The effect of process parameters on catalytic direct CO\textsubscript{2} hydrogenation to methanol

M K Koh\textsuperscript{1}, Y J Wong\textsuperscript{2,3} and A R Mohamed\textsuperscript{2}

\textsuperscript{1}School of Energy and Chemical Engineering, Xiamen University Malaysia, Jalan Sunsuria, Bandar Sunsuria, 43900 Sepang, Selangor, Malaysia
\textsuperscript{2}Low Carbon Economy (LCE) Research Group, School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
\textsuperscript{3}Department of Precision Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

Email: meikee.koh@xmu.edu.my

Abstract. The direct CO\textsubscript{2} hydrogenation to methanol is an attractive route to actively remove CO\textsubscript{2} and to promote sustainable development. Herein, the performance of Cu-Zn-Mn catalyst supported on mesoporous silica KIT-6 (hereafter, CZM/KIT-6) for methanol synthesis by direct CO\textsubscript{2} hydrogenation reaction was investigated by varying the process parameters, which included the weight-hourly space velocity, reaction temperature and reaction pressure. The CO\textsubscript{2} conversion was found to decrease with the increase of WHSV. On the other hand, CO\textsubscript{2} conversion increased with reaction temperature and pressure. Meanwhile, the methanol selectivity increased with WHSV and reaction pressure but decreased with the increase of reaction temperature. The apparent activation energy of methanol production at low reaction temperature (160 - 220 °C) was 10 kcal/mol. Non-Arrhenius behaviour of methanol formation was observed at high reaction temperature (220 - 260 °C). The performance of CZM/KIT-6 was maintained at high level, with the average methanol yield of 24.4 %, throughout the stability experiment (120-hour time-on-stream). In post-reaction XRD analysis, the copper crystallite growth was found to be 53.5 %, thus, resulting in 35.3 % loss of copper surface area.

1. Introduction

With the growing awareness on environmental protection and energy security issues, methanol production via direct CO\textsubscript{2} hydrogenation has been recognized as an advantageous approach to actively remove CO\textsubscript{2} and to promote sustainable development. The reaction is shown in equation (1).

\[
\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H_{298}^\circ = -49.5 \text{ kJ/mol}
\]

(1)

The approach reduces our dependence on fossil-based resources. It also provides an alternative to CO\textsubscript{2} sequestration, which requires suitable sequestration sites and continuous monitoring [1]. More recently, a new perspective on methanol production from direct CO\textsubscript{2} hydrogenation has emerged, wherein the process is considered as a way to store surplus electrical energy produced from renewable energy sources (RES) such as wind, hydraulic and solar energy [2,3]. The integration of RES and methanol production from CO\textsubscript{2} hydrogenation is also known as power-to-methanol (PtMeOH) process.
Efficient methanol production from CO₂ hydrogenation using inexpensive electricity generated from RES is important for abating global warming and to satisfy the world demand for renewable energy [4].

Despite relentless efforts, the reaction is yet to be operated efficiently due to the presence of the competing reverse water-gas shift reaction (RWGS), which often leads to low methanol production. The RWGS is shown in equation (2).

\[
CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H_{\text{298}}^\circ = 41.2 \text{ kJ/mol}
\]

At high reaction temperature (≥220 °C), most of the CO₂ are converted to CO through RWGS and/or methanol decomposition [5]. Hence, the methanol selectivity and yield are lowered at high reaction temperature. For instance, Xiao et al. [6] reported the methanol selectivity and yield obtained over Cu-ZnO-TiO₂ catalyst at 220 °C were approximately 50 % and 7.5 %, respectively. With the increase of reaction temperature to 260 °C, the methanol selectivity and yield decreased to approximately 33 % and 6.3 %, respectively.

Thermodynamically, the RWGS can be suppressed by low reaction temperature (≤200 °C) [7]. Yet, the CO₂ conversion at ≤200 °C is usually low and therefore limits the methanol yield. The CO₂ molecule is thermodynamically stable due to its negative electron affinity (-0.6 eV) and large ionization potential (13.73 eV) [8]. Besides, the Gibbs energy of formation (\(\Delta G^{\circ}_{\text{298K}}\)) of the molecule has a large negative value, -394.6 kJ/mol [9]. Consequently, a large input of energy is required to activate CO₂ molecules. Reaction temperatures of ≥220 °C are commonly reported to be the optimum to achieve reasonable CO₂ conversion but at the expense of lower methanol selectivity [10,11]. The approach to facilitate CO₂ conversion by increasing reaction temperature inevitably enhances the RWGS.

In order to address the aforementioned limitations, our research group has been dedicated to explore the reaction at low temperature, in which the kinetic limitation of CO₂ conversion is tackled through the development of Cu-Zn-Mn catalysts. The development of the catalysts has been presented in our earlier contributions [12,13]. Besides catalysts, it is equally important to apply suitable process conditions for achieving high methanol yield since the reaction is reversible and strongly competed by RWGS. In this sense, we investigated the effect of process parameters on direct CO₂ hydrogenation to methanol over Cu-Zn-Mn catalyst supported on mesoporous silica KIT-6. The weight-hourly space velocity (WHSV, 8 - 120 L/g-cat·h), reaction temperature (160 - 260 °C) and reaction pressure (1.0 - 5.0 MPa) were varied in the study. The range of these process parameters were selected by considering the relevant literature and the equipment limitation. The apparent activation energies of methanol and CO formation were also calculated. Finally, the stability of the catalyst in 120-hour time-on-stream was assessed.

2. Methods

The synthesis of CZM/KIT-6 has been reported elsewhere [13]. The catalyst was tested in a continuous flow tubular micro-reactor. The CO₂:H₂ mol ratio of the feed gas was fixed at 1:3. Other process conditions, i.e. WHSV, reaction temperature and pressure were investigated using change one separate factor at a time (COST) approach. The process parameters investigated are independent of each other, thus, suitable to be examined using COST approach. Traditionally, WHSV has been defined as the weight of feed flowing per unit weight of catalyst per hour. However, to ease reporting of results, the weight of feed flowing is now commonly substituted by the volume of feed flowing [14,15]. Therefore, it should be noted that the WHSV in this study was calculated based on the volume of feed flowing.

In a typical experiment, the catalyst was pre-reduced in hydrogen (60 ml/min) for 2 hours at 300 °C and atmospheric pressure. After cooling, reactant gases were fed into the reactor. Effluent products from reactor were analysed by on-line gas chromatograph (GC, Agilent 7890A) equipped with thermal conductivity detector (TCD) at 20-minute interval. After 6-hour time-on-stream, the conversion of CO₂ and the selectivity of methanol were recorded.

X-ray diffraction (XRD) analysis of the catalysts was conducted using diffractometer PANalytical X’Pert PRO MPD, equipped with Cu Kα radiation. Using Scherrer equation, the Cu crystallite size was calculated from the full width at half-maximum (FWHM) of diffraction peak at 2Θ value of 43.3°. Cu surface area was estimated by equation (3).


\[ S_{\text{Cu}}(m^2/g) = \frac{6000 \times X_{\text{Cu}}}{8.96 \times d_{\text{Cu}}} \]  

(3)

where \( X_{\text{Cu}} \) = mass fraction of Cu and \( d_{\text{Cu}} \) = Cu crystallite size from XRD analysis (nm) [16].

3. Results and Discussion

3.1. Effect of WHSV

The effect of WHSV on the performance of catalyst was investigated in the range of 8 - 120 L/g\(_{\text{cat}}\)·h. Meanwhile, the reaction temperature and pressure were held constant at 180 °C and 4.0 MPa, respectively. The CO\(_2\) conversion (\( C_{\text{CO}_2} \)), product selectivity (\( S_i \)) and methanol yield (\( Y_{\text{CH}_3\text{OH}} \)) are shown in figure 1. The CO\(_2\) conversion decreased from 24.2 % to 8.2 % with the increased of WHSV from 8 L/g\(_{\text{cat}}\)·h to 120 L/g\(_{\text{cat}}\)·h. The observation could be ascribed to the shorter contact time between reactants and catalytic active sites when WHSV was increased [17,18].

![Figure 1. Effect of WHSV on the performance of CZM/KIT-6 at constant reaction temperature (180 °C) and pressure (4.0 MPa).](image)

On stark contrast, the methanol selectivity was increased from 87.7 % to 99.0 % when WHSV was increased from 8 L/g\(_{\text{cat}}\)·h to 120 L/g\(_{\text{cat}}\)·h. The increasing trend of methanol selectivity contradicts the findings reported by Ren et al. [17], in which the ratio of activated CO\(_2\) to formate intermediates was speculated to decrease with the increase of space velocity (shorter contact time) and thereby lowering the methanol selectivity. The correlation observed between WHSV and methanol selectivity could also be related to the weakening of RWGS with the increased of WHSV. A similar trend has been reported by Razali [19]. Interestingly, it was found the methanol yield increased first with WHSV to a maximum of 22.4 % at 30 L/g\(_{\text{cat}}\)·h and then decreased with further increase of WHSV. As mentioned earlier, CO\(_2\) conversion and methanol selectivity responded in opposite manner with the increase of WHSV. Thus, it can be concluded that a balance between CO\(_2\) conversion and methanol selectivity was achieved at WHSV of 30 L/g\(_{\text{cat}}\)·h and therefore resulting in the high methanol yield (22.4 %).
3.2. Effect of reaction temperature

The effect of reaction temperature on the performance of catalyst was investigated in the range of 160-260 °C. Meanwhile, the WHSV and pressure were held constant at 60 L/gcat·h and 4.0 MPa, respectively. The catalyst performance is shown in figure 2.

![Figure 2](image)

**Figure 2.** Effect of reaction temperature on the performance of CZM/KIT-6 at constant WHSV (60 L/gcat·h) and reaction pressure (4.0 MPa).

As expected, the CO₂ conversion increased with the reaction temperature. This is because more external energy was supplied for CO₂ activation when reaction temperature was increased. The growth of CO₂ conversion was rapid at 160-200 °C and then became slow at 220 - 260 °C. The deceleration of CO₂ conversion points to the possibility of catalyst deactivation due to the loss of copper surface area when the reaction temperature was increased beyond 220 °C. Such effect of copper surface area on CO₂ conversion has been reported in other studies [20–22]. Using FWHM values from XRD analysis, the average copper crystallite size and copper surface area of CZM/KIT-6 spent in the experiments conducted at 180 °C, 220 °C and 260 °C were calculated and are shown in table 1. It was found that copper crystallite growth intensifies with the increase of reaction temperature, hence, resulting in the loss of copper surface area. The XRD results provide explanation to the deceleration of CO₂ conversion at reaction temperature above 220 °C.

The investigated temperature also showed significant effect on product selectivity. As the reaction temperature increased from 160 °C to 260 °C, the methanol selectivity decreased rapidly from >99.0 % to 33.0 %. On the contrary, the CO selectivity increased from <1.0 % to 67.0 %. These results corroborate well with the thermodynamics of CO₂ hydrogenation discussed earlier. The reaction of CO₂ conversion, either to produce methanol or CO, is highly dependent on the reaction temperature. The reaction of CO₂ hydrogenation to methanol is exothermic, hence, it is favoured at low reaction temperature. Meanwhile, RWGS is an endothermic reaction, thus, it is favoured at high reaction temperature.
Table 1. Average copper crystallite size and copper surface area of catalyst spent in the experiments conducted at 180 °C, 220 °C and 260 °C.

| Reaction temperature (°C) | Cu crystallite size (nm) | Cu surface area (m²/gcat.) |
|---------------------------|--------------------------|---------------------------|
| 180                       | 10.6                     | 19.5                      |
| 220                       | 11.3                     | 18.3                      |
| 260                       | 14.1                     | 14.6                      |

At temperature range 160 - 200 °C, the methanol yield increased with temperature due to the rapid increase of CO₂ conversion compared to the decrease of methanol selectivity. However, the methanol yield was decreased with further increase of temperature (220 - 260 °C) due to the drastic decrease of methanol selectivity compared to the gradual raise of CO₂ conversion. A balance between CO₂ conversion and methanol selectivity was attained at 200 °C, and the highest methanol yield (22.0 %) was recorded.

Frequently, the apparent activation energies (Ea) of methanol and CO formation were estimated from Arrhenius plot, in which the logarithms of formation rates are plotted against the reciprocal of absolute temperatures [23,24]. The Arrhenius plot of methanol formation in this study is depicted in figure 3. It is intriguing to note the Arrhenius plot of methanol formation in the overall temperature range (160 - 260 °C), figure 3(a), severely deviates from the theoretical linear plot, and a concave plot was obtained instead. The non-linearity of the Arrhenius plot is related to the decreased of methanol formation rate with the increase of reaction temperature from 220 - 260 °C. The corresponding apparent activation energy calculated for the high temperature region has a negative value of -10 kcal/mol. It should be noted that it is possible for a chemical reaction to have negative apparent activation energy though rare [25]. The deviation from Arrhenius law is rarely reported but very informative.

In current study, the deviation from Arrhenius law could be related to three factors. Firstly, the increase dominance of RWGS (endothermic) over the reaction of CO₂ hydrogenation to methanol (exothermic) when the reaction temperature was risen beyond 200 °C. The formation rates of methanol and CO in the investigated temperature range are shown in figure 4. It is observable that the formation rates of methanol decreased while CO increased at high temperature range, 220 - 260 °C. Secondly, the reduction of methanol formation rate at high reaction temperature due to catalyst deactivation. As seen in table 1, the increase of reaction temperature was accompanied by the growth of copper crystallites and the loss of copper surface area. The dependence of methanol production rate on the crystallite size and surface area of copper has been widely recognized [25,26]. As such, catalyst deactivation could have contributed to the reduced methanol formation rate at high reaction temperature. Thirdly, there could be a change in the reaction coordinate such as the increase of reverse reaction at high reaction temperature, thus, resulting in the overall negative apparent activation energy. This has been elaborated well by Revell and Williamson [25]. In this regard, Arena et al. [28] postulated the formation of CO via the decomposition of methanol at reaction temperature above 200 °C. This consumption of the formed methanol could have lowered the apparent methanol formation rate. Despite the non-Arrhenius behaviour of methanol formation at high reaction temperature, the apparent activation energy of methanol formation can be estimated from the low reaction temperature range, 160 - 200 °C. The apparent activation energy of methanol production at low reaction temperature was 10 kcal/mol.
Figure 3. Arrhenius plot for methanol formation in (a) overall temperature range and (b) according to high- and low-temperature range.

Figure 4. Methanol and CO production rate at reaction temperature of 160 – 260 °C.

The Arrhenius plot of CO formation is shown in figure 5. It should be noted that the formation rate of CO at 160 °C was not included in the Arrhenius plot because virtually no CO was detected at that reaction temperature. The CO production obeys the Arrhenius law, in which the formation rate increased
with reaction temperature. The apparent activation energy for CO formation was 22 kcal/mol. A comparison of apparent activation energies achieved in this study and the values reported in literature are shown in table 2. Generally, the apparent activation energies obtained in current study are consistent with other studies. According to table 2, the apparent activation energy of CO formation is generally higher than methanol by 2 - 3 folds. This explains the dominance of methanol formation at low reaction temperature while CO formation grows steeply at high reaction temperature. The experimental data collected in current investigation clearly reflects this trend.

![Figure 5. Arrhenius plot for CO formation.](image)

**Table 2.** Comparison of the apparent activation energies ($E_a$) for methanol and CO formation attained in current study and in the literature.

| Catalyst          | Methanol | CO     | Reference |
|--------------------|----------|--------|-----------|
| CZM/KIT-6          | 10       | 22     | This study|
| Cu/ZnO/Al$_2$O$_3$ | 13       | 28     | [29]      |
| La/Cu/ZrO$_2$      | 9        | 24     | [20]      |
| Ga-Cu/ZnO/ZrO$_2$  | 7        | 27     | [23]      |
| Cu/t-ZrO$_2$       | 9        | 25     | [24]      |
| CuCeTiO$_x$        | 9        | 18     | [21]      |
| Ni/In$_2$O$_3$     | 19       | -      | [30]      |

3.3. **Effect of reaction pressure**

The effect of reaction pressure on the performance of catalyst in CO$_2$ hydrogenation to methanol was investigated in the range of 1.0 - 5.0 MPa. Meanwhile, the WHSV and temperature were held constant at 60 L/g$_{cat}$·h and 220 °C, respectively. The catalyst performance is shown in figure 6. The presented results show the reaction pressure has marked influence on CO$_2$ conversion, in which the conversion increased steeply from 4.1 % to 26.1 % when the reaction pressure was increased from 1.0 MPa to 4.0 MPa. Further increase of reaction pressure to 5.0 MPa marginally increased CO$_2$ conversion to a maximum of 27.5 %. Under kinetic-controlled regime, the increased of reaction pressure could enhance the adsorptions of CO$_2$ and hydrogen on the catalyst, thus, improving CO$_2$ conversion [18].
Figure 6. Effect of reaction pressure on the performance of CZM/KIT-6 at constant WHSV (60 L/g_{cat}·h) and reaction temperature (220 °C).

From thermodynamic viewpoint, CO production from the RWGS is pressure-independent [31]. On the contrary, methanol synthesis from CO\textsubscript{2} hydrogenation is sensitive to reaction pressure since the reaction proceeds with the reduction of 4 moles of reactants to 2 moles of products. This is in accord with the Le Chatelier’s principle. The data collected shows the methanol selectivity steadily increased (74.6 - 83.5 %) with reaction pressure while CO selectivity decreased. The increased of methanol selectivity and the decreased of CO selectivity were slow when reaction pressure was increased beyond 2.0 MPa. An abrupt growth of methanol yield was observed when reaction pressure was increased from 1.0 MPa to 4.0 MPa (3.1 - 21.3 %), and then slow down with further increase to 5.0 MPa (23.0 %). Based on the observations, it can be concluded that the increase of reaction pressure has positive effect on methanol yield because it remarkably improves CO\textsubscript{2} conversion and to a lesser extend increases methanol selectivity.

3.4. Catalyst stability
The stability of CZM/KIT-6 was evaluated at 200 °C, with WHSV of 30 L/g_{cat}·h, and H\textsubscript{2}: CO\textsubscript{2} mole ratio of 3:1 under a reaction pressure of 5.0 MPa. The stability experiment was conducted under high methanol yield conditions for 120 hours. The process conditions applied were selected based on the investigations in Section 3.1-3.3. It should be noted that the effluent stream from the reactor was analysed at hourly interval. The catalyst performance is illustrated in figure 7.

Methanol and carbon monoxide (CO) were the only detectable carbon-containing products during the experiment. On the average, 27.6 % of CO\textsubscript{2} conversion and 88.3 % of methanol selectivity were achieved, leading to 24.4 % of methanol yield. More importantly, the catalytic performance of CZM/KIT-6 was maintained at high level throughout the 120-hour experiment.
The crystalline phase of CZM/KIT-6 after pre-reduction and after stability experiment were analysed by XRD and the results are shown in figure 8. The broad diffraction peak observed in both catalysts at 22° can be attributed to amorphous silica. Furthermore, the diffraction peaks of metallic Cu phase (JCPDS 04-0836) were observed at 43.3°, 50.4° and 74.1°.
The diffraction peak of ZnO phase (JCPDS 36-1451) was seen at 36.4°. In the spent CZM/KIT-6, a weak diffraction peak corresponds to copper hydroxide (Cu(OH)$_2$) (JCPDS 13-0420) was found at around 16°. Meanwhile, the diffraction peaks of Cu$_2$O and/or CuO were not detectable, thus, suggesting the re-oxidation of metallic Cu in CZM/KIT-6 was trivial even after 120-hour time-on-stream under high methanol yield conditions.

The average copper crystallite size and copper surface area in pre-reduced and spent catalysts are gathered in table 3. Compared to the pre-reduced catalyst, the copper crystallites in spent CZM/KIT-6 underwent 53.5 % growth. Accordingly, 35.3 % of copper surface area loss was estimated. Although substantial, the crystallite growth and the surface area loss had no significant effect on the catalyst performance in the 120-hour experiment.

**Table 3.** Average copper crystallite size and copper surface area of pre-reduced catalyst and spent catalyst (after 120 h time-on-stream).

| Catalyst treatment | CZM/KIT-6 |
|--------------------|-----------|
|                    | Cu crystallite size (nm) | Cu surface area (m$^2$/g$_{cat}$) |
| Pre-reduced        | 7.1       | 29.2 |
| Spent              | 10.9      | 18.9 |

A comparison between the performance of CZM/KIT-6 and other catalysts reported in literature during stability experiment is shown in table 4. In general, the stability of the performance of CZM/KIT-6 is on par with the catalysts reported in literature. Additionally, the high methanol yield achieved using CZM/KIT-6 indicates the catalyst was more active than the others in catalysing direct CO$_2$ hydrogenation to methanol. The performance demonstrated by CZM/KIT-6 in 120-hour time-on-stream infers the catalyst has the potential for industrial application.

**Table 4.** Comparison of the performance of CZM/KIT-6 and other catalysts reported in literature during stability experiment.

| Catalyst                | CO$_2$ conversion (%) | Methanol | Experiment duration (h) | Reference |
|-------------------------|-----------------------|----------|-------------------------|-----------|
|                         |                       | Selectivity (%) | Yield (%) |                        |           |
| CZM/KIT-6               | 27.6                  | 88.3     | 24.4                    | 120       | This work |
| Cu-ZnO-ZrO$_2$          | 12.0                  | 71.0     | 8.5                     | 100       | [32]      |
| Cu/SiO$_2$              | 28.0                  | 21.3     | 6.0                     | 120       | [33]      |
| Cu/ZnO                  | 16.1                  | 77.8     | 12.5                    | 100       | [34]      |
| Cu/ZnO/Al$_2$O$_3$      | 15.8                  | 63.4     | 10.0                    | 100       | [35]      |
| Cu/ZnO/Al$_2$O$_3$/ZrO$_2$ | 13.6               | 61.7     | 8.4                     | 170       | [36]      |

4. Conclusion

The performance of CZM/KIT-6 in catalysing direct CO$_2$ hydrogenation to methanol has been further assessed by considering the effect of process conditions (WHSV, reaction temperature and pressure) and the stability of the catalyst under high methanol yield conditions. The conversion of CO$_2$ and the selectivity towards methanol responded to the variation of process parameters according to the reaction thermodynamics and these have substantial effect on the methanol yield. Therefore, the effectiveness of methanol production relies greatly on the selection of operating conditions. The non-Arrhenius behaviour of methanol formation observed at high reaction temperature, 220 – 260 °C, are possibly the results of the increased rate of RWGS, catalyst deactivation and/or a change in the reaction coordinate such as the decomposition of methanol. The CZM/KIT-6 catalyst maintained high performance, with
average methanol yield of 24.4 %, throughout the stability experiment. The copper crystallite growth and the loss of copper surface area were 53.5 % and 35.3 %, respectively, after 120-hour time-on-stream under high methanol yield conditions.

Acknowledgments
We acknowledge the financial support given by Universiti Sains Malaysia-NanoMITE (203/PJKIMIA/6720009) and XMUM Research Fund (XMUMRF/2021-C7/IENG/0034).

References
[1] Yuan Z, Eden M R and Gani R 2016 Toward the development and deployment of large-scale carbon dioxide capture and conversion processes Ind. Eng. Chem. Res. 55 3383–419
[2] Rivarolo M, Bellotti D, Magistri L and Massardo A F 2016 Feasibility study of methanol production from different renewable sources and thermo-economic analysis Int. J. Hydrogen Energy 41 2105–16
[3] González-Aparicio I, Pérez-Fortes M, Zucker A and Tzimas E 2017 Opportunities of integrating CO$_2$ utilization with RES-E: A Power-to-Methanol business model with wind power generation Energy Procedia 114 6905–18
[4] Atsonios K, Panopoulos K D and Kakaras E 2016 Investigation of technical and economic aspects for methanol production through CO$_2$ hydrogenation Int. J. Hydrogen Energy 41 2202–14
[5] Arena F, Mezzatesta G, Zafarana G, Trunfio G, Frusteri F and Spadaro L 2013 Effects of oxide carriers on surface functionality and process performance of the Cu–ZnO system in the synthesis of methanol via CO$_2$ hydrogenation J. Catal. 300 141–51
[6] Xiao J, Mao D, Guo X and Yu J 2015 Methanol synthesis from CO$_2$ hydrogenation over CuO – ZnO – TiO$_2$ catalysts: the influence of TiO$_2$ Content Energy Technol. 3 32–9
[7] Saeidi S, Amin N A S and Rahimpour M R 2014 Hydrogenation of CO$_2$ to value-added products—A review and potential future developments J. CO$_2$ Util. 5 66–81
[8] Viswanathan B 2013 Electro-catalytic reduction of carbon dioxide New and Future Developments in Catalysis: Activation of Carbon Dioxide pp 275–95
[9] Havran V, Dudukovi M P and Lo C S 2011 Conversion of methane and carbon dioxide to higher value products Ind. Eng. Chem. Res. 50 7089–100
[10] Porosoff M D, Yan B and Chen J G 2016 Catalytic reduction of CO$_2$ by H$_2$ for synthesis of CO, methanol and hydrocarbons: Challenges and opportunities Energy Environ. Sci. 9 62–73
[11] Liu L, Jiang H, Liu H and Li H 2013 Recent advances on the catalysts for activation of CO$_2$ in several typical processes New and future developments in catalysis: Activation of carbon dioxide pp 189–222
[12] Koh M K, Wong Y J, Chai S P and Mohamed A R 2018 Carbon dioxide hydrogenation to methanol over multi-functional catalyst : Effects of reactants adsorption and metal-oxide(s) interfacial area J. Ind. Eng. Chem. 62 156–65
[13] Koh M K, Khavarian M, Chai S P and Mohamed A R 2018 The morphological impact of siliceous porous carriers on copper-catalysts for selective direct CO$_2$ hydrogenation to methanol Int. J. Hydrogen Energy 43 9334–42
[14] Wang G, Chen L, Sun Y, Wu J, Fu M and Ye D 2015 Carbon dioxide hydrogenation to methanol over Cu/ZrO$_2$/CNTs: effect of carbon surface chemistry Rsc Adv. 5 45320–30
[15] Yang H, Gao P, Zhang C, Zhong L, Li X, Wang S, Wang H, Wei W and Sun Y 2016 Core-shell structured Cu@SiO$_2$ and Cu/ZnO@SiO$_2$ catalysts for methanol synthesis from CO$_2$ hydrogenation Catal. Commun. 84 56–60
[16] Ahouari H, Soualah A, Le Valant A, Pinard L, Magnoux P and Pouillox Y 2013 Methanol synthesis from CO$_2$ hydrogenation over copper based catalysts React. Kinet. Mech. Catal. 110 131–45
[17] Ren H, Xu C, Zhao H, Wang Y, Liu J and Liu J 2015 Methanol synthesis from CO₂ hydrogenation over Cu/γ-Al₂O₃ catalysts modified by ZnO, ZrO₂ and MgO J. Ind. Eng. Chem. 28 261–7
[18] Portha J F, Parkhomenko K, Kobl K, Roger A C, Arab S, Commenga J M and Falk L 2017 Kinetics of methanol synthesis from carbon dioxide hydrogenation over copper-zinc oxide catalysts Ind. Eng. Chem. Res. 56 13133–45
[19] Razali N A M 2014 Synthesis, characterization and catalytic performance of Cu/ZnO/SBA-15 for hydrogenation of carbon dioxide to methanol (Universiti Sains Malaysia)
[20] Guo X, Mao D, Lu G, Wang S and Wu G 2011 The influence of la doping on the catalytic behavior of Cu/ZrO₂ for methanol synthesis from CO₂ hydrogenation J. Mol. Catal. A Chem. 345 60–8
[21] Chang K, Wang T and Chen J G 2017 Hydrogenation of CO₂ to methanol over CuCeTiOx catalysts Appl. Catal. B Environ. 206 704–11
[22] Li F, Zhan H, Zhao N and Xiao F 2017 CO₂ hydrogenation to methanol over La-Mn-Cu-Zn-O based catalysts derived from perovskite precursors Int. J. Hydrogen Energy 42 20649–57
[23] Ladera R, Pérez-Alonso F J, González-Carballo J M, Ojeda M, Rojas S and Fierro J L G 2013 Catalytic valorization of CO₂ via methanol synthesis with Ga-promoted Cu-ZnO-ZrO₂ catalysts Appl. Catal. B Environ. 142–143 241–8
[24] Witoon T, Chalornghtham J, Dumrongbunditkul P, Chareonpanich M and Limtrakul J 2016 CO₂ hydrogenation to methanol over Cu/ZrO₂ catalysts: effects of zirconia phases Chem. Eng. J. 293 327–36
[25] Revell L E and Williamson B E 2013 Why are some reactions slower at higher temperatures? J. Chem. Educ. 90 1024–7
[26] Natesakhatwat S, Lekse J W, Baltrus J P, Ohodnicki P R, Howard B H, Deng X and Matranga C 2012 Active sites and structure–activity relationships of copper-based catalysts for carbon dioxide hydrogenation to methanol ACS Catal. 2 1667–76
[27] Xiao S, Zhang Y, Gao P, Zhong L, Li X, Zhang Z, Wang H, Wei W and Sun Y 2017 Highly efficient Cu-based catalysts via hydrotalcite-like precursors for CO₂ hydrogenation to methanol Catal. Today 281 327–36
[28] Arena F, Mezzatesta G, Zafarana G, Trunfio G, Frusteri F and Spadaro L 2013 How oxide carriers control the catalytic functionality of the Cu – ZnO system in the hydrogenation of CO₂ to methanol Catal. Today 210 39–46
[29] Choi Y, Futagami K, Fujitani T and Nakamura J 2001 Role of ZnO in Cu/ZnO methanol synthesis catalysts - morphology effect or active site model? Appl. Catal. A Gen. 208 163–7
[30] Jia X, Sun K, Wang J, Shen C and Liu C jun 2020 Selective hydrogenation of CO₂ to methanol over Ni/In₂O₃ catalyst J. Energy Chem. 50 409–15
[31] Huš M, Dasireddy V D B C, Strah Štefančič N and Likozar B 2017 Mechanism, kinetics and thermodynamics of carbon dioxide hydrogenation to methanol on Cu/ZnAl₂O₄ spinel-type heterogeneous catalysts Appl. Catal. B Environ. 207 267–78
[32] Guo X, Mao D, Lu G, Wang S and Wu G 2010 Glycine-nitrile combustion synthesis of CuO-ZnO-ZrO₂ catalysts for methanol synthesis from CO₂ hydrogenation J. Catal. 271 178–85
[33] Wang Z-Q, Xu Z-N, Peng S-Y, Zhang M-J, Lu G, Chen Q-S, Chen Y and Guo G-C 2015 High-performance and long-lived Cu/SiO₂ nanocatalyst for CO₂ hydrogenation ACS Catal. 5 4255–9
[34] Lei H, Nie R, Wu G and Hou Z 2015 Hydrogenation of CO₂ to CH₃OH over Cu/ZnO catalysts with different ZnO morphology Fuel 154 161–6
[35] Lei H, Hou Z and Xie J 2016 Hydrogenation of CO₂ to CH₃OH over CuO/ZnO/Al₂O₃ catalysts prepared via a solvent-free routine Fuel 164 191–8
[36] Zhang Y, Zhong L, Wang H, Gao P, Li X, Xiao S, Ding G and Sun Y 2016 Catalytic performance of spray-dried Cu/ZnO/Al₂O₃/ZrO₂ catalysts for slurry methanol synthesis from CO₂ hydrogenation J. CO₂ Util. 15 72–82