UTILIZATION OF PALM OIL FUEL ASH (POFA) AS SILICA SOURCE OF Ni/SBA-15 FOR CO_2 REFORMING OF CH_4

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We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science.

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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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ABSTRAK

Karbon dioksida (CO_2) dan metana (CH_4) adalah penyumbang utama kepada gas rumah hijau (GRH) dengan komposisi 81% dan 10% yang membawa kepada pemanasan global. CO_2 pembentukkan semula CH_4 adalah proses yang sesuai untuk menukar CO_2 dan CH_4 kepada sintesis gas. Penghasilan sintesis gas daripada CO_2 pembentukkan semula CH_4 menggunakan pemangkin berasaskan Ni telah menarik perhatian ramai di seluruh dunia kerana aktiviti pemangkinnya yang baik, kos rendah, dan mudah didapati. Walau bagaimanapun, pemangkin berasaskan Ni menghadapi kelemahan yang serius dalam penyahaktifan permukaan pemangkin disebabkan oleh pembentukan kok. Pemilihan bahan sokongan yang bersesuaian didapati menjadi satu cara yang berkesan mengurangkan pembentukan kok yang tinggi pada permukaan pemangkin. Dalam kajian ini, SBA-15 telah dipilih sebagai bahan sokongan kerana sifat teksturnya yang menarik. SBA-15 boleh disintesiskan menggunakan templet dan pelbagai sumber silika seperti tetraetil orto silikat dan natrium silikat. Walau bagaimanapun, jenis prekursor silika ini tidak mesra alam dan memerlukan kos yang tinggi. Oleh itu, penggunaan bahan buangan abu minyak kelapa sawit (AMKS) sebagai sumber silika alternatif akan mengurangkan kos pengeluaran. Penyediaan POFA sodium silikat (POFA-Na_2SiO_3) telah dilakukan dengan menggunakan natrium hidroksida (NaOH) di bawah beberapa parameter termasuk nisbah jisim NaOH/POFA, suhu perlakuran, dan nisbah jisim H_2O/NaOH-POFA terlakur. Keadaan optimum telah dicapai pada nisbah NaOH/POFA jisim 2:1, suhu gabungan 550^oC, dan nisbah jisim H_2O/NaOH-POFA terlakur dari 4:1, dengan kandungan silika maksimum 40570 ppm. Hasil SiO_2 daripada POFA ialah 35 %. SBA-15 telah berjaya disintesis dan dibuktikan dengan keputusan XRD sudut rendah, N_2 penjerapan isoterma dan imej TEM, dengan ciri struktur meso bagi SBA-15. 3 peratus Ni telah dimuatkan pada SBA-15 menggunakan pelbagai jenis kaedah penyediaan seperti kaedah pengisitepuan (Ni/SBA-15 (IM)), kaedah bantuan penyejat berputar (Ni/SBA-15 (RE)), kaedah bantuan penggoncang (Ni/SBA-15 (SH)) dan kaedah bantuan ultrasonik (Ni / SBA-15 (US)). CO_2 pembentukkan semula CH_4 (CRM) telah disiasat dalam keluli tahan karat dengan dibungkus di katil reaktor pada 800°C dengan tekanan ambien dan suapan komposisi CO_2/CH_4 bersamaan dengan 1/1. Prestasi pemangkin tertinggi dicapai melalui Ni/SBA-15(US) dengan 81% penukaran CO_2 dan 90% penukaran CH_4. Ini disebabkan oleh penyebaran baik Ni pada permukaan pemangkin dengan beberapa Ni terletak di dalam kerangka SBA-15, interaksi Ni-O-Si yang kuat, dan asas pemangkin yang lebih tinggi. Pembentukan karbon grafit yang paling rendah pada Ni/SBA-15 (US) telah dikaitkan dengan penyebaran baik zarah Ni yang lebih kecil yang mampu menyekat pembentukan kok. Kewujudan penyinaran ultrasonik menawarkan kesan peronggaan untuk memusnahkan aglomerasi lembut zarah Ni dan dengan itu membawa kepada penyebaran Ni yang lebih baik daripada pengisitepuan konvensional (IM), kaedah bantuan penyejat berputar (RE), dan kaedah bantuan penggoncang (SH) . Kajian ini memberikan idea untuk menyediakan sifat pemangkin Ni/SBA-15 yang lebih baik untuk meningkatkan aktiviti dan kestabilan dalam proses CO_2 pembentukkan semula CH_4.

ABSTRACT

Carbon dioxide ($CO_{2)}$ and methane (CH_4) are the major greenhouse gases (GHGs) with 81% and 10 %, respectively, leading to global warming. CO_2 reforming of CH_4 is a promising route to convert CO_2 and CH_4 to synthesis gas. Production of synthesis gas by CO_2 reforming of CH_4 over Ni-based catalyst has been attracted extensive attention worldwide due to its good catalytic activity, low cost, and readily available. However, Ni-based catalyst faces a serious drawback in catalyst surface deactivation by coke formation. Selection of suitable support material was found to be an effective way to reduce the coke formation on catalyst surfaces. In this study, SBA-15 has been chosen as support material due to its interesting textural properties. SBA-15 can be synthesized using templates and variety of silica sources such as tetraethyl ortosilicate and sodium silicate. However, these types of silica precursors are non-eco-friendly and high cost. Therefore, the utilization of palm oil fuel ash (POFA) waste material as an alternative silica source would minimize the cost of SBA-15 production. The preparation of POFA sodium silicate (POFA-Na_2SiO_3) was done via sodium hydroxide (NaOH) fusion method by investigating several parameters including NaOH/POFA mass ratio, fusion temperature and H_2O/NaOH-fused POFA mass ratio. The optimum condition was achieved at NaOH/POFA mass ratio of 2:1, fusion temperature of 550^oC, and H_2O/NaOH-fused POFA mass ratio of 4:1, with maximum silica content of 40570 ppm. The yield of SiO_2 from POFA was 35%. The successful synthesized of SBA-15 was proved by the results of XRD low angle, N_2 adsorption-desorption isotherm, and TEM image, corresponding to the SBA-15 mesostructure characteristic. 3wt % of Ni was loaded on the synthesized SBA-15 using various preparation method including conventional impregnation (Ni/SBA-15(IM)), rotary evaporator-assisted impregnation (Ni/SBA-15(RE)), shaker-assisted impregnation (Ni/SBA-15(SH)) and ultrasonic-assisted impregnation (Ni/SBA-15(US)). CO_2 reforming of CH_4 (CRM) were investigated in a stainless steel fixed bed reactor at 800°C, atmospheric pressure and CO_2/CH_4 feed composition =1/1. The highest catalytic performance was achieved over Ni/SBA-15(US) with 81 % of CO_2 conversion and 90 % of CH_4 conversion. This is due to the well Ni distribution on the catalyst surfaces with some of the Ni were located inside the SBA-15 framework, stronger Ni-O-Si interaction, and higher catalyst basicity. Lowest formation of graphite carbon on Ni/SBA-15(US) was correlated to the well dispersion of smaller Ni particles that able to suppress the coke formation. The existence of ultrasonic irradiation offers a cavitation effect to destroy the soft agglomeration of Ni particles and thus lead to a better Ni distribution than conventional impregnation (IM), rotary evaporator-assisted impregnation (RE), and shaker-assisted impregnation (SH) methods. This study provides an idea in preparing a better properties of Ni/SBA-15 catalyst to enhance the activity and stability of CO_2 reforming of CH_4.

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LIST OF SYMBOLS

θ	Half-Braggs's angle
^{o}C	Degree Celsius
g	gram
h	hour
kg	kilogram
kJ/mol	kilo Joule per mol
kV	kilo Volt
m^2/g	meter cube per gram
Mt/year	Metric tonne per year
µm	micrometer
mg	milligram
mL	milli Liter
min	minute
nm	nanometer

LIST OF ABBREVIATIONS

Al_2O_3	Aluminium Oxide
APOFA	Acid leached –Palm Oil Fuel Ash
BET	Brunauer–Emmett–Teller
CaO	Calcium Oxide
Ce	Cerium
Comm.	Commercial
CRM	CO_2 Reforming of CH_4
CO_2-TPD	Carbon dioxide-Temperature Programed Desorption
Cu	Copper
DRM	Dry Reforming of Methane
F_{CO2}	Molar Flow Rate of Carbon Dioxide
GC	Gas Chromatography
GHGs	Greenhouse Gases
HCl	Hydrochloric Acid
HNO_3	Nitric Acid
H_2SO_4	Sulfuric Acid
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IE	Ion Exchange
Ir	Iridium
MCM-41	Mobil Composition of Matter No. 41
MCM-48	Mobil Composition of Matter No. 48
MgO	Magnesium Oxide
Na_2SiO_3	Sodium Silicate
NaOH	Sodium Hydroxide
Ni	Nickel
NiO	Nickel Oxide
Ni/SBA-15(IM)	Ni/SBA prepared by Impregnation
Ni/SBA-15(RE)	Ni/SBA prepared by Rotary evaporator
Ni/SBA-15(SH)	Ni/SBA prepared by Shaker
Ni/SBA-15(US)	Ni/SBA prepared by Ultrasound
P123	Triblock copolymer pluronic 123

Pd	Palladium
PM	Physical Mixing
POFA	Palm Oil Fuel Ash
POM	Partial Oxidation of Methane
Pt	Platinum
RHA	Rice Husk Ash
Rh	Rhodium
Ru	Ruthenium
SBA-15	Santa Barbara Amorphous 15
SiO_2	Silicon Dioxide
S.S	Sodium Silicate
TCD	Thermal Conductivity Detector
TEOS	Tetraethyl ortosilicate
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TOS	Time on Stream
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
Wt.%	Weight percentage

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