that the chemical environmental of Y did not change with the crystal size of Y₂O₃, and the impregnated LaCuO₃ did not react with Y₂O₃. The binding energy values of La 3d were recorded around 834 and 851 eV as shown in Figure 5.10(c). The other two peaks at 837 and 854 eV are La 3d satellite peaks (Sunding et al., 2011). These peak positions are similar to the values recorded from pure La₂O₃, indicating the La ions were in a trivalent state. Moreover, the La3d_{5/2} and La3d_{3/2} peaks shifted to higher energy for La_{0.75}Y_{0.25}CuO₃, which probably connected with different chemical surroundings.



Figure 5.10 XPS analyses of the spent (a) $La_{0.75}Y_{0.25}CuO_3$, (b) $La_{0.50}Y_{0.50}CuO_3$ and (c) $La_{0.25}Y_{0.75}CuO_3$ catalysts.

5.3.4 Scanning electron microscopy – Energy Dispersive X-Ray

The SEM micrographs of YCuO₃, La_{0.25}Y_{0.75}CuO₃, La_{0.50}Y_{0.50}CuO₃, and La_{0.75}Y_{0.25}CuO₃ after the EDR reaction are shown in Figure 5.11. The samples were zoomed in 3000 times. The morphology of small clusters in the sample having lanthanum distributed evenly and attached to continuous structure, which is more than 100 microns in size, can be seen in all samples. The clusters are well dispersed. They might be the convoluted cubes of perovskite units as also reported elsewhere by (Mahapatra et al., 2018). Various pore sizes are randomly distributed on the structure and the clusters. Filamentous structure was not present on the surface of all catalysts like what (Pechimuthu, Pant, & Dhingra, 2007) found in their EDR study.



Figure 5.11 SEM analyses of the spent (a) YCuO₃, (b) $La_{0.25}Y_{0.75}CuO_3$, (c) $La_{0.50}Y_{0.50}CuO_3$, (d) $La_{0.75}Y_{0.25}CuO_3$ catalysts.

Figure 5.12 shows the topography of elements on the catalyst surface after the EDR reaction. The surface carbon composition of $La_{0.75}Y_{0.25}CuO_3$ is the lowest and this indicates the oxidation effect of yttrium in the perovskite catalyst as compared to the

spent LaCuO₃ catalyst in Figure 4.18. However, the carbon decomposition increased at higher yttrium loading. Thus, its negative effect on the reaction activity of the catalysts presented before in Section 6.2.4 is supported.





Figure 5.12 EDX topography analyses of the spent (a) $YCuO_3$, (b) $La_{0.25}Y_{0.75}CuO_3$, (c) $La_{0.50}Y_{0.50}CuO_3$, (d) $La_{0.75}Y_{0.25}CuO_3$ catalysts.

5.4 Effect of potassium promotion

The potassium promotion is playing key role in especially, stabilized copper and, therefore, the two potassium-copper perovskite catalysts present a constant activity for the soot combustion. The activity of the potassium-copper perovskite catalysts, which is maintained during consecutive reactions, is related to their NO₂ production capacity. The metal addition method seems to influence the catalysts performance, the substituted catalyst (SrKTiCuO₃) being the most active and stable.

As the same time, it was also observed that the addition of alkali metals to the catalyst formulation offers substantial benefit for soot combustion. Potassium is a well-known catalyst for carbon gasification and, consequently, it was used as catalysts for soot combustion. It has been suggested that alkali metals, like potassium, are able to improve the catalyst/soot contact by increasing the surface mobility. Another positive effect of potassium is related to its electron donor properties, which can increase the oxygen reactivity of the M–O bond. Potassium has the ability to control the coke formation and improves the catalytic activity, selectivity and stability in various conditions during steam reforming of ethanol. By considering the inferences studied the potassium promoted on LaCuO₃ by varying loading to evaluate by EDR reactions and catalytic activity, carbon formation.

5.4.1 X-Ray Diffraction

The XRD spectrum of La_{0.75}K_{0.25}CuO₃, La_{0.50}K_{0.50}CuO₃, La_{0.25}K_{0.75}CuO₃ and KCuO₃ catalysts are shown in Figure 5.13. The lanthanum spectrum peaks are illustrated at $2\theta = 35.30^{\circ}$, 38.36° , 48.53° , 65.64° and 72.47° confirms with standard JCPDS card no. #83-1348 and had the hexagonal phase structure. The CuO peaks are identified at $2\theta = 30.98^{\circ}$, 33.23° , 35.39° , 38.63° and 54.29° with JCPDS card no. #48-1548. The K₂O peaks are identified at $2\theta = 24.14^{\circ}$, 26.84° , 41.51° and 43.22° and matched with the JCPDS card #26-1327. The size of K⁺ is larger than that of La3+, resultantly, the incorporation of K⁺ into the A (here A = La³⁺) sites would result in the lattice expansion corresponding to the shift of 2θ to lower value. The size of the crystallite can be seen in Table 5.2

KCuO3	Crystals	Crystallite Size (nm)
La _{0.25} K _{0.75} CuO ₃	La ₂ O ₃	3.97
	CuO	2.46
	Cu	-
	UK2OSA	3.59
$La_{0.50}K_{0.50}CuO_{3}$	La_2O_3	3.60
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La _{0.75} K _{0.25} CuO ₃	La_2O_3	3.22
	CuO	1.90
	Cu	-
	K ₂ O	3.12
KCuO ₃	CuO	2.90
	Cu	-
	K ₂ O	2.18

Table 5.2 Size of Crystallites for Each Catalyst



Figure 5.13 XRD analysis of La_{0.75}K_{0.25}CuO₃, La_{0.50}K_{0.50}CuO₃, La_{0.25}K_{0.75}CuO₃ and KCuO₃

5.4.2 Fourier Transform Infrared Spectroscopy

The FTIR spectrum of La_{0.75}K_{0.25}CuO₃, La_{0.50}K_{0.50}CuO₃, La_{0.25}K_{0.75}CuO₃ and KCuO₃ catalysts are shown in Figure 5.14. The wideband in the region from 3900 cm⁻¹ to 3000 cm⁻¹ centred around 3500 cm⁻¹ is attributed to y (O-H) bands from physisorbed and chemisorbed water. The band in the region of 2300-2400 cm⁻¹ with two peaks at 2359 cm⁻¹ and 2341 cm⁻¹ is assigned to physisorbed carbon dioxide. On the spectra, there are also present two connected bands with peaks at 1620 cm⁻¹ and 1362 cm⁻¹ indicating the presence of bridged carbonate species. The overlapped vibrations for La-O, K-O and Cu-O components are located in wave number region in the range of 500-1200 cm⁻¹.



Figure 5.14 FTIR analysis of La_{0.75}K_{0.25}CuO₃, La_{0.50}K_{0.50}CuO₃, La_{0.25}K_{0.75}CuO₃ and KCuO₃

5.4.3 Temperature Programmed Reduction

The TPR results of La_{0.75}K_{0.25}CuO₃, La_{0.50}K_{0.50}CuO₃, La_{0.25}K_{0.75}CuO₃ and KCuO₃ catalysts are shown in Figure 5.15. The H₂ consumption in the range of 250–550°C, is due to the copper species reduction, as bare perovskite does not show any reduction. The percentage of copper oxide reduced for the two catalysts, estimated from H₂ consumption (using CuO as the reference material). The maximum located at temperature lower than 400°C, indicates the presence of copper with a strong electronic interaction with the perovskite or to copper incorporated into the lattice as main copper species. Although the copper incorporation generates a distortion of the structure creating oxygen vacancies, the coordination of copper keeps being higher than that of the CuO.

The P1 peak appeared like the first peak of the lanthana-promoted catalyst in Section 5.2.3, probably due to the reduction of lanthana-copper oxide complex into LaCuO₃ as illustrated by Equation (4.1). The addition of yttrium might have increased its reduction temperature from $230 \rightarrow 345 \rightarrow 375$ °C for the La_{0.75}K_{0.25}CuO₃, La_{0.5}K_{0.5}CuO₃ and La_{0.25}K_{0.75}CuO₃ catalysts, respectively. The second peak, P2, was likely appeared due to the same copper reduction from two to one oxidation as well, but the reduction temperature peak decreased from 700 to 600 °C (Y. N. Lee et al., 2001). The third peak, P3 appeared in the presence of lanthana and potassium oxide as shown in Equation (5.1).

$$LaKCuO_4 + H_2 \rightarrow LaCuO_3 + H_2O \tag{5.1}$$

Nonetheless, the P3 peak did not appear without lanthana and $La_{0.5}K_{0.5}CuO_3$ might have it beyond 700 °C.



Figure 5.15 TPR analysis of La_{0.75}K_{0.25}CuO₃, La_{0.50}K_{0.50}CuO₃, La_{0.25}K_{0.75}CuO₃ and KCuO₃

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Figure 5.16 exhibits the reactant conversions for the potassium-promoted perovskite catalysts in the EDR reaction for 8 h. Their conversions are 10% lower than the yttrium-promoted ones (in Figure 5.4) but they are interestingly consistent within 10% variance. The error bar of 5% analysis revealed insignificant fluctuations of the potassium loading below than 0.75. Thus, the stability of the catalyst due to the potassium promotion conformed with the result reported by Tsounis et al. (2020) on their nickel-based perovskite catalysts. The stability of the catalysts began compromising after 0.75 loading. The CO₂ conversion profiles are same, which are generally 10% lower than the yttrium-promoted catalysts and they are all significantly consistent for 8 h with about 13% of variance. Thus, the basicity of the catalyst is probably better than the yttrium-based catalysts (Stebbins, 2020).



Figure 5.16 Conversions of C_2H_5OH and CO_2 from the EDR reactions for 8 h of TOS using potassium-promoted perovskite catalysts.

The product yields of the EDR reaction for the potassium-promoted perovskite catalysts are presented in Figure 5.17. Despite the hydrogen yields are fluctuated more than the methane yield, their fluctuation is generally not significant based on the error bar analyses of 5%. The highest hydrogen yield exhibited by $La_{0.75}K_{0.25}CuO_3$ was 49%, which is 5% lower than that of the $La_{0.75}Y_{0.25}CuO_3$ catalyst. Methane yields are only steady with potassium loading below 0.75, indicating that the ethanol decomposition reaction decreased, which was also corresponding to the perpetual conversion of carbon dioxide feedstock. The sustained yield of syngas might be due to the well dispersed and stable copper structure on the catalyst (Zhigalina et al., 2024).



Figure 5.17 Yields of H₂ and CH₄ from the EDR for 8 h of TOS using the potassiumpromoted perovskite catalysts.

Figure 5.18 shows the ratio of products between syngas and methane.



Figure 5.18 Ratios of the EDR products for 8 h of TOS using the potassium-promoted perovskite catalysts.

The influence of potassium ratio on the perovskite catalyst activity in the EDR reaction was investigated using the stoichiometric feed ratio ($P_{CO2} = P_{C2H5OH} = 20$ kPa) and the reaction temperature of 1023 K. Figure 5.19(a) exhibits the reactant conversions that did not follow the EDR stoichiometry and are identical to the result by the yttrium-promoted perovskite catalyst (Figure 5.7(a)). By increasing the potassium ratio from 0.25 to 1, ethanol conversion decrease began significantly, based on the error bars, after 0.25 while CO₂ conversions were steady for all the ratios. This indicates the strong basicity of potassium on the catalyst and resistance to coking (Sajjadi et al., 2019). The effect on the product yields is shown in Figure 5.19(c). Hydrogen yield decreased with the increase of potassium loading, but the H₂/CO ratio is still above unity as seen in Figure 5.19(d). CO and methane remained the same, which are around 30-38% and 12-18%, respectively. Methane to carbon monoxide ratio decreased with the increase of potassium ratio except in the catalyst without lanthana (x = 0), further confirming that the rate of ethanol decomposition decreased.

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Figure 5.19 The activity of potassium-based perovskite catalyst $P_{CO2} = P_{C2H5OH} = 20$ kPa and 1023 K: (a) C₂H₅OH & CO₂ conversion (b) H₂, CO and CH₄ Selectivity (c) H₂, CO and CH₄ Yield (d) H₂/CO and CH₄/CO product ratio.

5.5 Potassium-Promoted LaCuO₃ Catalyst After Reaction

The XRD spectrum of La_{0.75}K_{0.25}CuO₃, La_{0.50}K_{0.50}CuO₃, La_{0.25}K_{0.75}CuO₃ and KCuO₃ catalysts were compared with the JCPDS database, and the results are shown in Figure 5.20. The metallic phase of potassium was observed at $2\theta = 26.34^{\circ}$ and the other elements like copper and lanthanum are at $2\theta = 43.49^{\circ}$, 50.50° and 15.43°, 30.50°, 54.78° respectively. The average crystallite size of potassium and copper are 6.74 and 9.3 nm estimated by the Scherrer equation and similarly observed for the catalyst (López-Suárez et al., 2014). The presence of a single crystalline phase (x < 1) with a linear increase of the lattice parameter corroborating the incorporation of potassium in the perovskite structure (C. Lee, 2001). The potassium carbonates, oxides or hydroxides could be detected by the XRD in most of the potassium rich oxides that showed good activity and active catalyst for oxidation of graphite (Christoph Janiak, 1993). Most of surface CuO

^{5.5.1} X-ray Diffraction

phase was observed on the impregnated catalyst in comparison with substituted catalyst inferring that copper was properly incorporated within the perovskite lattice and if any CuO was present, it would not be detected by the XRD because its size was below the detection limit of the technique (Franz, 2014). The crystal appeared in the crystallite size results is Cu, which are 4.3, 4.93, 5.79 and 5.22 nm in KCuO₃, La_{0.25}K_{0.75}CuO₃, La_{0.5}K_{0.5}CuO₃, and La_{0.75}K_{0.25}CuO₃, respectively.



Figure 5.20 XRD analyses of the spent La_{0.75}K_{0.25}CuO₃, La_{0.50}K_{0.50}CuO₃, La_{0.25}K_{0.75}CuO₃ and KCuO₃ catalysts.
5.5.2 Fourier-Transform Infrared Spectroscopy

The FTIR analyses for potassium-promoted perovskite catalysts are shown in Figure 5.21. The spent catalysts obtained were inspected in the spectrum of wavenumbers spanning from $500 - 2500 \text{ cm}^{-1}$ for surficial functional groups of metals. The stretched frequency in the range of $400 - 1400 \text{ cm}^{-1}$ related to metal oxides bonds such as lanthana, potassium oxide and copper oxides (N. Kumar et al., 2021) of absorptions peaks are observed at 577, 808 and 1343 cm⁻¹ respectively. The peaks at 1967, 2113, 2366, 2500 cm⁻¹ are related to the hydroxyl functional groups. (L. Wang et al., 2016). The similar observation on introduction of KNO₃ on the catalyst surface 3 DOM La_{0.8}Ce_{0.2}Mn1-xFe_xO₃ perovskites, the peaks incorporated in between 400 and 600 cm⁻¹ remain unchanged indicates that the deposition of KNO₃ on the surface of the catalyst has no effect. Meanwhile a new signal is observed between the 1300 -1900 cm⁻¹ associated to

anti-symmetric stretching mode of free NO_3^- ions. The corresponding KNO₃ support of perovskites, emphasising the portion of KNO₃ remains stable in case of K/La_{0.5}Ce_{0.2}Mn₁₋ _xFe_xO₃ perovskites even after calcination at 600°C for 5 hrs due to its formation of bulk KNO₃ (Feng, 2016).



Figure 5.21 The FTIR spectroscopy analyses of the spent $La_{0.75}K_{0.25}CuO_3$, $La_{0.50}K_{0.50}CuO_3$, $La_{0.25}K_{0.75}CuO_3$ and $KCuO_3$ catalysts.

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The surface properties of potassium promoted copper-based perovskites catalysts were examined using XPS analysis as shown in Figure 5.22. The binding energy of Cu2p3 and Cu2p1 detected at 932.5 and 952.2 eV respectively. Furtherly, we observe for orbital states of La3d5, La3d3 and K2p3, K2p1 peaks are detected at 838.5, 855.2 and 292.2, 294.7 eV respectively. The similar observations seen that the reduced copper species such as metallic copper or Cu₂O usually appears below 933 eV and copper species with Cu²⁺ cations above 933.7 eV. These two differences can be clearly seen in K-Cu/SrTiO₃ (above 933 eV) and SrKTiCuO₃ (below 933 eV). A revision of literature data reveals that copper species (Cu²⁺, Cu¹⁺ and Cu⁰) avail in bulk phases can be differentiated by their characteristics binding energy. However, when copper is highly dispersed and in intimate contact with supports, as is the case of the catalysts under study, Cu2p_{3/2} energies (Franz, 2014). The Fernandez-Garcia et al (2016) observed that for Cu/CeO_x/Al₂O₃ catalyst (reduced with H₂ at 350 °C) Cu2p_{3/2} appears at 932.7 eV.


Figure 5.22 XPS Analysis of the spent (a) La_{0.75}K_{0.25}CuO₃, (b) La_{0.50}K_{0.50}CuO₃, (c) La_{0.25}K_{0.75}CuO₃ and (d) KCuO₃ catalysts.

5.5.4 Scanning Electron Microscopy with Energy Dispersive X-Ray

The surface morphology of the potassium-based perovskite catalysts is shown in Figure 5.23. The metal nanoparticles are well dispersed on the lanthanum oxide support potassium, which is evident from the potassium distribution. Due to the uniform and regular distribution of particles, it is possible to identify the metal content in the support. Additionally, filamentous carbon was observed on the surface of the metal catalysts. This observation was further confirmed by analysing the crystallite size using XRD. Notably, the carbon content was more pronounced in the KCuO₃ catalyst.

The morphology of the spent catalysts primarily consisted of spherical primary particles with a grain radius in the range of 80-120 nm. However, the particle size of La_{0.75}K_{0.25}CuO₃ decreased to less than 50 nm. These primary particles tended to condense

into agglomerates. After K promotion in the catalysts, the spherical particles became larger but less uniform, and a few impurities appeared at high K content (Fang, 2014). The composition of impurities can be seen in EDX, as shown in Figure 5.24. The larger dark regions in the EDX map consist of La, K, and Cu, which might be attributed to the perovskite phase. However, only small amounts of fine grains and nanofibers-like structures, along with the carbon formation, are less prone to the surface of $La_{0.75}K_{0.25}CuO_3$ catalyst.



Figure 5.23 SEM images of the spent (a) $La_{0.75}K_{0.25}CuO_3$, (b) $La_{0.50}K_{0.50}CuO_3$, (c) $La_{0.25}K_{0.75}CuO_3$, and KCuO₃ catalysts under 3000 times of magnification.



Figure 5.24 SEM-EDX images of (a) $La_{0.75}K_{0.25}CuO_3$, (b) $La_{0.50}K_{0.50}CuO_3$, (c) $La_{0.25}K_{0.75}CuO_3$ and (d) KCuO₃ catalysts.

5.6 The Longevity Tests on the Yttrium and Potassium promoted LaCuO₃.

The catalytic performances in the EDR for both promoted catalysts were determined for 72 h of run by using an equal molar reactant ratio fed at 20 atm. The EDR reaction occurred at 1023 K and atmospheric pressure. The reference of the LaCuO₃ catalyst run was stopped after 45 h due to 14% drop of activity. The activity and stability for the catalysts in the EDR reaction and carbon deposition was the focus of this test. Hence, the EDR reaction was carried out at the reaction temperature higher than most previous reports (in Table 2.4) to see the catalyst defect due to carbon formation and sintering. The effects of Y and K promotion on reactant conversions with time on stream (TOS) are illustrated in Figure 5.25. C₂H₅OH conversion was significantly four times more than CO₂ conversion probably due to the co-existence of side reactions (viz., ethanol decomposition and ethanol dehydrogenation) during EDR reactions (Fayaz et al., 2023). However, the CO₂ conversion drops were not as high as ethanol conversion drops after 20 h on stream. Perhaps the EDR reactions had been becoming prominent (M. Wang et al., 2024).

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An initial and considerable increase was particularly observed for C_2H_5OH and CO_2 conversions of the LaCuO₃ catalyst in 8 hours. However, the conversions dropped gradually after that until 64%. The results of characterization analyses revealed the possible cause of the declination. Carbon deposition structure was evidenced in the EDX of post-reaction catalyst result shown in Figure 4.18. The surface area of spent LaCuO₃ decreased by 52% while the pore size decreased about 14%, as similarly reported by Li Zhang et al. (2017) in their methane dry reforming test. The structure of the carbon deposition might be crystals as shown by the XRD result in Figure 4.16 and amorphous as exhibited by the Raman spectroscopy in Figure 4.20. The single covalent bonding of carbon crystals was exhibited by the FTIR result in Figure 4.17 (Sarno et al., 2018).

The 5% error bars reveal the change significance of ethanol conversion is less than that of carbon dioxide. Nonetheless, the drop of the ethanol conversion became obvious after 40 h. The conversion ended at 70% (only 5% drop) and 55% (32% drop) for $La_{0.75}Y_{0.25}CuO_3$ and $La_{0.75}K_{0.25}CuO_3$, respectively. This implies better activity and stability of the yttrium-promoted perovskite catalyst, which is similar to the results

reported by Ramírez-Hernández, Viveros-García, Fuentes-Ramírez, and Galindo-Esquivel (2016). CO_2 conversions between Y-promoted and K-promoted perovskite catalysts are different where the first catalyst resulted in constant value for 72 h. This result was similar to the report shown by (M. Wang et al., 2024) in their Ni-based catalyst study for the EDR reaction. Yttrium might have strong alkalinity to chemisorb CO_2 during the reaction relative to potassium(Ramírez-Hernández et al., 2016).





Figure 5.26 exhibits the product yields of the same reaction: hydrogen and carbon monoxide. The yields follow the same pattern of reactant conversions, as previously discussed, especially ethanol conversion. Both yields increased until 20 h for all catalysts. The reference catalyst, LaCuO₃, ended at 46% of hydrogen yield and 25% of carbon monoxide yield, which are about 5% drop from the initial state. The maximum yields are seen approximately after 18 h. This maximum trend of yield data is not found in any reference, which indicates the increment of activity after the reaction is started. The analyses of XRD to the spent catalysts exhibits metal crystal rather than metal oxide crystal. Oxygen from the metal oxide reduction might have been involved in the EDR reaction process to produce more hydrogen and carbon monoxide as what was reported by (Fayaz et al., 2023) who added oxygen as the feedstock.



Figure 5.26 H_2 and CO Yield of the best catalysts for the best yttrium and potassiumpromoted catalysts at 1:1 (C₂H₅OH:CO₂) and 1023 K

Figure 5.27 shows the methane yield. The EDR reaction from both promoted catalysts exhibit the yields lower than the reference catalyst. Based on the error bar of 5%, Y-promoted catalyst significantly produced between 11.2% and 14.5% of methane yield before 60 h on stream. After that, a consistent drop occurred. The K-promoted catalyst has the fluctuated methane yield between 9% and 13.8% of methane yield before steady drop after 54 h on stream. Both drop probably manifested the decrease of methane dehydrogenation (Fayaz et al., 2023) and consequent formation of carbon as revealed by the XPS and EDX analyses. Hence, La_{0.75}Y_{0.25}CuO₃ showed lower carbon formation than the others.



Figure 5.27 CH₄ yield for for the best yttrium and potassium-promoted catalysts at 1:1 (C₂H₅OH:CO₂) and 1023 K

Figure 5.28 exhibits product ratios referring to carbon monoxide for the best yttrium and potassium-promoted catalysts. Error bars for H₂/CO are high due to the fluctuation of data and the drop was not apparently significant. All catalysts, including the reference, had the H₂/CO ratios higher than unity that are suitable for the Fischer Tropsch synthesis to produce long-chain hydrocarbons (Bolívar Caballero et al., 2022). H₂/CO ratio was obtained about 1.0-1.4 and higher than unity for both catalysts because of the concomitant ethanol dehydrogenation reaction. Interestingly, this H₂/CO ratio suitable to be employed as feedstock for downstream methanol production and FTS to produce long-chain hydrocarbons. This is probably an advantage using copper compared to nickel and cobalt (M. Wang et al., 2024). The highest ratio was shown by potassium-promoted perovskite catalyst and the ratio declines with time consistently until 72 h due to the surface area and reduction of active sites of the catalysts. CH₄/CO ratios generally follow the same trend. Perhaps CO was formed more than the other products due to the reverse of water shift reaction as expressed in Equation (2.14).





5.7 Post-Longevity Test Characterization

As aforementioned that $La_{0.75}Y_{0.25}CuO_3$ catalyst stands as the best catalysts in this study, the spent catalysts used for longevity test was further selected for post-reaction characterization. The resulting physicochemical attributes, morphology and carbon content analyses for selected catalyst were compared with the $La_{0.75}Y_{0.25}CuO_3$ and $La_{0.75}K_{0.25}CuO_3$ catalysts.

5.7.1 X-ray Diffraction

XRD analyses were conducted on the catalysts used in the EDR reaction running at T=1023 K and stoichiometric feed ratio as seen in Figure 5.29Figure . From the JCPDS database no. 83-0927, Y₂O₃ phase was identified at 20 of 29.16°, 39.94° and 48.74°. As all catalysts were sufficiently reduced in H₂ prior to EDR, this presence of Cu₂O phase on both spent catalysts was not observed during the reaction. The re-oxidation of active metal to inactive metal oxide could probably explain the initial declination of catalytic activity within 50 h. However, the Cu⁰ metallic form resulted from H₂ activation was still detected at 20 of 43.27° (JCPDS No. 04-0836) on both spent catalysts after 72 h on stream. The preservation of active metal after EDR would account for the stability of

catalytic performance beyond 50 h. The typical peaks with $2\theta = 29.87^{\circ}$ and 53.42° belongs to La₂O₃ phase (JCPDS No. 83-1355) were detected on both catalysts.

The broad peak ranging from 20° to 30° with the tip at 26.38° was observed for both spent catalysts assigned to graphitic carbon (JCPDS No. 75-0444), most likely formed from ethanol decomposition and cracking of CH4 intermediate at high reaction temperature (Pechimuthu et al., 2007).



Figure 5.29 XRD analyses of the spent (a) La_{0.75}Y_{0.25}CuO₃ (b) La_{0.75}K_{0.25}CuO₃ catalysts

5.7.2 Scanning Electron Microscopy with Energy Dispersive X-Ray.

SEM images of spent samples in the longevity test in Figure 5.30 clearly revealed carbon structure similarly reported by (Ch Pichas, P. Pomonis, D. Petrakis, & A. Ladavos, 2010) and they are at nanoscale or called carbon nanofilament (CNF) (Fayaz, 2018). Perhaps it was the carbon on catalysts surface as confirmed by EDX topography in Figure 5.31. The sponge like aggregate CNFs covers nearly entire surface of both catalysts, thereby inducing the initial loss in reactant conversions within 10 h. However, these CNFs would not result in severe deterioration due to its high reactiveness with CO₂ reactant via reverse Boudouard reaction (Fayaz, 2018). Carbon content of La_{0.75}Y_{0.25}CuO₃ in Figure 5.31(a) is lower than in La_{0.75}K_{0.25}CuO₃ in Figure 5.31(b). This content is however higher than LaCuO₃, which is 20.9 wt%.



Figure 5.30 SEM analysis of the spent (a) $La_{0.75}Y_{0.25}CuO_3$ (b) $La_{0.75}K_{0.25}CuO_3$ catalysts



Figure 5.31 SEM-EDX of (a) La_{0.75}Y_{0.25}CuO₃ (b) La_{0.75}K_{0.25}CuO₃ catalysts

5.7.3 X-Ray Photoemission Spectroscopy

The surface properties of $La_{0.75}Y_{0.25}CuO_3$ and $La_{0.75}K_{0.25}CuO_3$ catalysts were examined using XPS analysis of survey scan as shown in Figure 5.32. The low intensity of binding energy of Cu2p3 and Cu2p1 detected at 932.5 and 952.2 eV, the orbital states of La3d5, La3d3 and K2p3, K2p1 peaks are detected at 838.5, 855.2 and 292.2, 294.7 eV respectively. Moreover, shows that the binding energy of Y3d_{5/2} for all these four spent catalysts is around 156.2 eV which is comparable with that of Y 3d_{5/2} for pure Y₂O₃. In clearly the binding energy of carbon peak is higher for La_{0.75}K_{0.25}CuO₃ and strongly supporting from the XRD and SEM-EDX data.



Figure 5.32 XPS spectroscopy (a) full spectra scan (survey scan) (b) Carbon element of the spent $La_{0.75}Y_{0.25}CuO_3$ and $La_{0.75}K_{0.25}CuO_3$ catalysts

5.8 Concluding Remarks

The promotion of yttrium and potassium onto LaCuO₃ was studied through several characterizations and reaction tests. X-Ray diffractograms of both promoted catalysts showed the appearance of crystals, which were identified by referring to the equipment library, but the CuO, La₂O₃ and yttrium oxide crystals only appeared in yttrium-promoted catalysts. Nevertheless, in FTIR results, the functional groups of several metal oxide peaks appeared in both promoted catalysts. The TPR results revealed that promotion of yttrium did not increase the reduction temperature like potassium, thus indicating the more active yttrium-promoted catalysts. The EDR results show superior activity at the lowest loading, which is 0.25 of x-fraction based on La_{1-x}B_xCuO₃ composition in both catalysts. However, the conversions of ethanol and CO₂, and hydrogen yield are 5%, 5% and 10% respectively more in yttrium-promoted catalysts. Crystals in the yttrium-promoted catalysts remained higher than potassium-promoted catalysts in the postreaction XRD results. The FTIR analysis after the EDR reaction the functional groups of metal oxides appeared in both catalysts with lower intensity. La_{0.75}Y_{0.25}CuO₃ showed the highest activity.

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CHAPTER 6

KINETICS STUDY

6.1 Overview

Results of kinetics study are discussed for $La_{0.75}Y_{0.25}CuO_3$ catalyst beginning with the power law model. The rate laws on EDR were examined at reaction temperatures ranged from 998 to 1073 K, and partial pressure of CO₂: C₂H₅OH ratios of 2.5:1 to 1:2.5. As discussed in subchapter 3.6.2, the flow rate and catalyst packing secured the negligible mass transfer limitation conditions.

6.1.1 Power Law Model



The power law rate expression of EDR was examined at reaction temperatures spanning from 998 to 1073 K, and the ratios were varied based on partial pressure. The kinetic parameters of power the law model is expressed in Equation (6.1)

-r' = kC^m_{C2H3OH}Cⁿ_{CO2} اونيورسيتي مليسيا فهغ السلطان (6.1) UNIVERSITI MALAYSIA PAHANG

were determined by using the Polymath software. The method of the least square regression by Levenberg-Marqardt (L-M) algorithm was used to fit the data and determine the activation energy and rate constants of reaction, and pre-exponential or frequency factor in the Arrhenius equation. Both reactant conversions increased as the reaction temperature increased primarily due to the endothermicity and irreversibility of the EDR reaction. The reaction rates calculated by using Equations 6.2) and (6.3) using data from Table 6.1

$$-r_i' = \frac{F_{io} - F_i}{\Delta W} \tag{6.2}$$

where F and ΔW are molar flow rate and catalyst mass, respectively. The molar flow was calculated from ideal gas law,

$$F_i = \frac{P_i}{RT} \tag{6.3}$$

where y, P, R and T are mole fraction, partial pressure, gas constant and reaction temperature (K), respectively.

$P_{C_2H_5OH}$	P_{CO_2}	$-r_{C_2H_5OH}^{\prime}$	$-r'_{CO_2}$			
kPa	kPa	mol gcat ⁻¹ s ⁻¹	mol gcat ⁻¹ s ⁻¹			
30	70	1.06E-04	1.89E-05			
40	60	1.20E-04	2.76E-05			
50	50	1.36E-04	1.33E-05			
50	50	8.59E-05	2.10E-04			
60	40	8. 39 E-05	1.34E-04			
70	30	7.49E-05	9.70E-05			
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Table 6.1 Rate of Reactions for Various Pressures of Reactants

The regression results such as degree of fitness (R^2) and deviation (Rmsd) values calculated are higher than 95 % and acceptably low, respectively. This fitness is similar to the work reported by Fayaz (2018) for other catalysts using a Langmuir Hinshelwood model. In Table 6.2, the activation energy was determined to be 44.2 kJ mol⁻¹, as obtained from the graph in Figure 6.1. This occurred when the consumption of C₂H₅OH exceeded the consumption of CO₂. Comparatively as shown in the same table, Bej et al. (2017) reported an activation energy of 97.87 kJ mol⁻¹ for the transformation of CO₂ to CO as the limiting step using nano-NiO/SiO₂catalyst. However, when the feed contained CO₂ pressure higher than ethanol at reaction temperatures exceeding 1023 K, the activation energy increased to 92.12 kJ mol⁻¹. This discrepancy may be attributed to the presence of reactions other than EDR that also consumed the excess reactant and occupied active side on the catalyst. Additionally, steric effects from different reactant molecules could play a role. Despite the experiment being conducted under free mass transfer limitation, the influence of side reactions on the rate law was noted, as previously reported by Z. Zhang et al. (2013)

Authors	m	n	Ea kJ mol ⁻¹	Α	R ²	Rmsd (10 ⁷)
This study	0.26	0.64	44.2	1.3 x 10 ⁻²	0.99	7.65
(Bej et al., 2017)	0.96	3.95	97.87	6.78 x 10 ⁵		

Table 6.2 Kinetics parameters of the reactant of $La_{0.75}Y_{0.25}CuO_3$ catalyst based the power law model.

Table 6.2 summarizes the kinetic parameters for the power law mode. The orders of C_2H_5OH (m) and CO_2 (n) partial pressures are 0.26 and 0.64, respectively indicating that the reaction rate is highly influenced by the C_2H_5OH partial pressure. This was also reported by J. Zhang et al. (2020) using Rh-based catalyst where the first order of ethanol and zero order of carbon dioxide were obtained. In steam reforming of ethanol, using nickel-based catalyst, the order of ethanol is lower than the order of water according to the power law model (Bepari, Sarkar, & Pradhan, 2022), which was 0.18. This is not like what was reported by Z. Zhang et al. (2013) where the order was close to the steam reforming of ethanol. They concluded that no other papers report the reaction kinetics because of highly exothermic of the EDR reaction. The activation energy, Ea = 44.2kJ/mol is lower than the ones obtained by (J. Zhang et al., 2020) and (Görke, Pfeifer, & Schubert, 2009), which were 71.1 and 95 kJ/mol using the Rh-based and Re/CeO2 catalysts. The parity plot of the experimental rates versus predicated rates of consumption and product formation over LaCuO₃ catalyst are illustrated in Figure 6.2(a) and (b). Interestingly, the predicted rate fitted well with the experimental rate over La_{0.75}Y_{0.25}CuO₃ catalyst. This result agrees with the parity plot presented by Nakajima et al. (2023) in terms of fitness of the power law model on Ni/Si-MCM-41 catalyst in the methane dry reforming. Bej et al. (2017) tested the EDR reaction using the catalyst of nickel oxide supported on silica. The orders of reactant concentrations are greater in the same power law model. The effect of carbon dioxide concentration is similarly higher. Unfortunately, their activation energy was higher than this study implying that our catalyst is more active than theirs.



Figure 6.1 Arrhenius plot of the power law model energy for the EDR reaction using equal pressure of feed on LaCuO₃ catalyst



Figure 6.2 Parity plots for the rates of consumption over La_{0.75}Y_{0.25}CuO₃ catalyst at the temperature of 998-1073 K on (a) C₂H₅OH, (b)CO₂.

The Langmuir Hinshelwood (L-H) model was employed to capture the data of the EDR reaction using the $La_{0.75}Y_{0.25}CuO_3$ catalyst over the EDR reaction. The kinetic parameters of the model were regressed by using the Polymath software as summarized in Table 6.3. Associative adsorption of both C_2H_5OH and CO_2 on the single site with bimolecular surface reaction was the best model to express the limiting step in the catalytic EDR reaction (Fayaz, 2018). The first L-H model is shown in Equation (6.4)

$$r = \frac{k_{rxn}(P_{C_2H_5OH}P_{CO_2})}{\left(1 + K_{C_2H_5OH}P_{C_2H_5OH} + K_{CO_2}P_{CO_2}\right)^2}$$
(6.4)

based on the single-mechanism steps of molecular adsorption of both ethanol and carbon dioxide as follows (Fayaz et al., 2023). The steps of the model are detailed below.

$$\begin{split} & C_2H_5OH + X \leftrightarrow C_2H_5OH - X \\ & CO_2 + X \leftrightarrow CO_2 - X \\ & C_2H_5OH - X + CO_2 - X \rightarrow HCOO - X + CH_2COH - X + H_2 \\ & HCOO - X \rightarrow CO_2 + H - X \\ & CH_2COH - X + H - X \rightarrow CH_3COH - X \\ & CH_3COH - X + X \rightarrow CH_2 - X + H_2CO - X \\ & CH_2 - X + H - X \rightarrow CH_3 - X + X \\ & CH_3 - X + H - X \rightarrow CH_4 + 2X \\ & H_2CO - X \rightarrow CO + H_2 + X \end{split}$$

Another second model of L-H is the single –site dissociative adsorption of both C_2H_5OH and CO_2 with bimolecular surface reaction is expressed in Equation (6.5)

$$r = \frac{k_{rxn}\sqrt{P_{C_2H_5OH}P_{CO_2}}}{\left(1 + \sqrt{K_{C_2H_5OH}P_{C_2H_5OH}} + \sqrt{K_{CO_2}P_{CO_2}}\right)^2}$$
(6.5)

Based on the dissociative adsorption of both C₂H₅OH and CO₂ according to the steps below. C₂H₅OH + 2X \leftrightarrow CH₂OH - X + CH₃ - X CH₃ - X + X \rightarrow CH₂ - X + H - X CH₂ - X \rightarrow CH - X + H - X CH - X \rightarrow CH - X + H - X H - X + H - X \leftrightarrow H₂ + 2X CH₂OH - X + H - X \rightarrow CH₃ - X + OH - X CH₃ - X + H - X \leftrightarrow CH₄ + 2X

- $CO_2 + 2X \leftrightarrow CO X + O X$
- $\mathrm{CO}-\!\!X \leftrightarrow \mathrm{CO} + X$

The third L-H dual site mechanism considers that the C_2H_5OH and CO_2 reactants to adsorb favourably on two different sites (X1 and X₂) available on the catalyst surface (Sahoo, Das, Babu, & Naik, 2007)and lumped as below. Figure 6.3 illustrates the simplified steps for all models.

$$C_{2}H_{5}OH + X_{1} \leftrightarrow C_{2}H_{5}OH - X_{1}$$

$$CO_{2} + X_{2} \leftrightarrow CO_{2} - X_{2}$$

$$C_{2}H_{5}OH - X_{1} + CO_{2} - X_{2} \rightarrow HCOO - X_{2} + CH_{2}COH - X_{1} + H_{2}$$

$$HCOO - X_{2} \rightarrow CO + HO - X_{2}$$

$$CH_{2}COH - X_{1} + H - X_{2} \rightarrow CH_{3} - X_{1} + CHO - X_{2}$$

$$CH_{3} - X_{1} + X_{2} \rightarrow CH_{2} - X_{1} + H - X_{2}$$

$$CH_{2} - X_{1} + H - X_{2} \rightarrow CH_{3} - X_{1} + X_{2}$$

$$CH_{3} - X_{1} + H - X_{2} \rightarrow CH_{3} - X_{1} + X_{2}$$

$$CH_{3} - X_{1} + H - X_{2} \rightarrow CH_{4} + X_{1} + X_{2}$$

$$CHO - X_{1} + X_{2} \rightarrow CO - X_{1} + H - X_{2}$$

$$CO - X_{1} + X \leftrightarrow CO + X_{1}$$

$$2H - X_{2} \leftrightarrow H_{2} + 2X_{2}$$

$$r = \frac{k_{rxn} P_{C_2 H_5 OH} P_{CO_2}}{\left(1 + K_{C_2 H_5 OH} P_{C_2 H_5 OH}\right) \left(1 + K_{CO_2} P_{CO_2}\right)}$$
(6.6)

simplifies the steps that are previously mentioned.



Figure 6.3 The simplified steps of Langmuir-Hinshelwood based on a) a singlemechanism step of molecular adsorption of both reactants, b) single –site dissociative adsorption of both reactants and d) dual site mechanism considers that the both reactants adsorb favourably on two different sites (X1 and X₂) available on the catalyst surface

The kinetic parameters of La_{0.75}Y_{0.25}CuO₃ catalyst calculated form L-H model by using Polymath software are illustrated in Table 7.3. The L-H models were carried out over ethanol consumption rate of La_{0.75}Y_{0.25}CuO₃ catalyst over 3 models in EDR. As observed in Table 7.3, the various parameters including rate constant of reaction (k_{rxn}), adsorption constants of $K_{C_2H_5OH}$ and K_{CO_2} , R^2 and Rmsd values are estimated at temperature 923-1073 K. the rate constants of model 1 increased with growing temperature. In addition, the ($R^2 > 0.98$), and smaller R_{msd} values were obtained for model 1. Therefore, model 1 with single site associative adsorption on EDR reaction surface gave good fitting as shown in Table 6.3. The Arrhenius plot for model 1 is presented in appendix F (see Figure 6). Model 1 is suitable for explaining the reaction mechanism in EDR over La_{0.75}Y_{0.25}CuO₃ catalyst.

The parameters such as rate constant of reaction (k_{rxn}), adsorption constants of $K_{C_2H_5OH}$ and K_{CO_2} , R² and Rmsd values were estimated at the temperatures spanning from 923 to 1073 K. the rate constants of the model increased with growing temperature. In addition, R² > 0.98, and smaller R_{msd} values were obtained for the L-H model. The model with single site associative adsorption on EDR reaction surface gave a good fitting. The model is suitable for explaining the reaction mechanism in EDR over La_{0.75}Y_{0.25}CuO₃ catalyst.

Table 6.3 Kinetic parameters calculated from L-H rate expressions for La_{0.75}Y_{0.25}CuO₃ catalyst

M.J.I	T	V	II.	L.	D 2	р
Niodei	Temp	A _{rxn}	К С2H50H	K _{CO2}	R ²	K _{msd}
No	(K)	(10 ⁷⁾	(10 ²)	(10 ²)		(10 ⁷)
	998	5.84	5.79	3.04	0.98	3.07
1	1023	6.49	4.72	5.13	0.99	3.86
	1048	3.50	3.98	6.54	0.98	3.13
	1073	1.140	2.62	7.02	0.96	2.02
	998	5.69	4.51	4.48	0.99	2.84
	1023	36.9	4.89	2.03	0.98	4.86
2	1048	2.83	3.23	3.56	0.98	3.68
	1073	4.51	1.51	4.34	0.99	6.63

Table 6.3 Continued

Model	Temp	K _{rxn}	К _{С2Н5} ОН	K _{CO2}	R ²	R _{msd}
No	(K)	(107)	(10 ²)	(10 ²)		(10 ⁷)
	998	5.02	2.14	7.67	0.99	2.59
	1023	4.36	1.11	1.01	0.98	4.06
3	1048	3.26	1.31	9.21	0.98	1.10
	1073	2.18	1.56	6.63	0.99	2.16

The L-H model was studied for further assessment to examine its thermodynamic consistency. The kinetic parameter such as $K_{C_2H_5OH}$ and K_{CO_2} were estimated by using Equations (7.3) – (7.4) and subsequent values of both enthalpy and entropy are presented in Table 6.4. The activation energy and thermodynamic properties are lower than the result obtained by Fayaz (2018).

Table 6.4.



Where,

K = adsorption constant

 $\Delta H = enthalpy (J mol^{-1})$

 $\Delta S = entropy (J mol^{-1}K^{-1})$

 $R = gas constant (8.314 mol^{-1} K^{-1})$

T = reaction temperature (K)

The activation energy and thermodynamic properties are lower than the result obtained by Fayaz (2018).

Table 6.4 Summary of kinetic parameter computed from L-H rate expression over catalysts

Catalyst	А	Ea	$\Delta H_{ads}^{C_2H_5OH}$	$\Delta S_{ads}^{C_2H_5OH}$	$\Delta H_{ads}^{CO_2}$	$\Delta S_{ads}^{CO_2}$
This study on	2.12	102.24	-61.33	-94.32	62.19	43.23
$La_{0.75}Y_{0.25}CuO_{3}$						
Fayaz (2018) on	2.34	106.48	-81.67	-110.96	81.32	63.46
3%La-10%Co/Al ₂ O ₃						

Figure 6.5 shows the parity plot between estimated values and experimental values for the rates of reactant consumptions and product formations over $La_{0.75}Y_{0.25}CuO_3$ catalyst by using the L-H model 1. Both the experimental & predicted C₂H₅OH consumption rates are in a good fit further confirming that the model is appropriate for the mechanism of $La_{0.75}Y_{0.25}CuO_3$ catalyst for EDR reaction.



Figure 6.4 Parity plot of experiment versus predicted of C₂H₅OH consumption rate for La_{0.75}Y_{0.25}CuO₃ catalyst using L-H model 1



Figure 6.5 Parity plot of experimental versus predicted for rate of (a) C_2H_5OH consumption, (b) CO_2 consumption, (c) H_2 synthesis and (d) CO synthesis for $La_{0.75}Y_{0.25}CuO_3$ catalyst using the L-H model 1.

6.1.3 Concluding Remarks

The EDR reaction data under $La_{0.75}Y_{0.25}CuO_3$ catalysis was captured by two models: power law and Langmuir Hinshelwood on reactant single steps. Both models were fitted well in the analysis. The results of the kinetics study manifest the mechanism of reactant chemisorption on the catalyst surface before the transformation into the desired products or carbonaceous side products, which might have become the limiting step to the reaction.

CHAPTER 7

CONCLUSION AND RECOMMENDATIONS

7.1 Conclusions

In the current scenario, among catalytic reforming techniques, EDR is gaining prominence in the production of syngas due to its eco-friendly nature. It utilizes CO_2 greenhouse gases and ethanol (a non-toxic feedstock). In this method, syngas is produced with a suitable H₂/CO ratio to produce long chain hydrocarbons through Fischer-Tropsch synthesis. The research objectives have been largely fulfilled, and the findings from the evaluation of EDR on copper-based perovskites catalysts promoted with lanthanum or cerium and yttrium or potassium are as follows:

- The copper-based perovskites were mixed with rare earth metals (i.e. La and Ce) to prepare the catalysts using the sol-gel method. The evaluation of EDR was performed in a quartz fixed reactor by varying the reaction temperature from 998 to 1073 K and reactant ratios (C₂H₅OH:CO₂) of 2.5:1 to 1:2.5 respectively under atmospheric pressure. The presence of perovskite structures was confirmed from the XRD, SEM, TEM and XPS results. Hence, Objective 1 was achieved.
- The catalytic activity of reaction temperature increased with respective rise in temperatures from 998 to 1073 K due to its endothermic nature. The LaCuO₃ catalyst exhibited the best activity in terms of reactant conversions and product yield. The increase in reactant conversions and product yields correlated with CO₂ partial pressure, which resulted from excess CO₂ adsorption. This excess adsorption contributed to the enhancement of intermediate CH₄ dry reforming in all catalysts. Conversely, the conversions decreased with increasing C₂H₅OH partial pressures due to competing reactant adsorption on the catalyst surface, especially in the presence of ethanol dehydrogenation side reactions.
- The reduction in BET surface area and CuO crystallite size occurred due to its diluting effect in the presence of La₂O₃ and CeO₂. The addition of promoters (Y

and K) enhanced the interaction evidence in TPR analyses. The increasing H_2 uptake with the promoters during TPR indicates an enhanced degree of CuO to Cu^0 reduction. The promoter loading of $La_{1-x}Y_xCuO_3$ and $La_{1-x}K_xCuO_3$ varied where x ranged from 0 to 1 with increments of 0.25. Among the tested catalyst samples, $La_{0.75}Y_{0.25}CuO_3$ and $La_{0.75}K_{0.25}CuO_3$ exhibited the best catalytic activity at a 1:1 ethanol to CO₂ stoichiometric ratio at 1023 K, owing to their high metal dispersion, basic property and H_2 reduction degree. Objective 2 was achieved.

- ➤ The longevity and stability performances of three catalysts (LaCuO₃, La_{0.75}Y_{0.25}CuO₃ and La_{0.75}K_{0.25}CuO₃) were studied for the EDR reaction. Among these, La_{0.75}Y_{0.25}CuO₃ exhibited higher catalytic activity at $P_{C_2H_5OH} = P_{CO_2} = 20 \ kPa$ for 72 h and 1023 K under atmospheric pressure. An interesting observation is that the H₂/CO ratios for all the catalyst were less than 2, indicating their suitability for downstream hydrocarbon productions.
- The kinetic model was studied for LaCuO₃, varying the reactant ratios from 1:2.5 to 2.5:1 and the reaction temperatures from 998 to 1073 K under atmospheric pressure. Power law calculations revealed an activation energy is 44.2 kJ mol⁻¹ and the order of ethanol and carbon dioxide are 0.26 and 0.64, respectively. A Langmuir-Hinshelwood model was additionally proposed for the catalytic EDR reaction. In the model, both reactants were associatively adsorbed on a single-site of the catalyst, corresponding to an activation energy of approximately 102.24 kJ mol⁻¹. Objective 3 was therefore achieved. A PAHANG

AL-SULTAN ABDULLAH

7.2 Recommendation

The following recommendations are put forward from the results of the entire EDR study:

- The catalyst preparation method used in this study was the sol-gel technique without the addition of any other chemicals. Another sol-method using polyethylene glycol and ammonium hydroxide can be proposed to improve the formation of perovskite structure and buffer pH of the solution (Abdel-Latif et al., 2015; Navas, Fuentes, Castro-Alvarez, & Chavez-Angel, 2021).
- The catalytic activity and stability were studied on rare earth elements (i.e. La, Ce and Y) and transition metals (i.e. K) mixed and prompted with copper-based

perovskites catalysts. There are other metal supports (i.e. Al₂O₃, Hydrotalacities etc.,) alkali metals, transition metals (Ni. Co) and rare earth (Sm, Nd) that can be studied.

Temperature programmed desorption of carbon dioxide should be employed to delineate the basicity of the catalyst active site.



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APPENDIX A

CALCULATION OF CATALYST PREPARATION

Catalysts used for this work are:

i. LaCuO₃ & CeCuO₃

- ii. $La_{1-x}K_xCuO_3$ where x = 0, 0.25, 0.75 & 1
- iii. $La_{1-x}Y_xCuO_3$ where x = 0, 0.25, 0.75 & 1

<u>5 g of LaCuO₃ Catalyst:</u>

$1 \text{ mol of } LaCuO_3 = 1 \text{ mol of } La(NO_3)_3.6H_2O$
mass of LaCu0 mass of La(NO)3.6H2Og
molar mass of LaCuO3g/mol molar mass of La(NO3)3.6H2Og/mol
$\frac{5g}{2} = \frac{mass of La(NO).6H2Og}{2}$
250.4 <i>g</i> /mol 433.01 <i>g</i> /mol
Mass of La(NO ₃) ₃ .6H ₂ Og = $\frac{5g \times 433.01 \ /mol}{250.4g/mol}$
= 8.64g
The solubility of $La(NO_3)_3.6H_2O = 168g/100mL$
168g → 100mLINIVERSITI MALAYSIA PAHANG
8.64 → n mL AL-SULTAN ABDULLAH
$nmL = \frac{100mL \times 8.64}{168g}$

= 5.14 mL

8.64g of lanthanum nitrate hexahydrate was mixed in the 5.14mL of D.I water.

1 mol of $LaCuO_3 = 1$ mol of $Cu(NO_3)_2.6H_2O$

 $\frac{mass of LaCuO3g}{molar mass of LaCuO3g/mol} = \frac{mass of Cu(NO).6H2Og}{molar mass of Cu(NO).6H2Og/mol}$ $\frac{5g}{250.4g/mol} = \frac{mass of Cu(NO3).6H2Og}{295.64 / mol}$ Mass of Cu(NO₃)₂.6H₂O = $\frac{5g \times 295.64g/mol}{250.4g/mol}$ = 5.90g The solubility of Cu(NO₃)₂.6H₂O = 156g/100mL 156g \rightarrow 100mL

 $5.90 \rightarrow nmL$

 $nmL = \frac{100mL \times 5.90}{156g}$ = 3.78mL

5.90g of copper nitrate hexahydrate was mixed in the 3.78mL of D.I water. the molar ratio of citric acid to total metal ions was selected to be 2:1

$$n_{CA}/n_{total ions} = 2/1;$$

$$n_{CA} = 2 \times (n_{La3+} + n_{Cu2+})$$

$$= 2 \times (\frac{5}{250.4} + \frac{5}{250.4})$$

$$= 0.0796 \text{ mol}$$

$$n_{CA} = \frac{mass \ of \ citric \ acid}{molar \ mass \ of \ citric \ acid}$$

Mass of citric acid = n_{CA} x molar mass of citric acid

= 0.0796 mol x 192.124g/mol

```
= 15.29g
```

The solubility of citric acid = 180.89 g/100 mL

180.89g → 100mL	
15.29g → n mL	
$m m I = \frac{100 m L \times 15.29 g}{m L \times 15.29 g}$	
$111112 - \frac{11112}{180.89}g$	
= 8.45 mL	UMPSA

Therefore, 15.29g of citric acid is added in 8.45ml of D.I.

5 g of CeCuO ₃ Catalyst:	اونيۇرسىتى مليسيا قهغ السلطا
1 mol of LaCuO ₃	1 mol of Ce(NO ₃) ₃ .6H ₂ O PAHANG
mass of CeCuO molar mass of CeCuO3g/mol	= mass of Ce(NO3)3.6H20 molar mass of Ce(NO3)3.6H2Og/mol
$\frac{5g}{251.662g/mol} =$	mass of Ce(NO3).6H2Og 434.22g/mol
Mass of Ce(NO ₃) ₃ .6H ₂ Og	$= \frac{5g \times 434.22g/mol}{251.662g/mol}$
	= 8.627g

The solubility of Ce(NO₃)₃.6H₂O = 175.4g/100mL175.4g \rightarrow 100mL

8.627 → n mL

 $nmL = \frac{100mL \times 8.627g}{175.4g}$ = 4.91mL

8.627g of Cerium nitrate hexahydrate was mixed in the 4.91mL of D.I water.

1 mol of $CeCuO_3 = 1$ mol of $Cu(NO_3)_2.6H_2O$

 $\frac{mass of CeCuO3g}{molar mass of CeCuO3g/mol} = \frac{mass of Cu(NO3).6H2Og}{molar mass of Cu(NO3).6H2Og/mol}$ $\frac{5g}{251.662g/mol} = \frac{mass of Cu(NO3).6H2Og}{295.64 / mol}$

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Mass of Cu(NO₃)₂.6H₂O = $\frac{5g \times 295.64g/mol}{251.662g/mol}$ = 5.87g

The solubility of $Cu(NO_3)_2.6H_2O = 156g/100mL$

 $156g \rightarrow 100mL$ $5.87 \rightarrow nmL$ $nmL = \frac{100mL \times 5.87}{2}$

 $nmL = \frac{100mL \times 5.87g}{156g}$ = 3.76mL

5.87g of copper nitrate hexahydrate was mixed in the 3.76mL of D.I water.

Most of literature has taken, the molar ratio of citric acid to total metal ions was selected to be 2:1

 $n_{CA}/n_{total ions} = 2/1 ;$ $n_{CA} = 2 \times (n_{La3^+} + n_{Cu2^+})$ $= 2 \times (\frac{5}{250.4} + \frac{5}{250.4})$ = 0.0796 mol $n_{CA} = \frac{mass \ of \ citric \ acid}{molar \ mass \ of \ citric \ acid}$ Mass of citric acid = $n_{CA} \times \text{molar mass of citric acid}$ = 0.0796 mol x 192.124 g/mol = 15.29 g

The solubility of citric acid = 180.89g/100mL

180.89g → 100mL

15.29g → n mL

n mL =
$$\frac{100 \ mL \times 15.29 \ g}{180.89 \ g}$$

= 8.45 mL

Therefore, 15.29g of citric acid is added in 8.45ml of D.I.

Molar mass of $La_{0.75}K_{0.25}CuO_3 = 0.75(La)+0.25(K)+Cu+3(O)$

= 0.75(138.9) + 0.25(39.09) + 63.5 + 3(16)

= 226.02 g/mol.

n La_{0.75}K_{0.25}CuO₃ = $\frac{5 g}{mw}$

 $=\frac{5 g}{226.02 g/mol}=0.02 \text{ mol } \text{La}_{0.75}\text{K}_{0.25}\text{CuO}_3$ n_{La} required = 0.75×0.02 the solubility of $La(NO_3)_3.6H_2O = 168$ g/100 mL = 0.015 mol $168 \text{ g} \rightarrow 100 \text{ mL}$ $1 \text{ mol La}(NO_3)_3.6H_2O = 1 \text{ mol of La}$ $6.49 \text{ g} \rightarrow \text{n mL}$ $\frac{mass of La(NO3)3.6H20}{Molar mass of La(NO3)3.6H20} = 0.015$ $n mL = \frac{100 \times 6.49}{168}$ mass of La(NO₃)₃.6H₂O = 0.015×433.01 = 6.49 g= 3.86 mL n_k required = 0.25×0.02 the solubility of $KNO_3 = 246 \text{ g}/100$ mL $246 \text{ g} \rightarrow 100 \text{ mL}$ = 0.005 mol $1 \mod KNO_3 = 1 \mod of K$ $0.50 \text{ g} \rightarrow \text{n mL}$ $\frac{mass of KNO3}{molar mass of KNO3} = 0.005$ $n mL = \frac{100 \times 0.50}{246}$ mass of KNO₃ = 0.005×101.10 = 0.50 g= 0.203 mLthe solubility of $Cu(NO_3)_2.6H_2O = 156$ n_{Cu} required = 1×0.02 g/100 mL = 0.02 mol $156 \text{ g} \rightarrow 100 \text{ mL}$ 1 mol of $Cu(NO_3)_2.6H_2O = 1$ mol of CuارImi g→nmL مليسيا فهة السلطان عبدالله $\frac{mass of Cu(NO3)2.6H20}{molar mass of Cu(NO3)2.6H20} \equiv 0.02$ AYSIA PAHANG $n mL = \frac{100 \times 5.91}{156}$ mass of Cu(NO₃)₂.6H₂O = 0.02×295.64 = 5.91 g= 3.78 mL $\frac{nCA}{ntotal} = \frac{2}{1}$ The solubility of citric acid = 180.89 g/100mL $nCA = 2 (nLa^{3+} + nCe^{3+} + nCu^{2+})$ $180.89 \text{ g} \rightarrow 100 \text{ mL}$ = 2 (0.018 + 0.002 + 0.02)15.36 g \rightarrow n mL = 0.08 moln mL = $\frac{100 \times 15.36}{180.89}$ mass of citric acid = 0.08×192.124 = 15.36 g= 8.49 mLLa(NO₃)3.6 D.I KNO₃ D.I Cu(NO₃)₂. D.I D.I(m Catalyst Citric H₂0 (g) (mL) (mL) 6H₂O (g) (mL) acid (g) L)

La _{0.75} K _{0.25} CuO ₃	6.4	3.8	0.50	0.20	5.9	3.7	1536	8.49
La _{0.50} K _{0.50} CuO ₃	4.3	2.5	1.0	0.40	5.9	3.7	15.36	8.49
La _{0.25} K _{0.75} CuO ₃	2.1	1.2	1.5	0.60	5.9	3.7	15.36	8.49

Catalyst	La(NO ₃) ₃ .6H ₂ 0 (g)	D.I (mL)	KNO3 (g)	D.I (mL)	Cu(NO ₃)2.6 H ₂ O (g)	D.I (mL)	Citric acid (g)	D.I (mL)
La _{0.75} K _{0.25} CuO ₃	6.4	3.8	0.50	0.20	5.9	3.7	15.36	8.49
La _{0.50} K _{0.50} CuO ₃	4.3	2.5	1.0	0.40	5.9	3.7	15.36	8.49
La _{0.25} K _{0.75} CuO ₃	2.1	1.2	1.5	0.60	5.9	3.7	15.36	8.49



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APPENDIX B

TRANSPORT RESISTANCE CALCULATIONS

B.1 Resistance of External Mass Transfer

The external mass transfer resistances can be ignored when the following condition is satisfied.

$$\frac{(-r_{exp})\rho_b R_p n}{k_c C_{Ab}} < 0.15$$
(B.1)

Where

3)

 $(r_{exp}) = reaction rate (4.88 \times 10^{-5} \text{ mol gcat}^{-1} \text{ s}^{-1})$ $\rho_{b} = \text{ bulk density of catalyst (0.67 g cm}^{-3})$ $R_{p} = \text{ catalyst particle radius (7.15 \times 10^{-5} m)}$ $C_{Ab} = \text{ bulk gas phase concentration of reactant (A) in (4.09 \times 10^{-5} mol cm}^{-1})$

Determination of Mass Transfer Coefficient (kc)

The mass transfer coefficient (kc) can be determined as follows

$$k_c = \frac{j_D U}{s_c^{\frac{2}{3}}} \tag{B.2}$$

Before the calculating the mass transfer coefficient, the dimensionless quantities has to find out such as Reynolds (R_e) and Schmidt number (S_c) and colbum's mass transfer factor (j_D) as given below;

The Reynolds number (R_e):

$$R_e = \frac{\rho_{g \, U \, d_p}}{\mu_g} \tag{B.3}$$

Where

$$\rho_g$$
 = gas mixture density (i.e. N₂, CO₂ and CH₄ kgm⁻³)

U = Superficial gas velocity (ms⁻¹)

 d_p = Average particle diameter (1.43 × 10-4 m)

 μ_g = Viscosity of gas mixture (kg m⁻¹ s⁻¹)

Gas mixture density (ρ_g)

$$\rho_g = \frac{W_g P}{RT} \tag{B.4}$$

Where

R = ideal gas constant (8.314 m³ Pa K⁻¹ mol⁻¹) T = reaction temperature (1023 K) P = standard pressure (101325 Pa) W_g = $\sum M_i y_i$ (where i: C₂H₅OH, CO₂ or N₂) = 0.035 kg mol⁻¹ $\rho_g = \frac{0.035 \text{ kg mol}^{-1} \times 101325 \text{ Pa}}{8.314 \text{ m}^3 \text{ Pa} \text{ K}^{-1} \text{ mol}^{-1} \times 1023 \text{ K}} = 0.436 \text{ kg m}^3$ PAHANG

The calculation of superficial gas as shown below

$$U = \frac{V}{A}$$

Where, V is the volumetric gas flow rate (70 mL min⁻¹) at temperature of 298 K.

 $U = \frac{70 \, mLmin^{-1} \times 1 \, m^3 \times 1 \, min \times 1023 \, K}{4.90 \times 10^{-5} \, m^2 \times 10^6 \, mL \times 60 \, s \times 298 \, K} = 7.63 \times 10^{-2} \, \text{m s}^{-1}$

Therefore, the gas mixture viscosity was derived from Equations (B.6), (B.7) and (B.8)

$$\mu_g = \Sigma \frac{y_{i\mu_i}}{\sum_{j+1} y_{i\phi_i}} \tag{B.6}$$

$$\phi_{ij} = \left(\frac{\mu_i}{\mu_j}\right) \left(\frac{M_i}{M_j}\right) \phi_{ij}$$
(B.7)
$$\phi_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_i}\right)^{\frac{1}{2}} \left(\frac{M_i}{M_j}\right)^{\frac{1}{4}}\right]^2}{\left[8 \left(1 + \left(\frac{M_i}{M_j}\right)\right)^{\frac{1}{2}}\right]}$$
(B.8)

Where

y = mole fraction of gases (C₂H₅OH = 0.197, CO₂ = 0.197 and N₂ = 0.605)

 $i, j = C_2H_5OH, CO_2 and N_2$

 $\mu = \text{Viscosity of gases } (C_2H_5\text{OH} = 2.59 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}, \text{ CO}_2 = 4.08 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ and $N_2 = 3.92 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$

M = Gas component molecular weight

The substitution of μ and M values in Eqns. (B.7) and (B.8) is to find the value of Φ_{ij} . Further substitution of values Φ_{ij} and y in Equation (B.6) to obtain μ_g , which is 3.46×10^{-5} kg m⁻¹s⁻¹. Therefore, the Reynolds number (Re) is obtained

$$Re = \frac{0.436 \, kg \, m^{-3} \times 7.63 \times 10^{-2} m s^{-1} \times 1.43 \times 10^{-4} \, m}{3.46 \times 10^{-5} kg m^{-1} s^{-1}} = 0.137$$

The diffusivity of components (C₂H₅OH, CO₂ and N₂) is determined from

$$D_g = \frac{1 - y_i}{\sum_j \frac{y_i}{D_{ij}}} \tag{B.9}$$

$$D_{ij} = \frac{1 \times 10^{-3} \ T^{1.75} \sqrt{\frac{M_{i+M_j}}{M_i M_j}}}{P\left[(\Sigma v)_i^{\frac{1}{3}} + (\Sigma v)_j^{\frac{1}{3}} \right]^2}$$
(B.10)

Where

 $i = CO_2$; $j = N_2$ and C_2H_5OH

P = standard pressure (1 atm)

T = temperature (1023 K)

 $M = molecular weight of gases (N_2 = 28.01 g mol^{-1}, CO_2 = 44.01 g mol^{-1} and C_2H_5OH = 46.07 g mol^{-1})$

v = molecular weight of gases (N₂ = 17.9 cm³ mol, CO₂ = 26.9 cm³ mol and C₂H₅OH = 48.38 cm³ mol)

$$D_g = \frac{1 - 0.197}{\sum \left(\frac{0.197}{8.10 \times 10^{-5} m^2 s^{-1}} + \frac{0.605}{1.30 \times 10^{-4} m^2 s^{-1}}\right)} = 1.13 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$$

The Schmidt number (S_c)

$$Sc = \frac{\mu_g}{\rho_g D_g}$$
(B.11)
$$S_c = \frac{3.46 \times 10^{-5} kg m^{-1} s^{-1}}{0.436 kg m^3 \times 1.13 \times 10^{-4} m^2 s^{-1}} = 0.703$$

Colburn's mass transfer factor (J_D)

Since Re <350, the calculation of colburn's mass transfer factor can be determined using Equation (B.12) proposed by (Dwivedi and Upadhyay, 1977)

$$j_{D} = \frac{1}{\varepsilon} \left[\left(\frac{0.765}{Re^{0.82}} \right) + \left(\frac{0.365}{Re^{0.386}} \right) \right]$$
(B.12)
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$$j_{D} = \frac{1}{\varepsilon} \left[\left(\frac{0.765}{0.137^{0.82}} \right) + \left(\frac{0.365}{0.137^{0.386}} \right) \right] = 4.69 \text{BDULLAH}$$

Thus, mass transfer coefficient (kc) is computed as

$$k_c = \frac{4.69 \times 7.63 \text{ ms}^{-1}}{0.703^{\frac{2}{3}}} = 45.15 \text{ cm s}^{-1}$$

Therefore, the mears value is estimated using Equation (B.1)

$$\frac{(-r_{exp})\rho_b R_p n}{k_c C_{AB}}$$

$$\frac{4.88 \times 10^{-5} mol \ g_{cat}^{-1} s^{-1} \times 0.67 g cm^3 \times 7.15 \times 10^{-3} \ cm \times 1}{45.15 \ cm \ s^{-1} \times 4.09 \times 10^{-5} \ mol \ cm^{-3}} = 1.26 \times 10^{-4} < 0.15$$

B.2 Internal (Intraparticle) Mass transfer Resistance

The Weisz-Prater criterion is employed for negligible pore diffusion resistance by using Equation (B.13)

$$\frac{(-r_{exp})\rho_b R_p^2}{D_{eff} c_{As}} < 1 \tag{B.13}$$

Where

 $(-r_{exp}) = 4.88 \times 10^{-5} \text{mol } g_{cat}^{-1} s^{-1}$ $R_p = 7.15 \times 10^{-5} \text{ m}$ $\rho_c = 3.35 \text{ g cm}^3$

 D_{eff} = effective diffusivity of CO₂ into a mixture of C₂H₅OH and N₂ (m²s⁻¹)

 $C_{Ab} = 4.09 \times 10^{-5}$ mol cm⁻³ ($C_{Ab}=C_{As}$ since external mass transfer limitations is negligible)

Estimation of effective diffusivity

$$D_{eff} = \frac{D_g \omega_p \sigma_c}{\tau} \tag{B.14}$$

Where

$$\tau$$
 = tortuosity (3)
 ω_p = porosity of the catalyst pellet (0.4)
 σ_c = construction factor (0.8)
 D_g = diffusivity of CO₂ into a mixture of C₂H₅OH and N₂ (1.13×10⁻⁴ m² s⁻¹)

$$D_{eff} = \frac{1.13 \times 10^{-4} m^2 s^{-1} \times 0.4 \times 0.8}{3} = 1.21 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$$

Thus, the Weisz-Prater criterion

$$\frac{(-r_{exp})\rho_c R_p^2}{D_{eff} C_{Ac}}$$

$$\frac{4.88 \times 10^{-5} molg_{cat}^{-1} s^{-1} \times 3.35 g cm^3 \times (7.15 \times 10^{-5} m)^2}{0.121 cm^2 s^{-1} \times 4.09 \times 10^{-5} molcm^3} = 1.69 \times 10^{-3} m^2 s^{-1}$$

B.3 External Heat Transfer Resistance

The limitation for negligible external heat transfer, mears criterion computed in Equation (B.15) (Fogler, 2004)

$$\frac{|(-\Delta H_r)|(-r_{exp})\rho_b R_p E_A}{hRT_b^2} < 0.15$$
(B.15)

Where

 $\rho_b = 670 \text{ kg m}^{-3}$ $R_p = 7.15 \times 10^{-5} \text{ m}$ $E_A = 125.04 \times 10^3 \text{ J mol}^{-1}$ $-\Delta H_r = 302.10 \times 10^3 \text{ J mol}^{-1}$ $R = \text{ideal gas constant (8.314 \text{ J mol}^{-1} \text{ K}^{-1})}$ $T_b = \text{reactant gas bulk temperature (1023 \text{ K})}$ $h = \text{heat transfer coefficient between catalyst and gas mixture (J m}^{-2} \text{ s}^{-1} \text{ K}^{-1})$ Pre calculation of Heat Transfer Coefficient (h)

Colburn-Chilton was proposed the relation of heat transfer coefficient, mass transfer and heat of j-factor.

$$j_D = j_H = \frac{h p_r^2}{c_{pg} \rho_g U}$$
 (B.16) او نبو (B.16) (B.

Pr = Prandtl number

U = superficial gas velocity $(7.63 \times 10^{-2} \text{ m s}^{-1})$

 $j_{\rm H}$ = heat factor of j-factor ($j_{\rm H}$ = $j_{\rm D}$)

 ρ_g = gas mixture density (4.35×10⁻¹ kg m⁻³)

 C_{pg} = specific heat capacity of feed gas mixture at constant pressure (J kg⁻¹ K⁻¹)

The formulation of heat capacity gas mixture is given in Equation (B.17)

$$C_{pg} = \sum_{i} y_i C_p^i \tag{B.17}$$

$$C_{pg} = 1.55 \times 10^3 \text{J} \, kg^{-1} K^{-1}$$

Where

i = C₂H₅OH, N₂ and CO₂

$$C_p$$
 = specific heat capacity of gases (CO₂ = $1.22 \times 10^3 J kg^{-1}K^{-1}$, N₂ = $1.16 \times 10^3 J kg^{-1}K^{-1}$ and C₂H₅OH = $3.06 \times 10^3 J kg^{-1}K^{-1}$)
y = mole fraction of component gases (C₂H₅OH = 0.197 , CO₂ = 0.197 and N₂ = 0.605)

The thermal gas mixture conductivity (λ_g)

$$\lambda_g = \sum_i \frac{y_i \lambda_i}{\sum_{j \neq 1} y_j \varphi_{ij}} \tag{B.18}$$

$$\varphi_{ij} = \frac{1}{4} \left\{ 1 + \left[\left(\frac{\mu_i}{\mu_j} \right) \left(\frac{M_j}{M_i} \right)^{\frac{3}{4}} \left(\frac{T+S_i}{T+S_j} \right) \right]^{\frac{1}{2}} \right\}^2 \left(\frac{T+S_{ij}}{T+S_i} \right)$$
(B.19)

 $S_{ij} = S_{ji} = C\left(S_i S_j\right)^{\frac{1}{2}}$

Where

i ,j = N₂, CO₂ and C₂H₅OH T = temperature of gas mixture (1023 K) C = 1 is non-polar; 0.73 is for polar. S = boiling point (K) × 1.5 (C₂H₅OH = 351.37 K, CO₂ = 194.5 K and N₂ = 77.2 K) **UNVERSITIALAYSA PAHANG** μ = gas viscosity (C₂H₅OH = 2.59×10⁻⁵ kg m⁻¹s⁻¹, N₂ = 4.08×10⁻⁵ kg m⁻¹s⁻¹ and CO₂ = 3.92×10⁻⁵ kg m⁻¹s⁻¹) M = molecular weight of gases (CO₂ = 44.01 g mol⁻¹, N₂ = 28.01 g mol⁻¹ and C₂H₅OH = 46.07 g mol⁻¹) λ = thermal conductivity of gases (C₂H₅OH = 0.13 J m⁻¹ s⁻¹ K⁻¹, N₂ = 0.07 J m⁻¹ s⁻¹ ¹ K⁻¹ and CO₂ = 0.07 J m⁻¹ s⁻¹ K⁻¹) y = gas component mole fraction (CO₂ = 0.197, C₂H₅OH = 0.197 and N₂ = 0.605)

(B.20)

Therefore, the values of thermal conductivity of gas mixture (λ_g)

$$\lambda_g = 7.53 \times 10^{-2} \text{ J m}^{-1} \text{ S}^{-1} \text{ K}^{-1}$$

Prandtl number (Pr)

$$Pr = \frac{c_{pg}\mu_g}{\lambda_g} \tag{B.21}$$

 $Pr = \frac{1.55 \times 10^3 J \, kg^{-1} K^{-1} \times 3.46 \times 10^{-5} kg m^{-1} s^{-1}}{7.53 \times 10^{-2} J m^{-1} s^{-1} K^{-1}} = 0.71$

The heat transfer coefficient (h)

$$h = \frac{J_D C_{pg} \rho_g U}{P r^{\frac{2}{3}}}$$
$$h = \frac{4.69 \times 1.55 \times 10^3 J K g^{-1} K^{-1} \times 0.436 \, kg \, m^{-3} \times 7.63 \times 10^{-2} m \, s^{-1}}{0.71^{\frac{2}{3}}} = 303.169 \, \mathrm{J} \, \mathrm{m}^2 \mathrm{s}^{-1} \mathrm{K}^{-1}$$

The external heat transfer resistances may be calculated as

$$\frac{|(-\Delta H_r)|(-r_{exp})\rho_b R_p E_A}{hRT_b^2}$$

$$\frac{302.10 \times 10^{3} Jmol^{-1} \times 4.88 \times 10^{-5} molg_{cat}^{-1} s^{-1} \times 670 \ kgm^{-3}}{\times 7.15 \times 10^{-5} m \times 125.04 \times 10^{3} Jmol^{-1}}$$

$$\frac{379.56 Jm^{-2} s^{-1} K^{-1} \times 8.314 Jmol^{-1} K^{-1} \times (1023)^{2} K^{2}}{MMPSA}$$

$$= 2.67 \times 10^{-5} < 0.15$$

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The Anderson criterion can be calculated by internal heat transfer resistance

$$\frac{|(-\Delta H_r)|(-r_{exp})\rho_b R_p^2 E_A}{\lambda_p T_s^2 R} < 0.75$$
(B.22)

Where

$$\rho_{b} = 670 \text{ kg m}^{-3}$$

$$R_{p} = 7.15 \times 10^{-5} \text{ m}$$

$$-\Delta H_{r} = 302.10 \times 10^{3} \text{ J mol}^{-1}$$

$$E_{A} = 125.04 \times 10^{3} \text{ J mol}^{-1}$$

$$(-r_{exp}) = 4.88 \times 10^{-5} \text{mol} g_{cat}^{-1} S^{-1}$$

$$R = \text{ideal gas constant (8.314 \text{ J mol}^{-1} \text{ K}^{-1})}$$

$$\lambda p = \text{catalyst pellet thermal conductivity (J m}^{-2} \text{ s}^{-1} \text{ K}^{-1})$$

 $T_b = T_s$ = temperature of reactant gas bulk at 1023 K (since resistance to external heat transport limitations is negligible)

Thermal conductivity of catalyst pellet (λ_p)

$$log(\lambda_p \times 10^5) = 0.859 + 3.12 \left(\frac{\lambda_m}{\omega_p}\right)$$
(B.23)

Where

1

 ω_p = porosity of catalyst pellet (0.4)

 λ_m = thermal of the catalyst material

Thus the value of thermal conductivity of catalyst pellet (λ_p) = 1.26×10²² J m⁻¹ s⁻¹ K⁻¹



 $\frac{302.10\times10^{3}J\,mol^{-1}\times4.88\times10^{-5}mol\,g_{cat}^{-1}s^{-1}\times670\,kg\,m^{-3}\times\left(7.15\times10^{-5}\right)^{2}m^{2}\times125.04\times10^{3}J\,mol^{-1}}{1.26\times10^{22}J\,m^{-2}s^{-1}K^{-1}\times8.314\,J\,mol^{-1}K^{-1}\times(1023)^{2}K^{2}}$

 $= 5.75 \times 10^{-29} < 0.75$ اونيۇرسىتى مليسيا قھڭ السلطان عبدالله B.5 Effect of wall and Radial Heat Dispersion IA PAHANG

DULLAF The effect of wall heat transfer is negligible shown in Equation (B.24) when the ratio of diameter is more than 4.

$$\frac{d_t}{d_p} > 4 \tag{B.24}$$

Where

$$d_t$$
 = diameter of tube reactor (7.9×10⁻³ m)

 d_p = diameter of catalyst surface (1.43×10⁻⁴ m)

$$\frac{7.9 \times 10^{-3} m}{1.43 \times 10^{-4} m} = 55.24 > 4$$

The effect of radial heat dispersion can be determined via the mears criterion in Equation (B.25)

$$\left(\frac{E_a}{RT_w}\right) \left(\frac{|(-\Delta H_r)|(-r_{exp})\rho_b R_p^2 \left[\frac{(1-\varepsilon)}{(1-b)}\right]}{4\lambda_p T_w}\right) \left(\frac{1}{8} + \frac{B_p}{Bi_w R_t}\right) < 0.05$$
(B.25)

Where

 $T_w = T_b$ = temperature (1023 K)

 R_t = radius of reactor tube (3.95×10⁻³ m)

b = inert solids fraction of catalyst bed

 ε = void function in the catalyst bed (0.8)

Wall biot number (Bi_w) is calculated by using Equation (B.26)

$$Bi_{w} = \frac{h_{w}d_{p}}{\lambda_{p}}$$
(B.26)

Where

$$d_{p} = \text{diameter of catalyst particle } (1.43 \times 10^{-4} \text{ m})$$

$$h_{w} = \text{reactor tube wall heat transfer coefficient (quartz tube)}$$

$$\lambda_{p} = \text{ thermal conductivity of catalyst pellet } (1.26 \times 10^{22} \text{ J M}^{-1} \text{ s}^{-1} \text{K}^{-1})$$

$$Bi_{W} = \frac{30 J m^{-2} s^{-1} K^{-1} \times 1.43 \times 10^{-4} m}{1.26 \times 10^{22} J m^{-1} s^{-1} K^{-1}} = 3.40 \times 10^{-25}$$

Thus, the radial heat dispersion value

$$= \left(\frac{125.04 \times 10^3 \, J \, mol^{-1}}{8.314 \, J \, mol^{-1} K^{-1} \times 1023 \, K}\right) \times$$

$$302.10 \times 10^{3} J \ mol^{-1} \times 4.88 \times 10^{-5} \ molg_{cat}^{-1} s^{-1}$$
$$\times 670 \ kgm^{-3} \times (7.15 \times 10^{-5})^{2} m^{2} \times \left[\frac{(1-0.8)}{(1-0)}\right]$$
$$4 \times 1.26 \times 10^{22} J \ m^{-2} s^{-1} K^{-1} \times 1023 \ K$$
$$\times \left(\frac{1}{8} + \frac{9.75 \times 10^{-5} m}{3.41 \times 10^{-25} \times 3.95 \times 10^{-3} m}\right) = 3.76 \times 10^{-8} < 0.05.$$

APPENDIX C

GRAPHS OF ISOTHERMAL ADOSRPTION FOR BET SURFACE ANALYSES.

C.1 Isothermal Adsorption of LaCuO₃



C.2 Isothermal Adsorption of CeCuO₃



Figure C. 2 Isothermal Adsorption of CeCuO₃

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APPENDIX D

CALIBRATION CURVE

D.1 Calibration Curve for Syringe Pump

Ethanol as a reactant material was used in a syringe pump for calibration using 30 ml syringe, 10 ml pipette, retort stand, and stopwatch as shown in Figure D.1.



Figure D.1 The calibration curve of syringe pump using C2H5OH. UNIVERSITI MALAYSIA PAHANG AL-SULTAN ABDULLAH

D.2 Calibration Curve for Mass Flow Controller (MFC)

All gases (CO₂, H₂ and N₂) were calibrated using Mass flow controllers, bubble flow meter and stopwatch as shown in Figures D.2, D.3 and D.4, respectively.



1. MFC used for CO₂ calibration (model No: MFC104205)

Figure D.2 The calibration curve of mass flow controller using CO₂.



Figure D.3 The calibration curve of mass flow controller using H2.



3. MFC used for N2 calibration (model no. MFC104205)

Figure D.4 The calibration curve of mass flow controller using N2.



D.3 Calibration Curve of GC Analysis

The calibration curve of GC-TCD was prepared by the laboratory staff namel Mrs Hafizah Ramli as shown in Figure D.5.

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7.2	273 MM	3209.40283 1.57853e-3 5.06615 CH4	
13.3	358	1.//94364 1.11/96e-3 19.89342 CO2	
13.8	92 MM	1.93483e4 1.27974e-3 24.76080 CO	
The Party Name of Street, or other			

Figure D.5 Calibration curve of GC-TCD analysis



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