



Enhanced dry reforming of methane over mesostructured fibrous Ni/MFI zeolite: Influence of preparation methods

Hambali Umar Hambali ^{a, c}, Aishah Abdul Jalil ^{a, b, *}, Abdulrahman A. Abdulrasheed ^a, Tan Ji Siang ^a, Dai-Viet N. Vo ^d

^a School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310, UTM Johor Bahru, Johor, Malaysia

^b Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, 81310, UTM Johor Bahru, Johor, Malaysia

^c Department of Chemical Engineering, University of Ilorin, P.M.B. 1515, Ilorin, Nigeria

^d Center of Excellence for Green Energy and Environmental Nanomaterials, Nguyen Tat Thanh University, 300A Nguyen Tat Thanh, District 4, Ho Chi Minh City, 755414, Viet Nam

ARTICLE INFO

Article history:

Received 20 November 2019

Received in revised form

29 December 2019

Accepted 13 January 2020

Available online 17 January 2020

Keywords:

Nickel

Mesostructured MFI

Dry reforming

Methane

Syngas

ABSTRACT

Dry reforming of methane is acknowledged to be an environmentally benign route for conversion of CO₂ and CH₄ into syngas (CO and H₂). Herein, unique mesostructured fibrous MFI support was synthesized by microemulsion method, and Ni incorporation via double solvent, physical mixing and wetness impregnation methods. Results revealed wetness impregnation catalyst had the highest activity and stability. Activation energy of reactants showed a reliance on acidity, where moderate acidity impeded deactivation by CH₄ cracking. Furthermore, degree of catalyst deactivation was negligible compared to what is attainable on conventional zeolite catalysts. Thus, fibrous morphology, microscopic dispersion and moderate acidity played a positive role in boosting reactants accessibility to active Ni sites which results in preservation of activity under the harsh conditions of DRM process.

© 2020 Energy Institute. Published by Elsevier Ltd. All rights reserved.

1. Introduction

With the current quest for environmentally friendly energy sources due to lingering climate issues and tropospheric air quality, synthesis gas production from methane (CH₄) has attracted ever growing attention [1–3]. Synthesis gas is a gaseous mixture comprising of carbon monoxide (CO) and hydrogen (H₂) in varying ratio based on production processes [4,5]. The syngas production processes are autothermal reforming of methane, partial oxidation of methane, steam reforming of methane and dry reforming of methane [6]. Among them, dry reforming of methane (DRM) is more desirable. The DRM reaction produces pure syngas mixture (equimolar ratio of CO and H₂) appropriate for subsequent Fischer-Tropsch process. In the DRM reaction (CH₄ + CO₂ → 2CO + 2H₂), proportional consumption of a mole of CO₂ per mole of CH₄ occur in gas phase which curbs CO₂ flaring and environmentally beneficial

CH₄ consumption [7,8]. However, secondary reactions such as reverse water gas shift (CO₂ + H₂ → CO + H₂O), CH₄ cracking (CH₄ → 2H₂ + C) and CO disproportionation (2CO → CO₂ + C) do occur during DRM [5,9]. Among these reactions, reverse water gas shift and CO disproportionation occur at lower temperatures, while the DRM and CH₄ cracking occur at high temperatures. The CH₄ cracking and CO disproportionation produce carbon which invoke catalyst deactivation by generating carbonaceous deposits on the catalyst surface [9].

The catalyst is adjudged as a key factor in the DRM reaction. As such, development of catalyst system able to effectively perform the reaction with less coke formation remains a challenge [5]. However, despite the demerit of nickel-based catalysts, their application in DRM seem reasonable. They offer high turnover frequency, relative abundance and moderate cost compared to noble based catalyst [10,11]. The demerit of the nickel-based catalysts is their rapid deactivation due to CO disproportionation and CH₄ cracking. It was reported that the agglomeration of nickel particles increases nickel particle size which have a significant effect on coke deposition during DRM reaction [5]. To improve the resistance to coke deposition, metal sintering should be impeded

* Corresponding author. School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310, UTM Johor Bahru, Johor, Malaysia.

E-mail address: aishahaj@utm.my (A.A. Jalil).

by improvement of metal-support interaction. These favour stabilization of active particles in the support, which consequently inhibit agglomeration of nickel particles at high DRM reaction temperature [9,11].

As we recently reviewed, revolutionary development of catalyst system can be achieved via controlled synthesis methods [12]. The various preparation methods have demonstrated pivotal effect on DRM catalysts. They resulted in altering catalysts composition, particles size, dispersion, and superficial interaction between catalyst components. These phenomena influence activity of DRM catalysts at high temperatures with better resistance to agglomeration and coking. It is known that size and dispersion of active metal particles affect the catalytic property [5,12]. Zhang et al. [10] fabricated Ni-SBA-15 via solid-state grinding metal loading method which displayed superior coke resistance as compared to the catalysts prepared by wet impregnation method. Zhang et al. [13] have found that homogeneous precipitation method (Ni-HP) produce better DRM performance than the conventional impregnation method (Ni-IM). H₂ reducibility studies demonstrates strong interaction of NiO nanoparticles with the SBA-15 support for Ni-HP catalyst. Similarly, X-ray diffractogram findings affirms high degree of dispersion on Ni-HP catalysts. Hao et al. [14] synthesized Ni/Al₂O₃ catalyst by sol gel method producing larger surface area and ultrafine dispersed Ni nanoparticles, which produced excellence DRM performance in contrast with catalysts prepared by impregnation method. Furthermore, controlled adsorption method provided high dispersibility and cooperative interaction compared to the dry impregnation catalysts [15].

The present work involves tuning physico-chemical properties of commercial MFI (Mobil-type five) support via micro emulsion method for enhanced catalyst performance, due to its inclinations to high dispersion and stabilization of metal particles [11,16–19]. To the best of our knowledge, this is the first report on the influence of physical mixing, wetness impregnation and double solvent methods on DRM catalytic behaviour of mesostructured fibrous MFI supported Ni catalyst. The catalytic tests were conducted at 500–800 °C temperature range to elucidate the reaction kinetics, and to evaluate the coking resistance of the catalysts under the harsh conditions of DRM process.

2. Experimental section

2.1. Materials

The materials used in the study are: Tetraethyl orthosilicate (TEOS), n-butanol, urea, Cetyltrimethylammonium bromide (CTAB) obtained from Merck Sdn. Bhd and MFI seed (Zeolyst International, CBV 2314) with Si/Al ratio of 23. Ni(NO₃)₂·6H₂O was used as Ni precursor purchased from Merck Co. H₂, air and N₂ gases were used for reduction, pre-treatment and carrier respectively.

2.2. Catalyst preparation

As elaborated and published in our laboratory, the mesoporous fibrous MFI support was synthesized by the microemulsion zeolite seed crystallization [18]. The Ni/MFI were synthesized by double-solvent (DS), physical mixing (PM), and wetness impregnation (WI) methods. The Ni/MFI-(PM) was made by physical grinding of the Ni precursor and mesoporous MFI support in a pestle for 20 min. The resultant powder was heat treated (at 800 °C for 2 h) [20]. The Ni/MFI-(DS) catalyst was prepared by suspending the MFI support in cyclohexane solvent. After rigorous stirring (at 25 °C for 2 h), the aqueous Ni precursor solution was dropwise added into the suspension. The corresponding mixture was continuously stirred (for 3 h), dried (for 12 h) and calcined (at 800 °C for 3 h) [21].

The Ni/MFI-(WI) catalyst on the contrary was prepared without the cyclohexane solvent.

2.3. Characterization technique of the catalysts

Crystal structural features of synthesized fibrous MFI supported Ni catalysts were determined using X-ray diffractometer (Bruker Advance D8) with monochromatic Cu K α radiation at 40 mA and 40 kV. The NiO crystallite size was calculated by the Scherrer equation based on the (200) diffraction peak. Fourier-Transform Infrared (FTIR) measurements were carried out using Agilent FTIR Spectrometer (Cary 640) to evaluate the chemical functional groups using the KBR method. The N₂ physisorption analysis was carried out on a Quantachrome Autosorb-1 analyzer at temperature of 77 K to determine the surface area and pore properties. To ascertain the formation of mesoporous fibrous MFI support and the effects of preparation methods on Ni dispersion and distribution on the support, Field emission scanning electron microscopy (FESEM) characterization was conducted on all catalysts in conjunction with elemental dot mapping from electron microscopy dispersive X-ray analyzer (JSM-6710F). The presence of acid sites on the catalysts were examined by probe 2,6-lutidine adsorption via in situ FTIR studies.

2.4. Catalytic performance

DRM catalytic testing was conducted in a fixed bed micro catalytic reactor. Typically for each test, 0.20 g of catalyst diluted with quartz sand (3 times the catalyst weight) was packed between two quartz layers and loaded. Prior to commencement of the testing, pre-treatment (for 1 h at 850 °C, and 50 mL min⁻¹ O₂ flowrate) and catalyst reduction (H₂ flow at 50 mL min⁻¹, for 1 h at 850 °C) was carried out. Thereafter, the reactants (CH₄:CO₂:N₂ = 1:1:3) were fed into the reactor. The product gases and excess reactant were monitored continuously and analyzed by gas chromatograph (GC7820 N, Agilent Technologies Inc.). Analysis of effluent products was carried out after 1-h reaction, and 20 min product sampling for each run. The reactants conversions and the H₂/CO ratio were computed by equations (1)–(5).

$$CH_4 \text{ conversion} = \frac{F(CH_4)_{in} - F(CH_4)_{out}}{F(CH_4)_{in}} \times 100 \quad (1)$$

$$CO_2 \text{ conversion} = \frac{F(CO_2)_{in} - F(CO_2)_{out}}{F(CO_2)_{in}} \times 100 \quad (2)$$

$$H_2 \text{ selectivity} = \frac{F(H_2)_{out}}{2[F(CH_4)_{in} - F(CH_4)_{out}]} \times 100 \quad (3)$$

$$CO \text{ selectivity} = \frac{F(CO)_{out}}{[F(CH_4)_{in} - F(CH_4)_{out}] + [F(CO_2)_{in} - F(CO_2)_{out}]} \times 100 \quad (4)$$

$$\frac{H_2}{CO} = \frac{F(H_2)_{out}}{F(CO)_{out}} \times 100 \quad (5)$$

3. Results and discussion

3.1. Thermodynamic considerations

Thermodynamic computations were conducted by HSC Chemistry 6 software at 500–800 °C and atmospheric pressure. The major sources of carbon deposition during DRM are CH₄ cracking (MC), CO disproportionation (CD) and reverse water gas shift (RWGS). The spontaneity of occurrence of these reactions were calculated by the Gibbs free minimization method and displayed in Fig. 1. The effect of gaseous feed compositions on H₂/CO ratio and formation of unavoidable carbon were determined. From the Gibbs free minimization plot, all the reactions displayed endothermic behaviour except for CD. The DRM reaction supremely take place above 650 °C with occurrence of the side reaction. This shows that DRM reaction is favorable around 700 °C, while MC seem favorable at 550 °C. On the other hand, CD is unfavorable above reaction temperature of 700 °C due to its exothermic nature [22]. Thus, meaningful conversions of reactants are possible in 650–800 °C temperature range, with less tendency of large carbon formation due to the side reactions.

Fig. 2A presents the effect of feed gas composition on H₂/CO ratio in DRM. It can be seen that irrespective of the feed gases concentration, the H₂/CO ratio reduces as temperature increases. At lower temperatures, large ratio of H₂/CO are obtained, while it is almost constant above 700 °C. However, increasing concentration of CH₄ in the feed led to decrease of H₂/CO ratio. This may be due to the fact that H₂ is produced from CH₄, so when its concentration is high, the concentration of H₂ also increases. The results are in accordance with literature [22,23]. Thus, attaining H₂/CO ratio near unity is only possible when the temperature is above 700 °C and CH₄:CO₂ ratios of 20:20, 15:25, 10:30 and 5:35. Generally, obtaining a H₂/CO ratio near unity signals pure syngas product which is crucial for future applications [12]. For instance, in steam reforming process, high H₂/CO ratio (3:1) makes it unfit for direct production of methanol [6].

Fig. 2B shows the equilibrium carbon deposition with respect to feed gas compositions for DRM reaction. The graph (Fig. 2B) reveals that the thermodynamic driving force for formation of carbon

species diminishes with respect to increasing temperature. However, only CH₄:CO₂ = 35:5 ratio showed a contrary trend. This may be related to the fact that fast increase in carbon formation is prominent when concentration of CH₄ is high in the feed. This behaviour indicates the prevalence of high carbon deposition in CH₄ cracking reaction as compared to the CO disproportionation. This is in accord with the study of Kim et al. [22] and Giehr et al. [23]. Hence, we need to fabricate a robust catalyst that can effectively retard coke deposition for a stellar DRM performance.

3.2. Phase identification

X-ray diffraction patterns portraying the structure of Ni loaded catalysts are shown in Fig. 3. All catalysts exhibited the characteristic MFI structure with peaks in 2θ range of 5–10° and 20–26° respectively [24,25]. Moreover, the NiO peaks were noticeable at 2θ = 37.2°, 43.1°, 63.0° and 79.3°, which can be assigned to (111), (200), (220) and (222) crystal planes of NiO crystallites, suggesting that the morphology of the catalysts did not change as a result of different Ni loading methods [8]. Nevertheless, for the intensity of diffraction peaks, differences in peaks intensity was observed. The peak intensities of NiO phases for Ni/MFI-(WI) was weaker, and full width at half maximum (FWHM) was broader, signalling that smaller NiO crystallites was obtained for wetness impregnation catalyst. The peaks intensity of Ni/MFI-(DS) and Ni/MFI-(PM) are slightly higher than those of Ni/MFI-(WI). The NiO crystallite size calculated by the Scherrer equation are presented in Table 1. The Ni/MFI-(WI), Ni/MFI-(DS) and Ni/MFI-(PM) have their average NiO crystallite sizes of 12.4, 13.5 and 14.39 nm, respectively.

3.3. Textural properties

Intrinsically, activity of a supported catalyst is dependent on the surface area. Catalyst system with large surface area promote high dispersion and better utilization of active metal components for better DRM activity and stability [12]. The textural features of the synthesized Ni loaded catalysts were estimated from N₂ physisorption isotherms and pore size distributions, displayed in Fig. 4A–C. The Non-Local Density Functional Theory (NLDFT) method was used for the parameters estimation as summarized in Table 1. N₂ physisorption isotherms are of type IV with H3 hysteresis loop in accordance to IUPAC classification, signifying the existence of micro-mesoporous material [18]. The surface area and pore volume of Ni/MFI-(WI) was slightly higher than that of Ni/MFI-(DS) and Ni/MFI-(PM). This may be as a result of higher coverage and better distribution of Ni crystallites in the wetness impregnation synthesized catalyst, which is in agreement with Ni crystallite size obtained from Scherrer equation and FESEM-Mapping results.

3.4. FESEM/elemental mapping

The FESEM images with mapping revealing NiO particles distribution on as-synthesized catalysts are shown in Fig. 5. The FESEM image depict the formation of mesostructured fibrous MFI morphology [18,19]. It was observed that Ni incorporation did not destroy the mesoporous MFI structure. However, slight variation of morphology arises from the different metal loading methods. The NiO species appeared as bright pink spots as shown in the elemental dot mapping images (Fig. 5). The wetness impregnation catalyst shows higher dispersion and homogenous distribution of NiO crystallites than those based on double solvent and physical mixing. This behaviour can be attributed to metal loading procedure. The hydrophobic precursor added to support during double solvent synthesis might have limited the capillary force that leads to penetration of aqueous nickel nitrate solution into support pores.

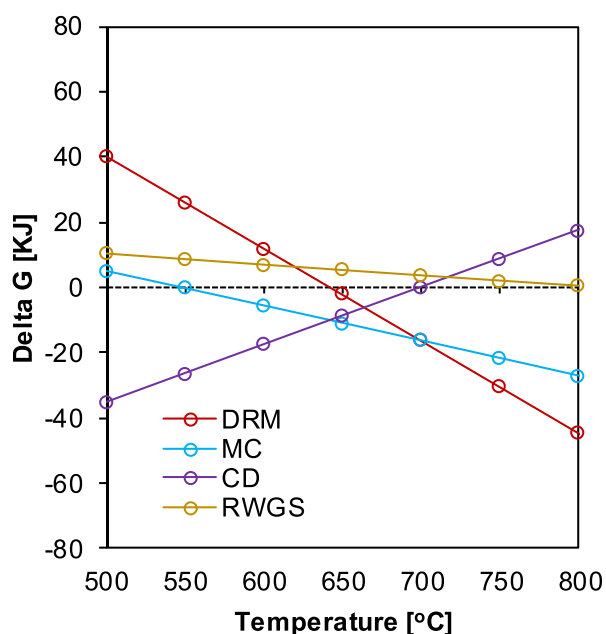


Fig. 1. Spontaneity of the various reactions occurring during DRM.

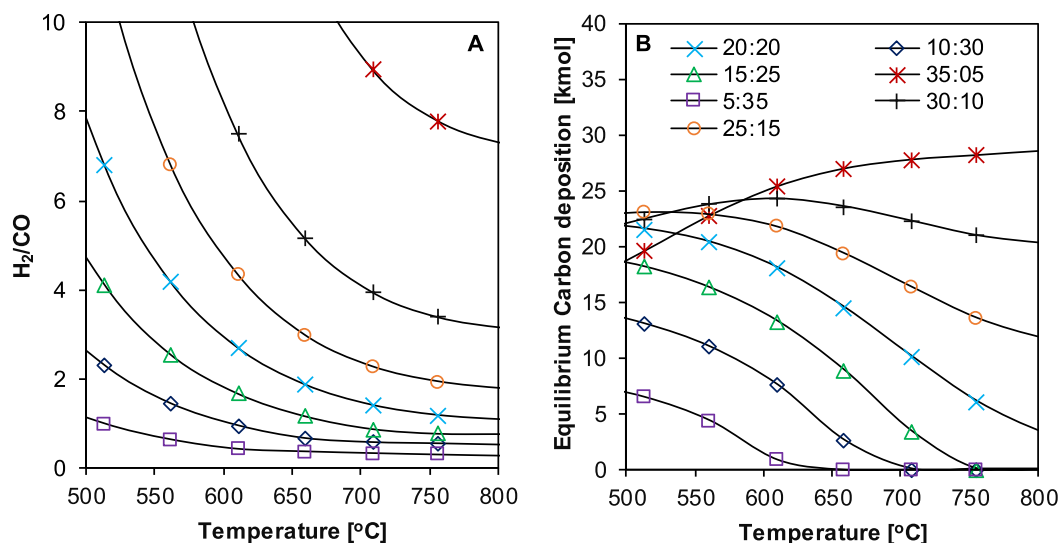


Fig. 2. (A) H₂/CO ratio at CH₄/CO₂ equilibrium composition as a function of temperature (B) Equilibrium carbon deposition with respect to feed gas compositions.

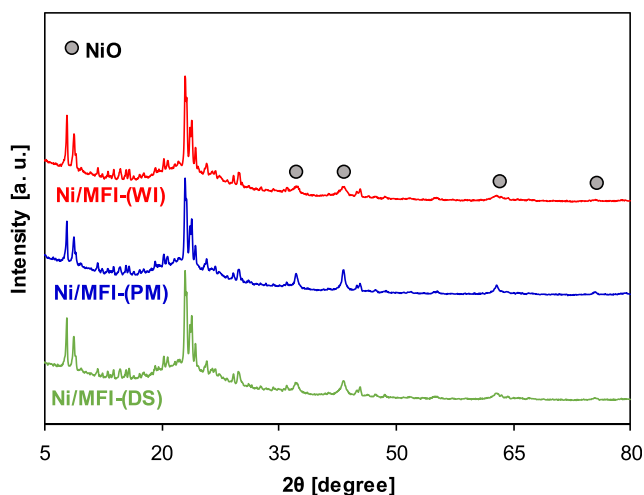


Fig. 3. XRD patterns of Ni loaded catalysts.

3.5. FTIR

The FTIR spectra analysis of the synthesized catalysts with wavenumber 4000–400 cm⁻¹ was performed as displayed in Fig. 6. The spectral bands near 3450 and 1640 cm⁻¹ are attributed to O–H and physically adsorbed water respectively [26]. It is known, that absorption band around 450–1200 cm⁻¹ verifies the existence of zeolite structure [26,27]. The formation of double five ring in MFI zeolite is characterized by bands in the range of 500–650 cm⁻¹, while bands around 350–470 cm⁻¹ are associated with pore opening modes. In addition, symmetric and asymmetric TOT modes are assigned to bands around 750–850 cm⁻¹ and 1050–1200 cm⁻¹ [27,28]. The bands near 460, 540, 796, 1095 and 1220 cm⁻¹ are fingerprint of MFI structure and were present on the synthesized catalysts. The existence of this bands affirms the formation of MFI-type zeolite which is in accordance with reported literature [28,29]. The ratio of the intensities of bands near 540 and 460 cm⁻¹ (I₅₄₀/I₄₆₀) provides information on relative crystallinity of the synthesized catalysts [26]. The increase in crystallinity follows the trend: Ni/MFI-(DS) < Ni/MFI-(WI) < Ni/MFI-(PM) < MFI. Considering the major frequencies, incorporation of Ni did not destroy the MFI structure. However, slight shift of the characteristic MFI bands to higher wavenumber is observed in the Ni loaded catalysts due to metal-support interaction. As it has been pointed out by Miskolcz et al. [28] introduction of metal cations in zeolite catalysts cause shift in position of infrared band due to structural modification.

Finally, the acidities of the catalysts were evaluated by 2,6-lutidine adsorbed FTIR spectrum method as presented in Fig. 7. The shoulder band around 1695 cm⁻¹ represents lutidine cation bonded to the catalyst protonic sites. The broad band in the region of 1585–1670 cm⁻¹ corresponds to interaction of probe lutidine with the acid sites [30]. The broader the band area, the more the total acidity. The band intensity of surface acid sites followed the trend Ni/MFI-(PM) > Ni/MFI-(DS) > Ni/MFI-(WI). This shows that various preparation methods slightly altered the catalyst acid properties. The presence of poorly dispersed Ni in the Ni/MFI-(PM) catalyst (Fig. 5) could explain the occurrence of a larger fraction of acid sites [31]. Conversely, the homogenous and high dispersion of Ni in Ni/MFI-(WI) led to much coverage of the acid supports surface. The pyrrole FTIR studies displayed no adsorption of probe pyrrole molecules over the examined catalysts (not presented here).

Table 1
Crystal and textural properties of Ni loaded catalysts.

Catalyst	NiO crystalline size (nm) ^a	S _{BET} (m ² /g) ^b	Pore volume (mL/g) ^b		
			V _{Mic}	V _{Meso}	V _{Total}
Ni/MFI-(DS)	13.5	391	0.01638	0.50442	0.5208
Ni/MFI-(PM)	14.39	365	0.06168	0.31842	0.3801
Ni/MFI-(WI)	12.4	413	0.02026	0.55984	0.5801

^a Scherrer equation.

^b BJH method.

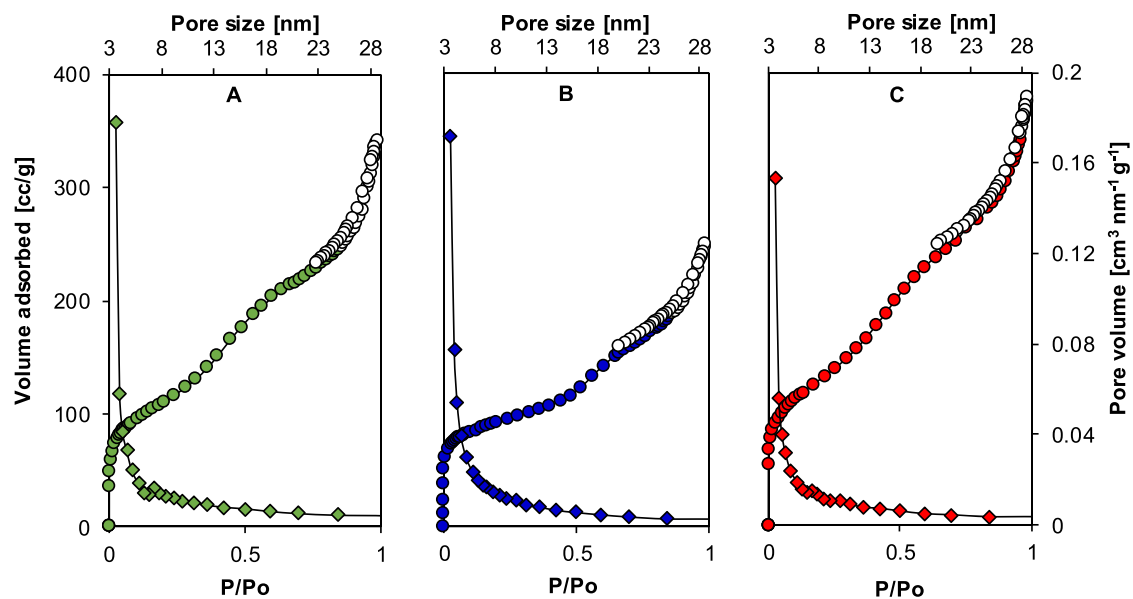


Fig. 4. N_2 physisorption of catalysts (A) Ni/MFI-(DS) (B) Ni/MFI-(PM) (C) Ni/MFI-(WI).

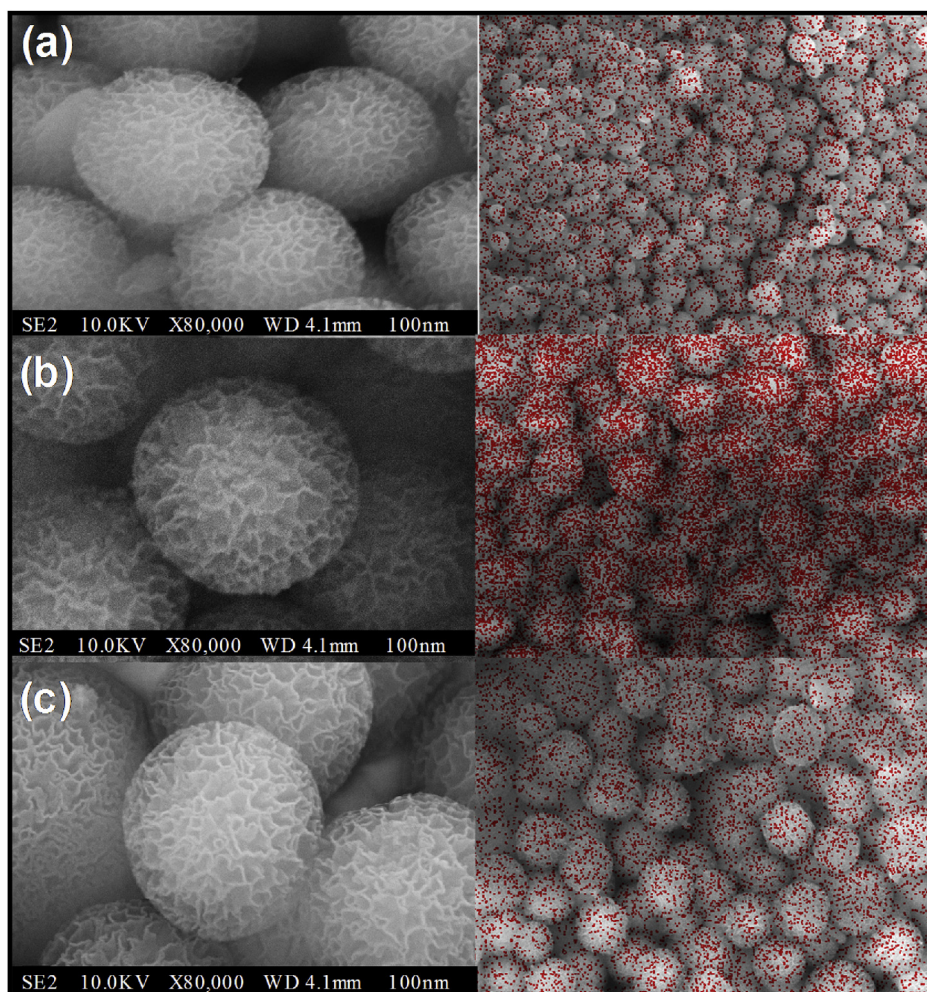


Fig. 5. FESEM images with mapping of Ni particles for the catalysts (a) Ni/MFI-(DS) (b) Ni/MFI-(PM) (c) Ni/MFI-(WI).

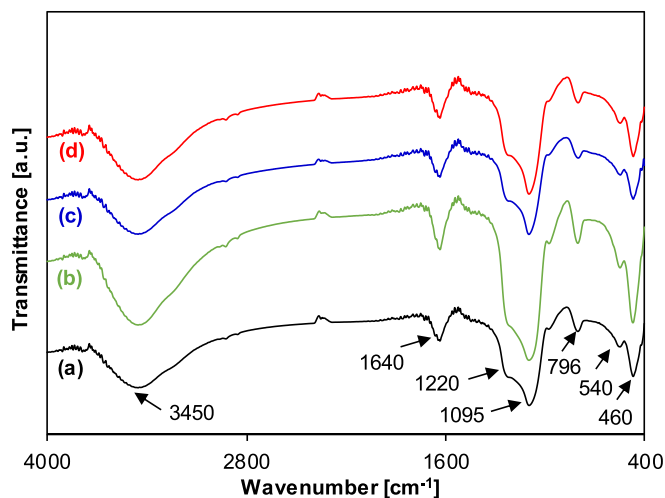


Fig. 6. KBr-FTIR profiles of catalysts (a) MFI (b) Ni/MFI-(DS) (c) Ni/MFI-(PM) (d) Ni/MFI-(WI).

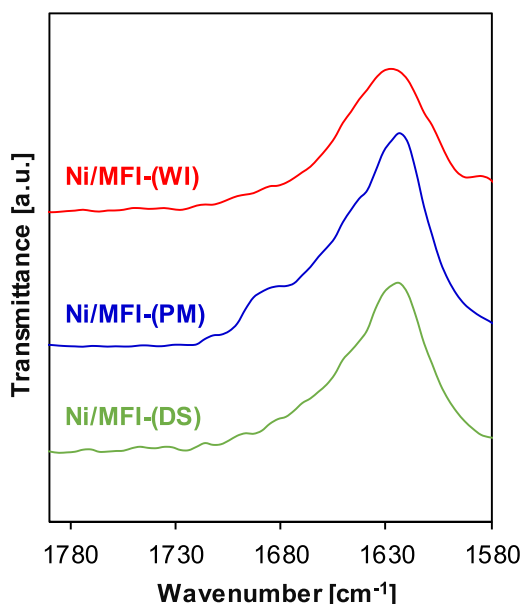


Fig. 7. Lutidine-FTIR profiles of Ni loaded catalysts.

Numerous studies have focused on development of low acidic catalyst system for coke free DRM operation [26,32,33]. We conclusively reported that excessive surface acidity promotes CH_4 cracking and deactivation by severe coke deposition on catalyst surface [12]. The acid sites inhibit dissociative chemisorption of CO_2 onto catalyst surface as a result of formed dehydrogenated carbon deposits leading to pulverization of catalyst pellets and graphitization of carbon deposits which renders catalyst inactive. Bawah et al. [34] tuned the DRM activity of silicalite-1 zeolite supported Ni catalyst by ion-exchanging with ceria promoter to reduce the surface acidity, which impeded carbon formation. Lovell et al. [35] reported the introduction of Na to moderate MCM-41 zeolite support acidity, which altered the extent of occurrence of side reaction during DRM. Conversely, loading KF on alumina supported Ni catalysts plays a crucial role in neutralizing the acidity of alumina and stabilized Ni particles from high temperature sintering for over 200 h time on stream [36]. Recently, experimental observations by Das et al. [33] showed that homogeneous distribution of basic Ceria

and Magnesia alleviated deactivation due to comparable (CH_4 and CO_2) activation energy.

3.6. Catalytic activity and longevity

The DRM catalytic activity of fibrous MFI supported Ni catalysts are shown in Fig. 8A–C with a phenomenal trend in reactants conversion as well as H_2/CO ratio increase. The DRM reaction was studied at temperatures ranging from 500 to 800 °C, gas hourly space velocity ($\text{GHSV} = 30 \text{ L g}^{-1} \text{ h}^{-1}$) and molar feed ratio ($\text{CH}_4/\text{CO}_2 = 1$). Conversion of reactants increased as temperature increases which is a general characteristic of DRM reaction [22,36]. The conversion of both reactants followed the order Ni/MFI-(WI) > Ni/MFI-(PM) > Ni/MFI-(DS) (Fig. 8A and B). The highest activity of Ni/MFI-(WI) was ascribed to: (1) its lower surface acidity (Fig. 7) which guarantee a better dissociative chemisorption of carbon dioxide. (2) its higher Ni dispersion guarantees higher reduction, thus increasing the availability of active sites for reaction. These factors also explained why Ni/MFI-(DS) has slightly higher activity than Ni/MFI-(PM). The H_2/CO ratio shown in Fig. 8C shows a dependence on temperature. For most reaction temperatures, desired product ratio attained were near to the expected thermodynamic ratio of 1. The H_2/CO ratio obtained on Ni/MFI-(WI) is more favored towards unity at 700 °C, signalling formation of pure syngas and less coke formation.

The catalytic longevity studies were conducted as shown in Fig. 9. The synthesized catalysts were subjected to the DRM reaction at 800 °C and 30 h on stream. The conversion on Ni/MFI-(PM) was stable for 12 h of reaction but suffered around 61% decline in both reactant conversions. This could be explained by the poor Ni dispersion and high acidity causing swift coke deposition. The Ni/MFI-(WI) was stable throughout the 30 h period with no noticeable deactivation, while for Ni/MFI-(DS) catalyst, slight deactivation was recorded.

3.7. Comparative catalytic performances

A major bottleneck in development of zeolite supported Ni catalysts for DRM is the undesired accumulation of hotspots, which facilitates the driving force for Ni particle sintering and coke formation [12]. Basically, the anti-carbon deposition behaviour can be achieved by: (1) utilizing a zeolite support with low acidity. (2) higher Ni particle dispersion which lead to more active sites on the catalyst surface and (3) cooperative interaction of catalysts components due to topology of support in reducing Ni sintering and retain activity over long time on stream [26,33]. As discussed previously, mesoporous support enhances metal dispersion coupled with easy access to the active sites which is prerequisite for high catalytic performance in DRM.

Conclusive reports by our group [17,18] demonstrated the potential of mesoporous fibrous architecture over commercial coffin shaped zeolite materials. The microemulsion engineered fibrous MFI support resulted in mesostructured material with moderate acidity and thermal stability as compared to commercial MFI supports. The mesoporous topology enhance dispersion, surface basicity, metal support interaction and mass transfer of gaseous reactant to boost catalytic activity and stability. Besides, the homogenous dispersion obtained by Ni/MFI-(WI) limited metal agglomeration and result in preservation of activity during the high temperature reaction. However, the behaviour of our as-synthesized catalysts showed a better DRM performance than prevailing catalysts as listed in Table 2. The conversion of both reactants over Ni/MFI-(WI) at reaction temperature of 700 °C were competitive with what is attainable in literature, and stable performance recorded at longer reaction period exceed most of those

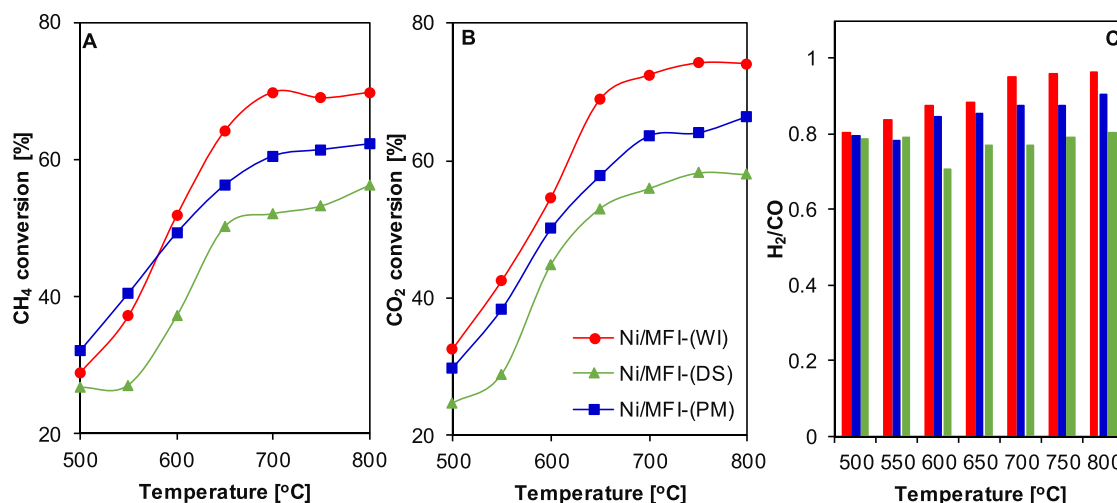


Fig. 8. Effect of temperature on DRM activity (A) CH₄ conversion (B) CO₂ conversion and (C) H₂/CO ratio.

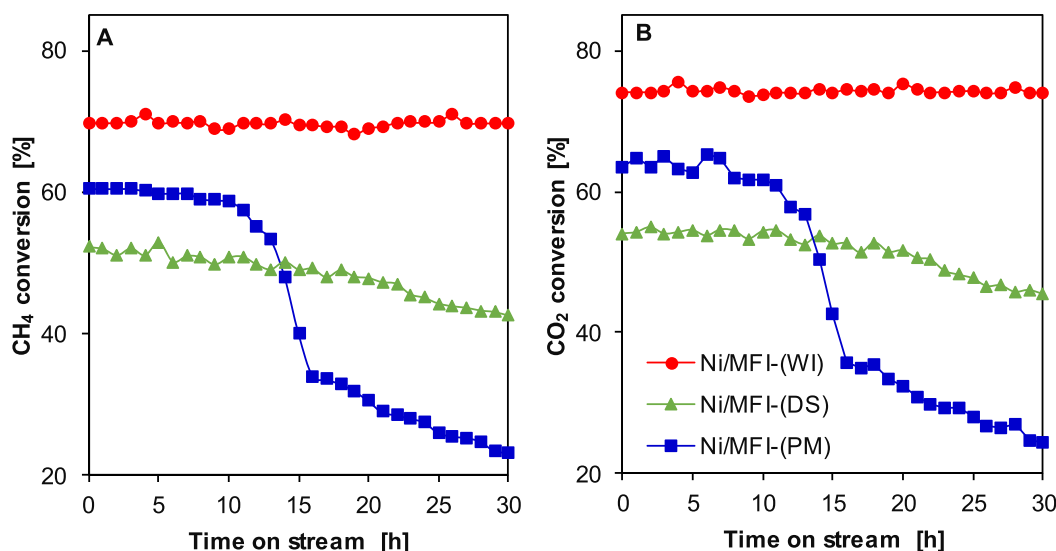


Fig. 9. Stability tests of the catalysts (A) CH₄ conversion (B) CO₂ conversion. (CH₄:CO₂:N₂ = 1:1:3, T = 800 °C, P = 1 atm, GHSV = 30 L g⁻¹ h⁻¹).

investigated in literature.

Concerning the excellent stability of the Ni/MFI-(WI) catalyst, its degree of deactivation was compared with literature as summarized in Table 2. The degree of deactivation over Ni/MFI-(WI) was negligible over the 30 h of reaction. Nevertheless, despite the shorter TOS considered by Dai et al. [37], Sarkar et al. [38], Estephane et al. [39] and Vafaeian et al. [26], their degree of deactivation during the stipulated TOS were quite high. Additionally, GHSV

shows dependence on the degree of deactivation. The GHSV of 72 and 60 Lg⁻¹h⁻¹ considered by Dai et al. [37] and Estephane et al. [39] gave deactivation degree of 11.1 and 13.6% respectively. While, Kaengsilalai et al. [40] and Vafaeian et al. [26] reported lower GHSV values with deactivation degree of 0.6 and 0.5% respectively. Thus, operating at low GHSV over zeolite supported catalyst system seem beneficial for stable DRM performance attainment.

Table 2

Comparison of deactivation degree of nickel-based catalysts in DRM.

Catalyst	T (°C)	GHSV (Lg ⁻¹ h ⁻¹)	TOS (h)	Initial CH ₄ conversion	Final CH ₄ conversion	D ^a (%)	Ref.
Ni/KIT-6	600	40.0	100	65.1	55	15.5	[43]
1.5Ni@Hol S-1	800	72.0	6	81	72	11.1	[37]
8% Ni/KH zeolite	700	30.0	5	91	90.5	0.6	[40]
5%Ni-ZSM	800	32	9	96.2	72.9	24.2	[38]
Ni (8%)/ZSM-5	850	24	24	82	81.6	0.5	[26]
2Ni1Co/ZSM5	800	60.0	12	66	57	13.6	[39]
5Ni/MFI-(WI)	800	30	30	69.85	69.72	0.1	This study

^a D = ((Initial CH₄ conversion – Final CH₄ conversion)/Initial CH₄ conversion).

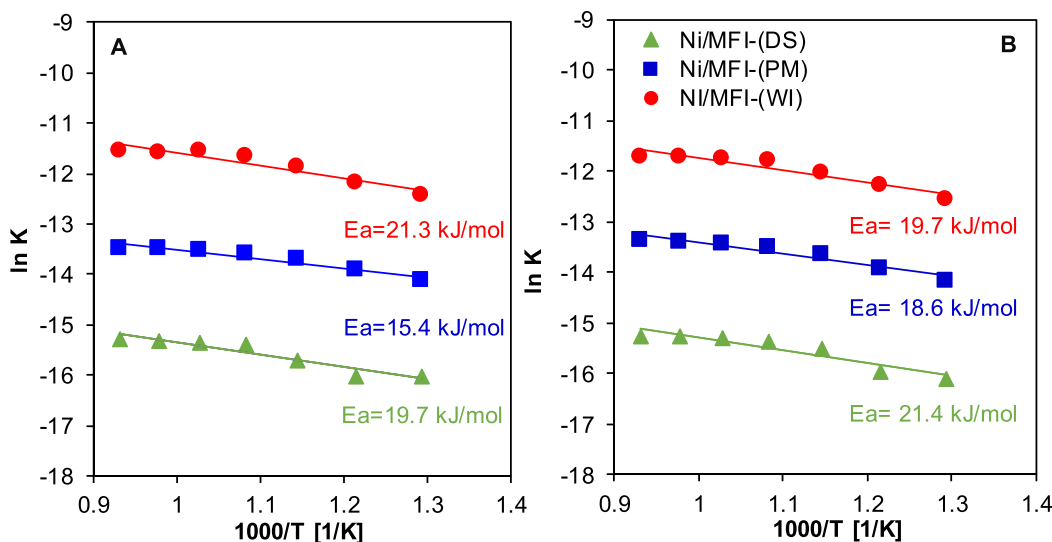


Fig. 10. Arrhenius plot for (A) CH₄ conversion and (B) CO₂ conversion.

3.8. Reaction kinetics

The kinetics of DRM was investigated over as-synthesized catalysts as shown in Fig. 10. The respective activation energy values of CH₄ and CO₂ were computed from slopes of the Arrhenius plot [41]. The activation energy of CH₄ (Fig. 10A) increased in the order Ni/MFI-(WI) > Ni/MFI-(DS) > Ni/MFI-(PM). Although Ni/MFI-(WI) has the highest activity and stability, it requires more energy for CH₄ conversion possibly due to its moderate acidity. Besides, the acidity measurement (Fig. 7), showed Ni/MFI-(PM) has the highest surface acidity in contrast to Ni/MFI-(DS) and Ni/MFI-(WI). Therefore, the higher the surface acidity, the lower the energy requirement for CH₄ conversion. This suggest vulnerability to CH₄ cracking over other side reactions; thus, more coke deposition. This is concomitant with rapid deactivation of Ni/MFI-(PM) observed during the long TOS (Fig. 9). The activation energy of CO₂ (Fig. 10B) follows the trend Ni/MFI-(DS) > Ni/MFI-(WI) > Ni/MFI-(PM). Interestingly, the activation barrier for CO₂ is slightly lower than that for CH₄ consumption over Ni/MFI-(WI). This can be attributed to better adsorption of CO₂ over Ni/MFI-(WI), which favour removal of carbon deposits. Similarly, the moderate acidity and higher metal deposition of wetness impregnation catalyst improved the stability over 30 h on stream. The conclusive report by Kathiraser et al. [41] showed that type of carrier material influences activation energy. The activation energies obtained are lower compared to the findings of Tang et al. [42]. Thus, the superior performance of meso-structured fibrous MFI supported Ni catalyst can be rationalized by optimal synergism of metal and support, mass transfer and accessibility to active sites.

4. Conclusion

To conclude, we have synthesized mesostructured fibrous MFI support by microemulsion zeolite seed crystallization method, and Ni incorporation via double solvent, physical mixing and wetness impregnation methods. The unique support plays a major role in impeding deactivation by stabilizing the Ni particles due to strong metal-support interaction. Catalytic test and kinetic studies showed activation energy of CH₄ and CO₂ is dependent on surface acidity, where high acidity foster deactivation due to occurrence of CH₄ cracking and other side reactions. The wetness impregnation catalyst was found to have the highest DRM activity and stability,

which was attributed to its moderate surface acidity that impede deactivation. Similarly, microscopic dispersion fostered accessibility of reactants to active Ni sites for enhanced performance. In addition, in order to get deeper insights on the stable behaviour and influence of other process conditions, studies are ongoing in our laboratory and will be reported in a later study.

Acknowledgements

The authors acknowledge the Transdisciplinary Research Grant (06G52 and 06G53) from Universiti Teknologi Malaysia for the financial support of the research.

References

- [1] V.V. Thyssen, D.M. Sartore, E.M. Assaf, Effect of preparation method on the performance of Ni/MgO–SiO₂ catalysts for glycerol steam reforming, *J. Energy Inst.* 92 (2019) 947–958.
- [2] Y. Gambo, A.A. Jalil, S. Triwahyono, A.A. Abdulrasheed, Recent advances and future prospect in catalysts for oxidative coupling of methane to ethylene : a review, *J. Ind. Eng. Chem.* 59 (2018) 218–229.
- [3] A.A. Abdulrasheed, A.A. Jalil, S. Triwahyono, M.A.A. Zaini, Y. Gambo, M. Ibrahim, Surface modification of activated carbon for adsorption of SO₂ and NO_x : a review of existing and emerging technologies, *Renew. Sustain. Energy Rev.* 94 (2018) 1067–1085.
- [4] M.A. Hossain, B.V. Ayodele, C.K. Cheng, M.R. Khan, Optimization of renewable hydrogen-rich syngas production from catalytic reforming of greenhouse gases (CH₄ and CO₂) over calcium iron oxide supported nickel catalyst, *J. Energy Inst.* 92 (2019) 177–194.
- [5] S. Singh, T.D. Nguyen, T.J. Siang, P.T.T. Phuong, N.H.H. Phuc, Q.D. Truong, S.S. Lam, D.-V.N. Vo, Boron-doped Ni/SBA-15 catalysts with enhanced coke resistance and catalytic performance for dry reforming of methane, *J. Energy Inst.* (2019), <https://doi.org/10.1016/j.joei.2019.04.011>.
- [6] T.J. Siang, L.G. Bach, S. Singh, Q.D. Truong, V.T.T. Ho, N.H.H. Phuc, F. Alenazey, D.-V.N. Vo, Methane bi-reforming over boron-doped Ni/SBA-15 catalyst: longevity evaluation, *Int. J. Hydrogen Energy* 44 (2019) 20839–20850.
- [7] Z. Yu, L. Zhang, C. Zhang, G. Gao, Z. Ye, S. Zhang, Q. Liu, G. Hu, X. Hu, Steam reforming of acetic acid over nickel catalysts: impacts of fourteen additives on the catalytic behaviors, *J. Energy Inst.* (2019), <https://doi.org/10.1016/j.joei.2019.09.002>.
- [8] T.J. Siang, S. Singh, O. Omogbe, L.G. Bach, N.H.H. Phuc, D.-V.N. Vo, Hydrogen production from CH₄ dry reforming over bimetallic Ni-Co/Al₂O₃ catalyst, *J. Energy Inst.* 91 (2018) 683–694.
- [9] N. Abdullah, N. Airirazali, C.C. Chong, H.A. Razak, H.D. Setiabudi, A.A. Jalil, D.-V.N. Vo, Influence of impregnation assisted methods of Ni/SBA-15 for production of hydrogen via dry reforming of methane, *Int. J. Hydrogen Energy* (2019), <https://doi.org/10.1016/j.ijhydene.2019.09.089>.
- [10] Q. Zhang, T. Zhang, Y. Shi, B. Zhao, M. Wang, Q. Liu, J. Wang, K. Long, Y. Duan, P. Ning, A sintering and carbon-resistant Ni-SBA-15 catalyst prepared by solid-state grinding method for dry reforming of methane, *J. CO₂ Utilization*

- 17 (2017) 10–19.
- [11] A.A. Abdulrasheed, A.A. Jalil, M.Y.S. Hamid, T.J. Siang, N.A.A. Fatah, S.M. Izan, N.S. Hassan, Dry reforming of methane to hydrogen-rich syngas over robust fibrous KCC-1 stabilized nickel catalyst with high activity and coke resistance, *Int. J. Hydrogen Energy* (2019), <https://doi.org/10.1016/j.ijhydene.2019.04.126>.
 - [12] A.A. Abdulrasheed, A.A. Jalil, Y. Gambo, M. Ibrahim, H.U. Hambali, M.Y.S. Hamid, A review on catalyst development for dry reforming of methane to syngas: recent advances, *Renew. Sustain. Energy Rev.* 108 (2019) 175–193.
 - [13] Q. Zhang, J. Wang, P. Ning, T. Zhang, M. Wang, K. Long, J. Huang, Dry reforming of methane over Ni/SBA-15 catalysts prepared by homogeneous precipitation method, *Korean J. Chem. Eng.* 34 (2017) 2823–2831.
 - [14] Z. Hao, Q. Zhu, Z. Jiang, B. Hou, H. Li, Characterization of aerogel Ni/Al₂O₃ catalysts and investigation on their stability for CH₄-CO₂ reforming in a fluidized bed, *Fuel Process. Technol.* 90 (2009) 113–121.
 - [15] J.L. Ewbank, L. Kovarik, F.Z. Diallo, C. Sievers, Effect of metal–support interactions in Ni/Al₂O₃ catalysts with low metal loading for methane dry reforming, *Appl. Catal., A* 494 (2015) 57–67.
 - [16] M.Y.S. Hamid, A.A. Jalil, A.F.A. Rahman, T.A.T. Abdullah, Enhanced reactive CO₂ species formation via V₂O₅-promoted Ni/KCC-1 for low temperature activation of CO₂ methanation, *React. Chem. Eng.* 4 (2019) 1126–1135.
 - [17] A.A. Jalil, Y. Gambo, M. Ibrahim, A.A. Abdulrasheed, N.S. Hassan, M.G.M. Nawawi, U.A. Asli, M.H. Hassim, A. Ahmad, Platinum-promoted fibrous silica Y zeolite with enhanced mass transfer as a highly selective catalyst for n-dodecane hydroisomerization, *Int. J. Energy Res.* (2019), <https://doi.org/10.1002/er.4545>.
 - [18] H.U. Hambali, A.A. Jalil, S. Triwahyono, S.F. Jamian, N.A.A. Fatah, A.A. Abdulrasheed, T.J. Siang, Unique structure of fibrous ZSM-5 catalyst expedited prolonged hydrogen atom restoration for selective production of propylene from methanol, *Int. J. Hydrogen Energy* (2019), <https://doi.org/10.1016/j.ijhydene.2019.11.236>.
 - [19] S.M. Sidik, S. Triwahyono, A.A. Jalil, M.A.A. Aziz, N.A.A. Fatah, L.P. Teh, Tailoring the properties of electrolyzed Ni/mesoporous silica nanoparticles (MSN) via different Ni-loading methods for CO₂ reforming of CH₄, *J. Co₂ Util.* 13 (2016) 71–80.
 - [20] P.J. Miedziak, S.A. Kondrat, N. Sajjad, G.M. King, M. Douthwaite, G. Shaw, G.L. Brett, J.K. Edwards, D.J. Morgan, G. Hussain, G.J. Hutching, Physical mixing of metal acetates: optimisation of catalyst parameters to produce highly active bimetallic catalysts, *Catal. Sci. Technol.* 3 (2013) 2910.
 - [21] M. Tao, Z. Xin, X. Meng, Y. Lv, Z. Bian, Impact of double-solvent impregnation on the Ni dispersion of Ni/SBA-15 catalysts and catalytic performance for the syngas methanation reaction, *RSC Adv.* 6 (2016) 35875.
 - [22] W.Y. Kim, J.S. Jang, E.C. Ra, K.Y. Kim, E.H. Kim, J.S. Lee, Reduced perovskite LaNiO₃ catalysts modified with Co and Mn for low coke formation in dry reforming of methane, *Appl. Catal., A* 575 (2019) 198–203.
 - [23] A. Giehr, L. Maier, S.A. Schunk, O. Deutschmann, Thermodynamic considerations on the oxidation state of Co/ γ -Al₂O₃ and Ni/ γ -Al₂O₃ catalysts under dry and steam reforming conditions, *ChemCatChem* (2017), <https://doi.org/10.1002/cctc.201701376>.
 - [24] X. Li, W. Dong, J. Zhang, S. Shao, Y. Cai, Preparation of bio-oil derived from catalytic upgrading of biomass vacuum pyrolysis vapor over metal-loaded HZSM-5 zeolites, *J. Energy Inst.* (2019), <https://doi.org/10.1016/j.joei.2019.06.005>.
 - [25] A. Kostyniuk, D. Key, M. Mdleleni, 1-hexene isomerization over bimetallic M-Mo-ZSM-5 (M: Fe, Co, Ni) zeolite catalysts: effects of transition metals addition on the catalytic performance, *J. Energy Inst.* (2019), <https://doi.org/10.1016/j.joei.2019.06.009>.
 - [26] Y. Vafaiean, M. Haghighi, S. Aghamohammadi, Ultrasound assisted dispersion of different amount of Ni over ZSM-5 used as nanostructured catalyst for hydrogen production via CO₂ reforming of methane, *Energy Convers. Manag.* 76 (2013) 1093–1103.
 - [27] O. Mazaheri, R.J. Kalbasi, Preparation and characterization of Ni/mZSM-5 zeolite with a hierarchical pore structure by using KIT-6 as silica template: an efficient bi-functional catalyst for the reduction of nitro aromatic compounds, *RSC Adv.* 5 (2015) 34398.
 - [28] N. Miskolci, T. Juzsakova, J. Soja, Preparation and application of metal loaded ZSM-5 and y-zeolite catalysts for thermo-catalytic pyrolysis of real end of life vehicle plastics waste, *J. Energy Inst.* (2017) 1–10, <https://doi.org/10.1016/j.joei.2017.10.017>.
 - [29] I.C. Freitas, R.L. Manfro, M.M.V.M. Souza, Hydrogenolysis of glycerol to propylene glycol in continuous system without hydrogen addition over Cu-Ni catalysts, *Appl. Catal., B* 220 (2018) 31–41.
 - [30] N.A.A. Fatah, S. Triwahyono, A.A. Jalil, N. Salamun, C.R. Mamat, Z.A. Majid, n-Heptane isomerization over molybdenum supported on bicontinuous concentric lamellar silica KCC-1: influence of phosphorus and optimization using response surface methodology (RSM), *Chem. Eng. J.* 314 (2017) 650–659.
 - [31] Z. Boukha, C. Jiménez-González, B.D. Rivas, J.R. González-Velasco, J.C. Gutiérrez-Ortiz, R. López-Fonseca, Synthesis, characterisation and performance evaluation of spinel-derived Ni/Al₂O₃ catalysts for various methane reforming reactions, *Appl. Catal., B* 158–159 (2014) 190–201.
 - [32] F. Mirzaei, M. Rezaei, F. Meshkani, Coprecipitated Ni-Co bimetallic nanocatalysts for methane dry reforming, *Chem. Eng. Technol.* 37 (2014) 973–978.
 - [33] S. Das, M. Sengupta, J. Patel, A. Bordoloi, A study of the synergy between support surface properties and catalyst deactivation for CO₂ reforming over supported Ni nanoparticles, *Appl. Catal., A* 545 (2017) 113–126.
 - [34] A. Bawah, Z.O. Malaibari, O. Muraza, Syngas production from CO₂ reforming of methane over Ni supported on hierarchical silicalite-1 fabricated by microwave-assisted hydrothermal synthesis, *Int. J. Hydrogen Energy* 43 (2018) 13177–13189.
 - [35] E. Lovell, Y. Jiang, J. Scott, F. Wang, Y. Suhardja, M. Chen, J. Huang, R. Amal, CO₂ reforming of methane over MCM-41-supported nickel catalysts: altering support acidity by one-pot synthesis at room temperature, *Appl. Catal., A* 473 (2014) 51–58.
 - [36] L. Chen, J. Ni, J. Zhao, J. Lin, S. Kawi, Lewis acid sites stabilized nickel catalysts for dry (CO₂) reforming of methane, *ChemCatChem* (2016), <https://doi.org/10.1002/cctc.201601002>.
 - [37] C. Dai, S. Zhang, A. Zhang, C. Song, C. Shi, X. Guo, Hollow Zeolite encapsulated Ni-Pt bimetallics for sintering and coking resistant dry reforming of methane, *J. Mater. Chem.* (2013), <https://doi.org/10.1039/x0xx00000x>.
 - [38] B. Sarkar, R. Tiwari, R.K. Singha, S. Suman, S. Ghosh, S.S. Acharyya, K. Mantri, L.N.S. Konathala, C. Pendem, R. Bal, Reforming of methane with CO₂ over Ni nanoparticle supported on mesoporous ZSM-5, *Catal. Today* 198 (2012) 209–214.
 - [39] J. Estephane, S. Aouad, S. Hany, B. El Khoury, C. Gennequin, H.E. Zakhem, J.E. Nakat, A. Abouka, E.A. Aad, CO₂ reforming of methane over Ni-Co/ZSM5 catalysts. Aging and carbon deposition study, *Int. J. Hydrogen Energy* (2015), <https://doi.org/10.1016/j.ijhydene.2015.05.147>.
 - [40] A. Kaengsilalai, A. Luengnaruemitchai, S. Jitkarnka, S. Wongkasemjit, Potential of Ni supported on KH zeolite catalysts for carbon dioxide reforming of methane, *J. Power Sources* 165 (2007) 347–352.
 - [41] Y. Kathiraser, U. Oemar, E.T. Saw, Z. Li, S. Kawi, Kinetic and mechanistic aspects for CO₂ reforming of methane over Ni based catalysts, *Chem. Eng. J.* 278 (2015) 62–78.
 - [42] M. Tang, L. Xu, M. Fan, Effect of Ce on 5 wt% Ni/ZSM-5 catalysts in the CO₂ reforming of CH₄ reaction, *Int. J. Hydrogen Energy* 39 (2014) 15482–15496.
 - [43] D. Xia, Y. Chen, C. Li, C. Liu, G. Zhou, Carbon dioxide reforming of methane to syngas over ordered mesoporous Ni/KIT-6 catalysts, *Int. J. Hydrogen Energy* (2018), <https://doi.org/10.1016/j.ijhydene.2018.09.059>.