

PAPER • OPEN ACCESS

## Effect of transition metals (Mo, Mn and Co) on mesoporous ZSM-5 catalyst activity in carbon dioxide reforming of methane

To cite this article: H U Hambali *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **808** 012005

View the [article online](#) for updates and enhancements.



**ECS** **240th ECS Meeting**  
Digital Meeting, Oct 10-14, 2021

**Register early and save  
up to 20% on registration costs**

Early registration deadline Sep 13

**REGISTER NOW**

# Effect of transition metals (Mo, Mn and Co) on mesoporous ZSM-5 catalyst activity in carbon dioxide reforming of methane

H U Hambali<sup>1,3</sup>, A A Jalil<sup>1,2\*</sup>, A A Abdurashed<sup>1</sup>, T J Siang<sup>1</sup>, N A A Fatah<sup>1</sup>, A F A Rahman<sup>1</sup>, M A H Aziz<sup>4</sup> and I Hussain<sup>4</sup>

<sup>1</sup> School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

<sup>2</sup> Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

<sup>3</sup> Department of Chemical Engineering, University of Ilorin, PMB 1515, Ilorin, Nigeria

<sup>4</sup> Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia

\*aishahaj@utm.my

**Abstract.** This paper investigates the effect of transition metals (Mo, Mn and Co) on mesoporous ZSM-5 support in carbon dioxide reforming of methane reaction. The mesoporous ZSM-5 support was synthesized by micro emulsion technique and the metals were loaded by wet impregnation method. It was observed that ZSM-5 supported Co catalyst had higher surface area in comparison to other catalysts, which could favour well dispersion and wider utilization of active component. In addition, the ZSM-5 supported Co catalyst exhibited the highest methane and carbon dioxide conversions of 69 % and 65 % respectively at 850°C. The Co species were more active to decompose methane and carbon dioxide compared to Mo and Mn loaded catalysts. Hence, loading Co on mesoporous ZSM-5 produce an active catalyst in carbon dioxide reforming methane reaction.

## 1. Introduction

The challenge for cleaner energy sources has continued to receive tremendous attention due to lingering issues of climate change, global energy crisis and tropospheric air quality [1,2]. Hence, processes for conversion of harmful molecules into valuable products are being pursued. Syngas (H<sub>2</sub>/CO) is a valuable intermediate for production of chemicals via Fischer-Tropsch process, methanol and oxygenates synthesis [3–5]. Carbon dioxide reforming of methane (CRM) involves conversion of natural gas and carbon dioxide into syngas. The process is considered a viable route to produce pure syngas with H<sub>2</sub>/CO ratio of unity. During the transformation process, methane reacts with an equimolar amount of carbon dioxide over a catalyst to yield syngas according to:  $\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$ . As such, it is an auspicious technology to address the issues of the two greenhouse gases with high global warming potentials [6]. The emission problems associated with carbon dioxide could be sequestered by CRM process that is cheap as considered to current carbon capture technologies [7]. The critical issue associated with CRM is the fabrication of highly active and stable catalyst. The catalyst system must be robust to impede carbon deposition and high temperature sintering. A variety of support materials has



been developed for CRM such as KCC-1 [3], Al<sub>2</sub>O<sub>3</sub> [8], SBA-15[9], MSN [10], SiO<sub>2</sub> [7] and zeolite [11].

The nature of support material is pivotal in controlling the dispersion of metal particles and the stability of active metal particles. CRM has been studied with noble metal (Pt, Rh, Pd, Ru, Ir) based catalysts. Noble metal catalysts displayed remarkable coke resistance, stability and activity [6]. However, their high cost is a major demerit for application as an industrial CRM catalyst. In this scenario, other non-noble metals (Ni, Co, Fe) with low cost becomes potential option. Transition metal catalysts show reasonable performance in CRM reaction with the noble metals producing superior activity and high coke resistance [3]. Reasonable methane and carbon dioxide conversion was recorded by Ni/MCM-41 catalyst at reaction temperature of 750°C [12]. ZSM-5 support with 8 wt.% Ni produced reasonable syngas from CRM reaction [13]. Similarly, the incorporation of nickel on hydroxyapatite support displayed high CRM activity [14]. In addition, Zeng et al. prepared 20% Co/γ-Al<sub>2</sub>O<sub>3</sub> catalyst, which showed good potential as an active CRM catalyst [15]. Thus, the present study investigates the activity of transition metals (Mo, Mn and Co) supported on mesoporous ZSM-5 catalyst in CRM reaction. In this paper, a mesoporous ZSM-5 support was synthesized via micro emulsion technique and employed as carrier material in CRM reaction. This study focused on the activity of mesoporous ZSM-5 supported Mo, Mn and Co catalysts in production of syngas from CRM reaction.

## 2. Experimental

### 2.1. Materials

The materials used in this study are: Tetraethyl orthosilicate (TEOS), Urea, 1-butanol (C<sub>4</sub>H<sub>9</sub>OH), Cetyltrimethylammonium bromide (CTAB), ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and ZSM-5 seed (Si/Al= 23) (MERCK Sdn. Bhd., Malaysia). MoO<sub>3</sub>, Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were used as Mo, Mn and Co precursors respectively obtained from Merck Co. Industrial grade gases (CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>) were used in catalytic testing. H<sub>2</sub> was used as reducing agent, while N<sub>2</sub> and O<sub>2</sub> were used as carrier and pre-treatment gases respectively.

### 2.2. Catalyst Preparation

In this study, microemulsion synthesis technique coupled with ZSM-5 seeds crystallization was adopted to prepare mesoporous ZSM-5 according to the previous reported procedure [16,17]. Metal loading was fixed at 5 wt% for all samples via wet impregnation method. The catalysts prepared were denoted as MoZ, MnZ and CoZ representing Mo, Mn and Co loaded mesoporous ZSM-5 catalysts respectively.

### 2.3. Catalyst Characterization

The phase of the prepared catalysts was confirmed by utilizing a Bruker D8 X-ray diffraction (XRD) analyzer. Specific surface area of all synthesized catalysts was determined from N<sub>2</sub> adsorption-desorption (at 77 K) in an analyzer (Beckman Coulter SA 3100). Catalytic tests were carried out in a micro catalytic fixed bed reactor over different temperature range 550-850°C. 20 mg catalyst with 40–60 meshes size was packed into the isothermal reaction zone of the fixed bed reactor.

Pre-treatment was done for an hour at 850°C under O<sub>2</sub> flowrate of 50 mL min<sup>-1</sup>. Thereafter, reduction was done at 850°C under H<sub>2</sub> flow rate of 50 mL min<sup>-1</sup> which was maintained for 1 h. Then, the gaseous feed comprising of CH<sub>4</sub>:CO<sub>2</sub>:N<sub>2</sub> in a ratio of 1:1:3 were feed into the reactor at flow rate of 100 mL min<sup>-1</sup>. An online gas chromatograph device (Agilent GC, 7820 N) was used to continuously detect and analyze the product gases. Product sampling at the considered temperatures were conducted an hour after commencement of the reaction. The sampling for each reaction run is 20 min. The feed conversion and corresponding products yield were computed by the following equations:

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

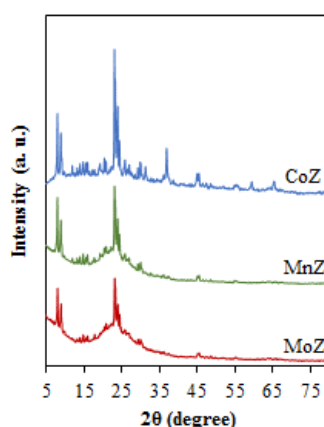
$$CO_2 \text{ conversion} = \frac{F(CO_2)_{in} - F(CO_2)_{out}}{F(CO_2)_{in}} \times 100 \quad (2)$$

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

$$CO \text{ yield} = \frac{F(CO)_{out}}{[F(CH_2)_{in} + F(CO_2)_{out}]} \times 100 \quad (4)$$

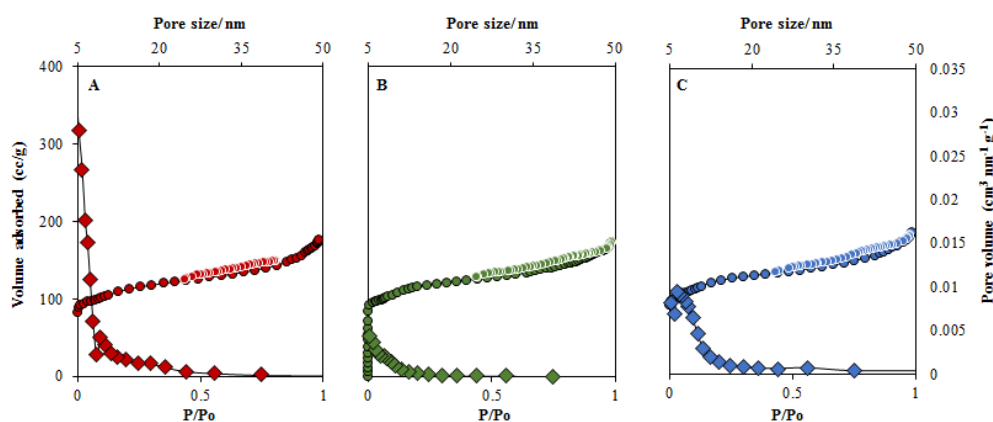
### 3. Results and discussion

The X-ray diffractogram of the synthesized catalysts are shown in figure 1. From the XRD analysis, reflections were observed corresponding to ZSM-5 structure as indicated by sharp diffraction peaks in  $2\theta$  range of 5–10 and 20–26 respectively [16,18]. The intensity of peaks (figure 1) below  $10^\circ$  slightly increased in the order  $CoZ > MnZ > MoZ$ . These might be due to Al removal from the framework, which did not invoke significant damage to the lattice [19]. The peak intensities of ZSM-5 supported Co catalyst had obvious increase, which may be attributed to increase of framework Si species [20]. Furthermore, XRD patterns of MoZ and MnZ seem to be identical. There exist no Mo and Mn species peaks in the XRD patterns, while CoZ demonstrated presence of  $Co_3O_4$  cubic phase by diffraction peaks at  $2\theta = 31.3^\circ, 36.7^\circ, 45.1^\circ, 55.9^\circ, 59.8^\circ$  and  $65.5^\circ$  (JCPDS 01-076-1802) [21].



**Figure 1.** X-ray diffractogram of the catalysts.

Generally, activity of a supported catalyst is significantly related to surface area. Catalyst system with large surface area promote well dispersion and wider utilization of active metals component which result in high CRM performance [22]. Figure 2 illustrates the  $N_2$  physisorption isotherms and the estimated pore volumes of the catalysts are presented in Table 1.



**Figure 2.**  $N_2$  adsorption–desorption and the pore size distribution (a) MoZ (b) MnZ and (c) CoZ.

The catalysts portrayed type IV isotherms with H3 hysteresis loops. This signals the existence of non-uniform slit-shaped mesopores structure. The surface area was MoZ= 395 m<sup>2</sup>/g, Mn= 404 m<sup>2</sup>/g and CoZ= 419 m<sup>2</sup>/g respectively. The MoZ catalyst had the lowest surface area as compared to other catalysts. The MnZ and CoZ catalysts displayed higher N<sub>2</sub> uptake as compared to MoZ, signifying more porosity. The N<sub>2</sub> uptake at partial pressure (P/Po) are characteristics of micropore presence. Furthermore, the step P/Po of 0.2 and 0.9 are attributed to inter and intra particle pores respectively [23,24]. As reported in literatures [25–27], the microemulsion synthesis condition invoke large amount of interparticle pores, which shows the presence of large surface area materials.

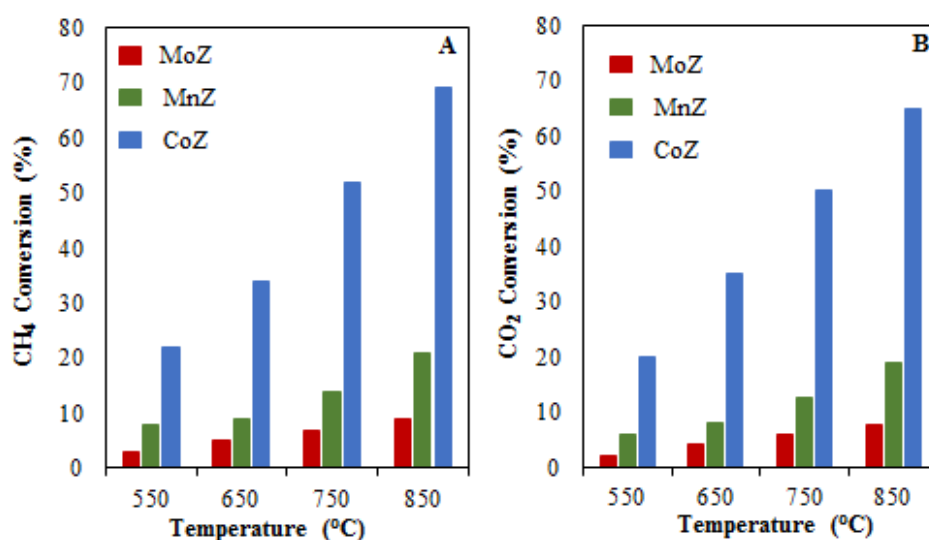
**Table 1.** Physical catalytic properties.

Sample	Surface area (m <sup>2</sup> /g) <sup>a</sup>	Total pore volume (mL/g) <sup>a</sup>	Mesopore volume (mL/g) <sup>b</sup>
MoZ	395	0.2626	0.1722
MnZ	404	0.2838	0.1862
CoZ	419	0.2694	0.1925

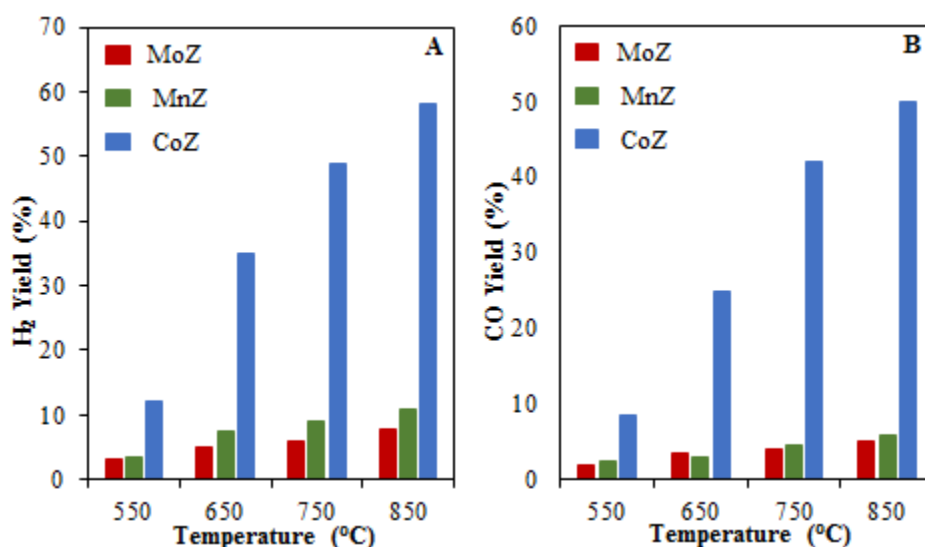
<sup>a</sup>Obtain by the BJH method.

<sup>b</sup>Computed by subtracting micropore volumes from total pore volume.

To determine the effect of prepared catalysts in the CRM process, series of tests were conducted in the micro catalytic fixed bed reactor over 550–850°C temperature range. The results are depicted in figure 3. As can be seen, temperature increase led to enhanced conversion and yield due to the endothermicity of CRM reaction. CoZ displayed high reactants conversion of 69 % and 65 % for CH<sub>4</sub> and CO<sub>2</sub> respectively. The CoZ catalyst produced the highest activity than other catalysts. This suggest that ZSM-5 supported Co catalyst is highly active for transformation of CH<sub>4</sub> and CO<sub>2</sub> gases into syngas. These is in accordance with findings in the catalyst characterizations. CoZ catalyst had higher activity as a result of larger amount of pore sizes and higher surface area which lead to better dispersion of active Co species [14]. These observations are affirmed by the XRD and N<sub>2</sub> adsorption–desorption analysis. Moreover, these features aid higher CH<sub>4</sub> and CO<sub>2</sub> adsorption which is pivotal in CRM reaction. Large surface area enhances the adsorption of the reactants. Hence, this observation is directly related to decomposition of CH<sub>4</sub> and CO<sub>2</sub> dissociation. However, the higher conversion of CH<sub>4</sub> than CO<sub>2</sub> suggest suppression of side reactions [11].



**Figure 3.** Effect of metal loaded catalysts on (a) CH<sub>4</sub> and (b) CO<sub>2</sub> conversions.



**Figure 4.** Effect of metal loaded catalysts on (a) H<sub>2</sub> and (b) CO yield.

It is reported that active metal sites play crucial role in CH<sub>4</sub> adsorption to produce CH<sub>x</sub> fragments [28,29]. Thus, Co species are more active to decompose CH<sub>4</sub> and CO<sub>2</sub> compared to Mo and Mn loaded catalysts. Fayaz et al. achieved initial H<sub>2</sub> and CO yield of 37.5 % and 39 % respectively over 10Co/Al<sub>2</sub>O<sub>3</sub> catalyst. This is in accordance with findings of Khan et al. [30] and Zeng et al. [15]. Similarly, the catalysts investigated displayed different effect on product yield as shown in figure 4. The H<sub>2</sub> and CO yield for CoZ is 58 % and 50 % respectively. There is significant difference in CRM activity of the CoZ and other catalysts as seen in figure 4. This performance is due to the higher activity of Co, coupled with the greater adsorption and dissociation of reactants which was remarkable on CoZ than other catalysts.

#### 4. Conclusion

Mesoporous ZSM-5 support was synthesized by micro emulsion technique and the metals were loaded by wet impregnation method. This study revealed that ZSM-5 supported Co catalyst is a highly active catalyst system for CRM reaction as compared to MoZ and MnZ catalysts. Higher surface area resulted in higher activity of CoZ catalyst in CRM. The Co species and mesoporous ZSM-5 support had a beneficial interaction which led to the suitable CRM activity. The Co species were more active to decompose CH<sub>4</sub> and CO<sub>2</sub> compared to Mo and Mn loaded catalysts. Thus, CoZ is an efficient catalyst in the quest for a viable CRM catalyst.

#### Acknowledgments

This work was supported by the Fundamental Research Grant (Scheme Grant No. FRGS/1/2017/STG07/UTM/01/1) and UTM Transdisciplinary Research Grant (Grant No. 06G53).

#### References

- [1] Gambo Y, Jalil A A, Triwahyono S, Abdurashed A A 2018 Recent advances and future prospect in catalysts for oxidative coupling of methane to ethylene: A review. *J. Ind. Eng. Chem.* **59** 218–229.
- [2] Abdurashed A A, Jalil A A, Triwahyono S, Zaini M A A, Gambo Y, Ibrahim M 2018 Surface modification of activated carbon for adsorption of SO<sub>2</sub> and NO<sub>x</sub>: A review of existing and emerging technologies. *Renewable Sustainable Energy Rev.* **94** 1067–1085.
- [3] Abdurashed A A, Jalil A A, Hamid M Y S, Siang T J, Fatah N A A, Izan S M, Hassan N 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* (doi:10.1016/j.ijhydene.2019.04.126).
- [4] Siang T J, Jalil A A, Hambali H U, Hussain I, Saifulddin M S 2019 Catalytic partial oxidation of methane to syngas over perovskite catalysts. *E3S Web of Conferences*. **6** 1–7.
- [5] Hussain I, Jalil A A, Mamat C R, Siang T J, Azami M S, Hambali H U 2019 Role of Promoters in Hoisting the Catalytic Performance for Enhanced CO Methanation. *J. Energy Safety Technology* **02** 15–20.
- [6] Abdurashed A A, Jalil A A, Gambo Y, Ibrahim M, Hambali H U, Hamid M Y S 2019 A review on catalyst development for dry reforming of methane to syngas : Recent advances. *Renewable Sustainable Energy Rev.* **108** 175–193.
- [7] Ayodele O B, Abdullah A Z 2019 Exploring kaolinite as dry methane reforming catalyst support: influences of chemical activation, organic ligand functionalization and calcination temperature. *Appl. Catal. A.* **576** 20–31.
- [8] Siang T J, Singh S, Omoregbe O, Bach L G, Phuc N N H, Vo D N 2018 Hydrogen production from CH<sub>4</sub> dry reforming over bimetallic Ni–Co/Al<sub>2</sub>O<sub>3</sub> catalyst *Energy Inst.* **91** 683–694.
- [9] Siang T J, Pham T L M, Cuong N V, Phuong P T T, Huu N, Phuc H, Duc Q, Vo D N 2018 Combined steam and CO<sub>2</sub> reforming of methane for syngas production over carbon-resistant boron-promoted Ni/SBA-15 catalysts *Microporous Mesoporous Mater.* **262** 122–132.
- [10] Sidik S M, Triwahyono S, Jalil A A, Majid Z A, Salamun N, Talib N B, Abdullah T A T 2016 CO<sub>2</sub> reforming of CH<sub>4</sub> over Ni–Co/MSN for syngas production: Role of Co as a binder and optimization using RSM *Chem. Eng. J.* **295** 1–10.
- [11] Bawah A, Malaibari Z O, Muraza O 2018 Syngas production from CO<sub>2</sub> reforming of methane over Ni supported on hierarchical silicalite-1 fabricated by microwave-assisted hydrothermal synthesis *Int. J. Hydrogen Energy* **43** 13177–13189.
- [12] Liu D, Lau R, Borgna A, Yang Y 2009 Carbon dioxide reforming of methane to synthesis gas over Ni-MCM-41 catalysts *Appl. Catal. A.* **358** 110–118.
- [13] Vafaeian Y, Haghghi M, Aghamohammadi S 2013 Ultrasound assisted dispersion of different amount of Ni over ZSM-5 used as nanostructured catalyst for hydrogen production via CO<sub>2</sub> reforming of methane *Energy Convers. Manag.* **76** 1093–1103.
- [14] Boukha Z, Pilar M, Angel M, Gonzalez-velasco J R 2019 Influence of Ca/P ratio on the catalytic performance of Ni/hydroxyapatite samples in dry reforming of methane. *Appl. Catal. A.* **580** 34–45.
- [15] Zeng S, Zhang L, Zhang X, Wang Y, Pan H, Su H 2012 Modification effect of natural mixed rare earths on Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts for CH<sub>4</sub>/CO<sub>2</sub> reforming to synthesis gas *Int. J. Hydrogen Energy* **37** 9994–10001.
- [16] Hambali H U, Jalil A A, Triwahyono S, Jamian S F, Fatah N A A, Abdurashed A A., Siang T J 2019 Unique structure of fibrous ZSM-5 catalyst expedited prolonged hydrogen atom restoration for selective production of propylene from methanol *Int. J. Hydrogen Energy*. (doi.org/10.1016/j.ijhydene.2019.11.236).
- [17] Teh L P, Triwahyono S, Jalil A A, Firmansyah M L, Mamat C R, Majid Z A 2016 Fibrous silica mesoporous ZSM-5 for carbon monoxide methanation. *Appl. Catal. A.* **523** 200–208.
- [18] Hambali H U, Jalil A A, Siang T J, Abdurashed A A, Fatah N A A, Hussain I, Azami M S 2019 Effect of ZSM-5 Acidity in Enhancement of Methanol-to-Olefins Process *J. Energy Safety Technology* **4** 9–13.
- [19] Rostamizadeh M, Taeb A 2015 Highly selective Me-ZSM-5 catalyst for methanol to propylene (MTP) *J. Ind. Eng. Chem.* **27** 297–306.
- [20] Jin Z, Liu S, Qin L, Liu Z, Wang Y, Xie Z, Wang X 2013 Methane dehydro-aromatization by Mo-supported MFI-type zeolite with core–shell structure *Appl. Catal. A.* **453** 295–301.
- [21] Abdollahifar M, Haghghi M, Sharifi M 2015 Dry reforming of methane over nanostructured Co/Y catalyst or hydrogen production: Effect of ultrasound irradiation and Co-loading on catalyst properties and performance *Energy Convers. Manag.* **103** 1101–1112.

- [22] Pang Y, Dou Y, Zhong A, Jiang W, Gu L, Feng X, Ji W 2018 Nanostructured Ru-Co@SiO<sub>2</sub>: Highly efficient yet durable for CO<sub>2</sub> reforming of methane with a desirable H<sub>2</sub>/CO ratio *Appl. Catal. A*. **555** 27–35.
- [23] Jalil A A, Gambo Y, Ibrahim M, Abdulrasheed A A, Hassan N S, Nawawi M G M, Asli U A, Hassim M H, Ahamd A 2019 Platinum-promoted fibrous silica Y zeolite with enhanced mass transfer as a highly selective catalyst for n-dodecane hydroisomerization *Int. J. Energy Research* 1–16 (doi: 10.1002/er.4545).
- [24] Fatah N A A, Triwahyono S, Jalil A A, Salamun N, Mamat C R, Majid Z A 2017 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** 650–659.
- [25] Hussain I, Jalil A A, Mamat C R, Siang T J, Rahman A F A, Azami M S, Adnan R H 2019 New insights on the effect of the H<sub>2</sub>/CO ratio for enhancement of CO methanation over metal-free fibrous silica ZSM-5: Thermodynamic and mechanistic studies *Energy Convers. Manag.* **199** 1120562.
- [26] Hamid M Y S, Jalil A A, Rahman A F A, Abdullah T A T 2019 Enhanced reactive CO<sub>2</sub> species formation via V<sub>2</sub>O<sub>5</sub>-promoted Ni/KCC-1 for low temperature activation of CO<sub>2</sub> methanation. *React. Chem. Eng.* **4** 1126–1135.
- [27] Azami M S, Jalil A A, Hitam C N C, Mamat C R, Siang T J, Hussain I, Hambali H U 2019 A Contemporary Assessment on Composite Titania onto Graphitic Carbon Nitride-Based Catalyst as Photocatalyst *J. Energy Safety Technology* **02** 21–25.
- [28] Hambali H U, Jalil A A, Abdulrasheed A A, Siang T J, Vo D V N 2020 Enhanced dry reforming of methane over mesostructured fibrous Ni/MFI zeolite: Influence of preparation method. *J Energy Inst.* 2020 (doi:10.1016/j.joei.2020.01.016).
- [29] Abdulrasheed A A, Jalil A A, Hamid M Y S, Siang T J, Abdullah T A T 2020 Dry reforming of CH<sub>4</sub> over stabilized Ni-La@KCC-1 catalyst: Effects of La promoter and optimization studies using RSM *J CO<sub>2</sub> Util.* **37** 230–239 (doi:10.1016/j.jcou.2019.12.018).
- [30] Khan N A, Kennedy E M, Dlugogorski B Z, Adesina A A, Stockenhuber M 2018 A proposed reaction mechanism for the selective oxidation of methane with nitrous oxide over Co-ZSM-5 catalyst forming synthesis gas (CO+H<sub>2</sub>) *Int. J. Hydrogen Energy* **43** 13133–13144.