

**SYNTHESIS AND CHARACTERIZATION OF
SAMARIUM-COBALT-TRIOXIDE
PEROVSKITE CATALYST FOR THE KINETIC
AND LONGEVITY STUDIES OF METHANE
DRY REFORMING**

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Doctor of Philosophy of Engineering in Chemical Engineering.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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Thesis submitted in fulfilment of the requirements
for the award of the degree of
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Faculty of Chemical and Natural Resources Engineering

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LIST OF SYMBOLS

A	Reaction order with respect to reactant CH ₄
B	Order of reaction with respect to CO ₂
Θ	Diffraction angle
λ	Wavelength (nm)
r _i	Reaction rate of species i
ρ _s	Density of the catalyst particle
T	Reaction temperature
R	Universal gas constant
ΔH	Enthalpy changed (kJ mol ⁻¹)
D	Crystallite catalyst size
φ	Co metallic site
%	Percentage
F	Molar flowrate
X	Conversion
Y	Yield
W _{cat}	Weight of catalyst

LIST OF ABBREVIATIONS

BET	Brunauer – Emmett –Teller
BJH	Barrett, Joyner, Halenda
CRM	Combine reforming of methane
DRM	Dry reforming of methane
DTG	Differential thermogravimetric
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
FTS	Fischer – Tropsch Synthesis
FWHM	Full Width at Half Maximum
GC	Gas Chromatography
GHSV	Gas Hourly Space Velocity
LH	Langmuir – Hinshelwood
POM	Partial oxidation of methane
R ²	Coefficient of Determination
RMSD	Root Mean Square Deviation
TEM	Transmission Electron Microscopy
TCD	Thermal Conductivity Detector
TOS	Time on stream
TPD	Temperature Programmed Desorption
TG	Thermogravimetric
TGA	Thermogravimetric Analysis
TPO	Temperature Programmed Oxidation
TPR	Temperature Programmed Reduction
XRD	X- ray Powder Diffraction

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ABSTRAK

Kadar pemanasan global yang berada di tahap membimbangkan memerlukan penggunaan gas rumah hijau seperti metana (CH_4) dan karbon dioksida (CO_2). Salah satu daripada cadangan adalah tindak balas pembentukan semula kering metana. Tindak balas pembentukan semula kering metana memerlukan pemangkin heterogen kerana sifat endotermiknya yang kuat. Beberapa jenis pemangkin telah digunakan untuk tindak balas pembentukan semula kering metana dengan penyahaktifan pemangkin sebagai kelemahan utama.

Di dalam kajian ini, pemangkin perovskit SmCoO_3 telah digunakan untuk tindakbalas pembentukan semula kering metana. Pemilihan pemangkin Sm_2O_3 ini adalah disebabkan mempunyai Co yang kurang cenderung terhadap karbon dan kapasiti simpanan oksida (O_2) yang tinggi. Pemangkin perovskit SmCoO_3 telah disintesis dengan menggunakan kaedah sol-gel sitrat dengan samarium (Sm) menduduki lokasi ‘A’ dan kobalt (Co) yang menduduki lokasi ‘B’. Model Toleransi Goldschmidt telah digunakan untuk memperolehi faktor toleransi 0.96 untuk struktur perovskit SmCoO_3 .

Teknik pembelauan X-ray mengesahkan struktur hablur monofasa untuk SmCoO_3 . Penyaherapan teraturcara suhu menunjukkan kekuatan bersih berasid untuk pemangkin. Kaedah sebaran tenaga X-ray dan spektroskopi fotoelektron X-ray mengesahkan unsur dan komposisi kimia bagi perovskit SmCoO_3 sintesis. Sebelum pemodelan kinetik, kesan suhu (antara 973 - 1073 K), nisbah suapan (0.5 - 2.0) dan tekanan separa (antara 6.8 - 60.8 kPa) telah dikaji. Keputusan daripada kajian menunjukkan penukaran suapan melebihi 90% dan hasil produk melebihi 60%, pada 1073 K. Data kinetik yang diperoleh telah disuaikan ke dalam model hukum kuasa dan model Langmuir-Hinshelwood. Tenaga pengaktifan yang diperolehi daripada hukum kuasa adalah 41 kJ mol^{-1} bagi CH_4 dan 25 kJ mol^{-1} bagi CO_2 . Kajian selanjutnya dengan menggunakan model Langmuir-Hinshelwood telah mencatatkan tenaga pengaktifan sebanyak 44 kJ mol^{-1} bagi CH_4 dan 22 kJ mol^{-1} bagi CO_2 . Ujian kelanjutan untuk pemangkin telah diuji pada nisbah suapan antara 0.5 - 2.0 pada 1073 K, untuk 72 jam. Tindakbalas pada nisbah suapan 0.75, 1.0 dan 1.33 menunjukkan kestabilan yang sangat baik. Pemangkin perovskit SmCoO_3 yang terpakai, dicirikan dengan teknik mikroskop elektron pengimbasan pancaran medan, sebaran tenaga X-ray, pengoksidaan teraturcara suhu, spektroskopi inframerah transformasi Fourier, mikroskop elektron pancaran dan spektroskopi fotoelektron X-ray telah menunjukkan bukti wujudnya spesis karbon jenis bermisai yang mana tidak menyahaktifkan pemangkin. Karbon ini digegaskan oleh species dwi-oksida yang hadir di dalam perovskit SmCoO_3 seperti terbukti melalui analisa spektroskopi fotoelektron X-ray. Penurunan species Co seperti yang dibuktikan melalui analisa TPR telah menambahkan prestasi pemangkin perovskit SmCoO_3 . Sifat-sifat ini bertanggungjawab kepada prestasi pemangkin perovskit SmCoO_3 yang menakjubkan dibandingkan dengan pelbagai pemangkin jenis logam lain yang telah dilaporkan sebelum ini.

ABSTRACT

The alarming rate of global warming necessitates the utilization of greenhouse gases such as methane (CH_4) and carbon dioxide (CO_2). One of such propositions is methane dry reforming. Methane dry reforming requires the use of heterogeneous catalyst due to its strong endothermicity. Several catalysts have been employed for methane dry reforming with catalyst deactivation as the major drawback.

In the present study, samarium cobalt trioxide (SmCoO_3) perovskite catalyst has been applied for methane dry reforming. The reduced affinity of cobalt (Co) for carbon and the rich oxygen (O_2) storage capacity of samarium oxide (Sm_2O_3) are responsible for the choice of this catalyst. The SmCoO_3 perovskite catalyst was synthesized using the sol-gel citrate method with samarium (Sm) occupying the ‘A’ site and Co occupying the ‘B’ site. The Goldschmidt tolerance model was employed to obtain a tolerance factor of 0.96 for the SmCoO_3 perovskite structure.

X-ray diffraction confirmed a monophasic crystalline structure for the synthesized SmCoO_3 . Temperature programmed desorption showed net-acidic catalytic site strength. Energy dispersive X-ray and X-ray photoelectron spectroscopy confirmed the elemental and chemical composition of the synthesized SmCoO_3 perovskite. Prior to the kinetic modelling, the effects of temperature (ranged 873 - 1173 K), feed ratio (0.5 – 2.0) and partial pressure (ranged 6.8 – 60.8 kPa) were studied. Results from the studies showed that conversion of reactants were above 90% and products yield were above 60%, at 1073 K. The kinetics data acquired were fitted into the power law and Langmuir–Hinshelwood model. Activation energy of 41 kJ mol^{-1} and 25 kJ mol^{-1} were obtained from the power law model for CH_4 and CO_2 , respectively. Further studies using the Langmuir–Hinshelwood model gave activation energy of 44 kJ mol^{-1} and 22 kJ mol^{-1} for CH_4 and CO_2 , respectively. The longevity of the catalyst was tested in a feed ratio range of 0.5 – 2.0 at 1073 K, for 72 h. Reactions at 0.75, 1.0 and 1.33 feed ratios had very good stability. The spent SmCoO_3 perovskite catalyst, characterized by field emission scanning electron microscope, energy dispersive X-ray, temperature programmed oxidation, Fourier transform infrared spectroscopy, transmission electron microscope and X-ray photoelectron spectroscopy techniques showed evidence of whisker carbon species which did not deactivate the catalyst. The carbon was gasified by the dual oxygen species present in the SmCoO_3 perovskite as evident in the X-ray photoelectron spectroscopy analysis. The reducibility of the Co species as evident in the TPR analysis enhanced the performance of the SmCoO_3 perovskite catalyst. These properties are responsible for the superior performance of SmCoO_3 perovskite catalyst over various metallic catalysts previously reported.

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