



I-CAT-O-139-07

## DIRECT STEPWISE OXIDATION OF METHANE TO METHANOL VIA ZINC-PROMOTED COPPER-CONTAINING MORDENITE

Chalermpol Meesub<sup>1</sup>, Phakpum Tannititam<sup>1</sup>, Pronpimol Kruemek<sup>1</sup>, Narit Triamnak<sup>2</sup> and Nutchapon Chotigkrai<sup>1,\*</sup>

<sup>1</sup> Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom, Thailand 73000

<sup>2</sup> Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom, Thailand 73000

\*Corresponding author's e-mail address: chotigkrai\_n@silpakorn.edu

### Abstract

Zinc-promoted copper-mordenite is an interesting material as a catalyst because it can be used to directly stepwise oxidize methane to methanol. In this research, the effects of zinc content in the catalysts and additional processes such as ion-exchange and dry impregnation were studied. The synthesized catalysts were characterized by XRD, N<sub>2</sub>-physisorption, ICP and H<sub>2</sub>-TPR. The catalytic activity was tested in the stepwise manner consisting of three steps of O<sub>2</sub> activation (450 °C), methane loading, and methanol extraction, respectively. The physical properties revealed that the structure of mordenite zeolite remained after Cu and Zn incorporation. The H<sub>2</sub>-TPR suggested the creation of small ZnO particles in zinc-impregnated samples while these species rarely were found in zinc-exchanged samples. The catalytic test showed that zinc could act as an active center itself in the reaction without copper. For zinc-exchanged samples, zinc addition decreased the methanol yield at the beginning and gradually increased with further zinc concentration increase. Interestingly, zinc addition via dry impregnation increased the methanol yield as high as 63% with 1 wt.% of zinc content. Moreover, the 1 wt.% zinc-impregnated catalyst was then tested at lower O<sub>2</sub>-activation temperature of 400 and 250 °C. It was found that the methanol yields were similar at 400 °C and 65.5%-decreased at 250 °C, comparing to the catalyst activated at 450 °C. This result indicated that Zn incorporation significantly promoted the O<sub>2</sub> activation. The promotional effects of zinc addition could be attributed to itself catalytically active and promoting O<sub>2</sub> activation by small ZnO particles.

**Keywords:** Methane to methanol, Zinc addition, Cu-mordenite, Zn-mordenite, Activation temperature

### Introduction

Biomethane, the main component in biogas, is an interesting feedstock because it is renewable and it can be produced from wastewater in conventional industrial plants and ranches. It is expected that Thailand has the potential amount of biogas more than 500 million cubic meters which have not been produced [1]. Biogas is mostly used as fuel for electrical generation, which may not convince the small industry to invest in the construction of biogas generation system and power plant. Therefore, the utilization of biogas for small-scale industry is great significant and challenge. One way is to synthesize value-added chemicals from methane at mild condition. Methanol is one of an interesting product due to its wide applications such as solvent, precursor of fuels, additives, olefins and etc. [2]. It is worth noting that methanol has been imported to Thailand more than 500,000 metric tons annually in 2012-2016, which costs over 6,000 million baht per year [3]. The recent commercial technology for methanol synthesis from methane is based on the indirect process consisting syngas production at high temperature (800 °C) and methanol synthesis at high pressure (50 bar), which allows only large-scale plant is economic feasible [2].

The direct stepwise conversion of methane to methanol at mild condition over Cu-containing ZSM-5 was introduced by M. Groothaert et al. [4] in 2005 and showed the high selectivity of methanol. The stepwise manner includes three steps; the first is O<sub>2</sub> activation at high temperature (~450 °C), CH<sub>4</sub> loading at a lower temperature (~200 °C), and off-line methanol extraction in liquid water, subsequently. Lately, van Bokhoven et al. developed the on-line extraction step by using steam vapor to extract methanol in the reactor, resulting in the more effective process because of easier operation and higher production rate [5]. In addition, they also reported the direct stepwise oxidation

of methane to methanol over Cu-containing mordenite zeolite with very high selectivity (97%) [6] and compared the catalytic activity of CuMOR catalyst activated O<sub>2</sub> at high temperature (450 °C) and isothermal temperature (200 °C) [2]. It was found that the catalyst activated at 450 °C gave higher methanol yield than the catalyst activated at 200 °C and the isothermal O<sub>2</sub> activation needed much higher pressure of methane to restore methanol yield. Interestingly, Román-Leshkov et al. demonstrated that the continuous conversion of this process is possible by flowing the stream of CH<sub>4</sub>, O<sub>2</sub>, and H<sub>2</sub>O simultaneously at 210 °C over Cu-ZSM-5, giving the methanol selectivity about 70% [7]. Therefore, the O<sub>2</sub> activation at a lower temperature is essential and may lead to the upgrading of direct oxidation of methane to methanol from stepwise to continuous process. Gabrienko et al. [8] reported that Zn-exchanged ZSM-5 zeolites could activate methane towards methyl species at low temperature and even at room temperature, in addition, the creation of methoxy species (methanol precursor) at the Zn active sites by flowing O<sub>2</sub> after the methyl species were formed. Moreover, Reule et al. [9] reported that addition of Zn into Cu-exchanged mordenite zeolite resulted in stabilizing high Cu dispersion in carbonylation reaction. These suggested that Zn could be a promoter for Cu-exchanged mordenite catalysts to improve methanol yield and lower O<sub>2</sub> activation temperature.

In this study, we report that zinc could promote Cu-exchanged MOR catalysts for direct stepwise oxidation of methane to methanol. The effects of zinc content in the catalysts, incorporation methods such as ion-exchange and dry impregnation, and O<sub>2</sub> activation temperature were studied. The catalysts were characterized by XRD, N<sub>2</sub> – physisorption, ICP-OES, and H<sub>2</sub> – TPR. This work may guide the way to develop copper-containing mordenite catalyst for direct isothermal-stepwise oxidation of methane to methanol by using zinc as a promoter.

## Materials and methods

### Materials

H-form mordenite zeolite (Si/Al = 9) was purchased from Tosoh corporation. Copper nitrate trihydrate (98.0 - 103 %) and zinc nitrate hexahydrate (≥ 98%) were purchased from Sigma Aldrich (Singapore). All materials were used without further purification.

### Methods

#### Catalyst preparation

Copper-exchanged mordenite catalyst was prepared by ion-exchange method. 10 g of mordenite was stirred in aqueous solutions of copper (II) nitrate trihydrate (0.05 M) at room temperature overnight. The suspension was then vacuum filtered at room temperature. The ion-exchange step was repeated twice, denoted as CuMOR (reference catalyst). The Zn-promoted CuMOR catalysts were prepared by 2 methods such as ion-exchange and dry impregnation. For zinc-exchanged CuMOR catalyst, 2 g of the filtered Cu-exchanged mordenite (without calcination) was stirred in aqueous solution of zinc (II) nitrate hexahydrate at room temperature overnight as the forth ion-exchange cycle with various concentrations of 0.05, 0.1, and 0.15 M, respectively. The Zn-exchanged CuMOR catalyst was denoted as xZn-CuMOR where x is concentration. For zinc-impregnated CuMOR catalyst, 2 g of the dried Cu-exchanged mordenite (dried at 120 °C overnight without calcination) was impregnated with aqueous solution of zinc (II) nitrate hexahydrate with desired amount to result in 0.5, 1, and 2 wt.% of zinc on a dry basis. The Zn-impregnated CuMOR catalyst was denoted as yZn/CuMOR where y is weight percent of zinc. All the final catalysts were dried overnight at 120 °C in an oven and calcined in dry air at 500 °C for 5 hours with a heating rate of 3 °C/min.

#### Catalyst characterization

The crystallinity of mordenite zeolite and Cu-containing catalysts were investigated by XRD technique using a Bruker (D5000). N<sub>2</sub> – physisorption was used to determine pore structure and specific surface area of all catalysts. The catalysts were degassed at 180 °C for 3 h. The elemental composition of the samples was determined by inductively coupled plasma optical emission spectrometry (Agilent 710 series). The sample was digested with 1.2 M of HCl. The reducibility of catalysts was examined by temperature programmed reduction in H<sub>2</sub> technique using a Micrometric Auto Chem 2910 instrument (thermal conductivity detector). Approximately, 0.1 g of catalyst was placed in a quartz U-tube reactor. The catalyst was pretreated in N<sub>2</sub> flow (30 ml/min) at 150 °C for 1 h. The reducibility profile from 100 – 800 °C was conducted in 10% H<sub>2</sub>/N<sub>2</sub> flow (30 ml/min) with a ramp rate of 10 °C/min. The generated water was trapped in a cold alcohol bath before entering the detector.

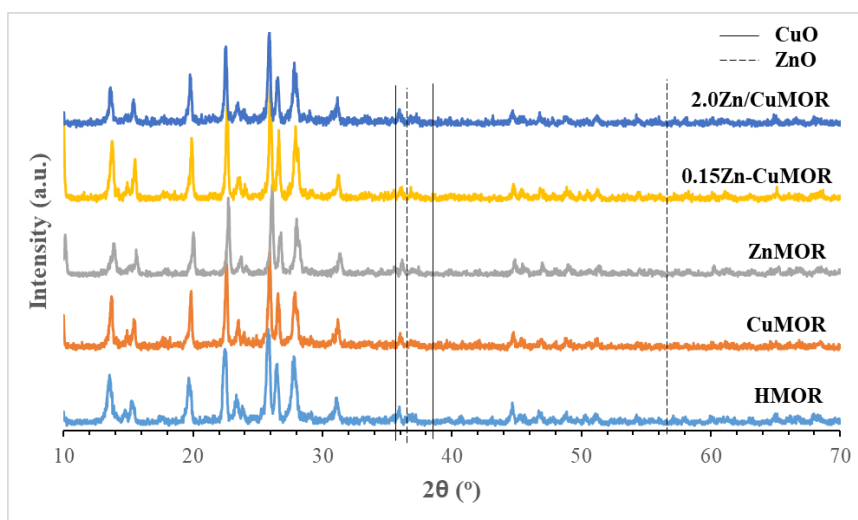
## Direct stepwise oxidation of methane to methanol

The stepwise reaction was carried out in a tubular flow reactor (stainless steel tube, O.D. 9.5 mm) at ambient pressure. 1 g of catalyst was packed between two quartz wool layers at the center of the reactor tube, which was mounted inside a furnace. First, the catalyst was activated in O<sub>2</sub> flow (30 ml/min) at desired temperatures (250, 400 and 450 °C) for 5 h with a heating rate of 10 °C/min before cooling down in O<sub>2</sub> to the reaction temperature (200 °C). Then, O<sub>2</sub> was flushed with helium (30 ml/min) for 15 min before switched to methane (50 ml/min) for 0.5 h. After that, the methane was flushed with helium (30 ml/min) for 15 min and cooling down to ambient temperature. The catalyst was unpacked, stirred in deionized water for 24 h, and filtered. Acetonitrile was added in the extract solution (10% V/V) as an internal standard. The product solution was analyzed by gas chromatography equipped with FID (flame ionization detector).

## Results and discussion

### X-ray Diffraction

The XRD patterns of catalysts are shown in Figure 1. H-form mordenite zeolite (HMOR) revealed the intense peaks between 10° and 54°, corresponding to the primary diffraction peaks of MOR pattern [10]. Cu-, and Zn-exchanged mordenite catalysts (CuMOR and ZnMOR) showed the similar patterns, indicating that ion-exchange of Cu or Zn into mordenite did not alter the crystalline structure of mordenite zeolite as expected. Moreover, the XRD peaks of crystalline copper oxide at 35.6 and 38.7° [11], and zinc oxide at 36.5 and 56.5° [12] were not found in all samples. It suggested that incorporation of copper and zinc by both methods including ion-exchange and dry impregnation provided well-dispersed copper and/or zinc species on the mordenite surface.



**Figure 1** XRD patterns of catalysts

### N<sub>2</sub> – Physisorption

The analysis of N<sub>2</sub> – physisorption results is summarized in Table 1. The BET surface area of a reference catalyst was 356 m<sup>2</sup>/g, corresponding to Le work [10]. For Zn-exchanged catalysts, the BET surface area and micropore volume slightly increased at the beginning and declined to 323 and 281 m<sup>2</sup>/g when further increased concentration of zinc solution to 0.10 and 0.15 M. The similar trend was also observed for the Zn-impregnated catalysts and the BET surface area substantial dropped to 238 m<sup>2</sup>/g for 2.0Zn/CuMOR. The slightly increase at the lowest amount of zinc addition could be ascribed to a part of Zn deposited on the external surface of mordenite that then formed to ZnO during the calcination. The drop of BET surface area at higher metal loading is typical and can be explained by pore filling and partial pore blockage of mordenite zeolite by incorporated metal.

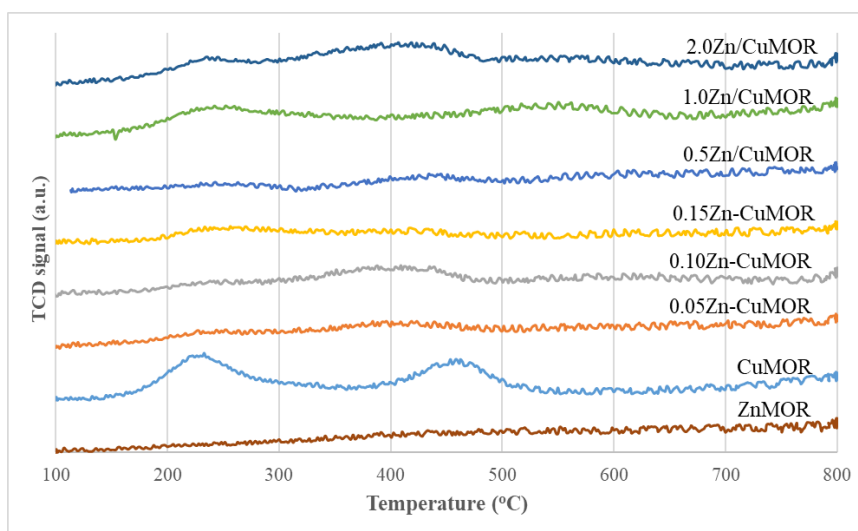
**Table 1** N<sub>2</sub> – physisorption analysis and elemental composition of catalysts

Catalyst	Specific surface area (m <sup>2</sup> /g)	t-plot micropore volume (cm <sup>3</sup> /g)	Elemental composition (wt. %)	
			Cu	Zn
CuMOR	356	0.169	-	-
0.05Zn-CuMOR	357	0.182	-	-
0.10Zn-CuMOR	323	0.161	0.62	0.75
0.15Zn-CuMOR	281	0.130	0.51	0.83
0.5Zn/CuMOR	364	0.180	-	-
1.0Zn/CuMOR	307	0.155	1.03	0.89
2.0Zn/CuMOR	238	0.128	-	-

### Inductively Coupled Plasma Optical emission spectrometry

The elemental composition of selected catalysts is shown in Table 1. The result indicated that Cu content in a series of Zn-exchanged catalysts decreased from 0.62 to 0.51 wt.% with increasing of Zn content from 0.75 to 0.83 wt.% as increased concentration of Zn exchange solution, in addition, Cu content was lower than the 1.0 wt.% Zn-impregnated catalyst. This result implied that Zn<sup>2+</sup> partially substituted Cu<sup>2+</sup> during ion-exchange while Zn species only deposited on the surface without Cu leaching for the impregnation samples.

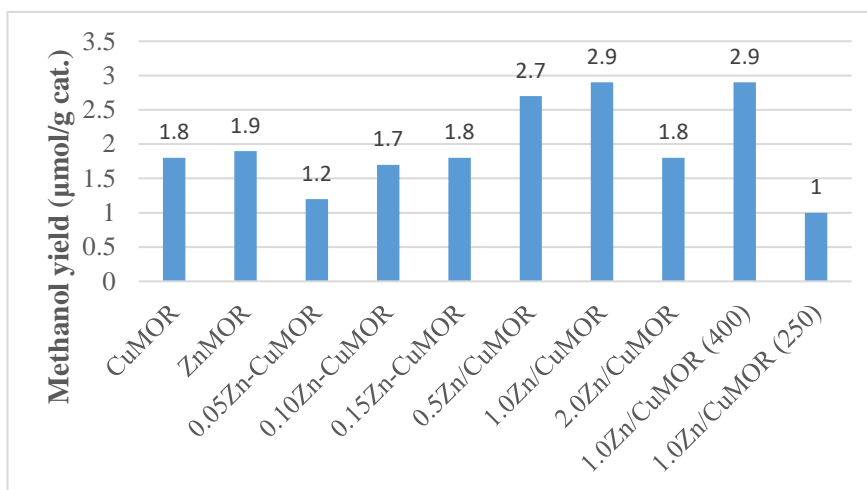
### H<sub>2</sub> – Temperature Programmed Reduction

**Figure 2** H<sub>2</sub> – TPR profiles of catalysts

The TPR profiles of all samples are shown in Figure 2. The TPR profiles of CuMOR catalyst revealed two major regions at 150 - 300 and 400 - 510 °C, respectively. The H<sub>2</sub> consumption at low temperature region was attributed to the reduction of Cu<sup>2+</sup> in the more accessible pore (12-MR channel) or small CuO particles on the external surface of mordenite. At high temperature region, the peaks were assigned to the reduction of Cu<sup>2+</sup> in a smaller channel of mordenite such as 8-MR [13]. The reduction peaks were not found for ZnMOR catalyst, suggesting that bivalent Zn<sup>2+</sup> highly dispersed at the exchange sites in mordenite pores as this behavior was also found in Zn-exchanged H-ZSM-5 zeolite [14]. In a good agreement with Reule et al. work [13], they reported the Zn<sup>2+</sup> preferably exchanged in the 8-MR pore. For all Zn-promoted CuMOR catalysts, it can be seen that the reduction peaks of Cu species were decreased substantially, which might be contributed to the effects of Cu leaching and/or preventing CuO formation (CuO revealed reduction peaks) when Zn was doped [13]. For xZn-CuMOR, the first and second regions were substantially decreased with a shift of the second region to lower temperatures around 420 °C. The decrease of

the first region can be explained by the partial substitution of Cu<sup>2+</sup> by Zn<sup>2+</sup> in the 12-MR channel, corresponding to the Zn<sup>2+</sup> preferably exchanged in 12-MR of mordenite pore when the Cu<sup>2+</sup> presence in the ion-exchange solution [13]. Additionally, the substitution of Cu by Zn in the Zn-exchanged CuMOR was demonstrated by the ICP result, as the amount of Cu in the Zn-exchanged samples was lower than in the Zn-impregnated samples. For *y*Zn/CuMOR, the peaks in the first region were reduced with the lower extent compared with the *x*Zn-CuMOR catalysts. It is suggested that the Cu sites in the 12-MR channels were partially covered but not substituted by the addition Zn when prepared via dry impregnation. Compared with the Zn-exchanged samples, the Zn-impregnated samples showed the additional peaks at 560 °C, which can be implied to the presence of ZnO, matching with the reduction peak of ZnO bulk oxide [12]. However, the H<sub>2</sub> consumption at around 420 °C can be observed for the samples prepared by both methods and increase with increasing of Zn content, these species can be assigned to the very small ZnO particles. The incline of this region is more clear for the Zn-impregnated samples, suggesting that these species were more favorable for the sample prepared by dry impregnation method and more aggregation of ZnO when Zn content was increased.

### Direct stepwise oxidation of methane to methanol



**Figure 3** Methanol yields of all catalysts

The methanol yields of all catalysts are depicted in Figure 3. The methanol yield of CuMOR and ZnMOR were 1.8 and 1.9 µmol/g, respectively, indicating that ZnMOR is catalytically active itself in this reaction. The work of Gabrienko et al. [8] described that zinc can activate methane to methyl species and even oxidize methyl to methoxy species (methanol precursor) after flowing O<sub>2</sub> but we have not found the literature describing that zinc supported on mordenite zeolite can oxidize methane to methanol with this stepwise manner. For *x*Zn-CuMOR catalysts, the methanol yields were 1.2, 1.7, and 1.8 µmol/g for the samples exchanged with aqueous zinc solution at concentration of 0.05, 0.1, and 0.15 M, respectively. The zinc incorporation via ion exchange method substituted the copper active sites as indicated by the ICP and H<sub>2</sub>-TPR results, resulting in the decrease of methanol yield. For *y*Zn/CuMOR catalysts, it is interesting to note that the methanol yields increased to 2.7 and 2.9 µmol/g for 0.5 and 1.0Zn/CuMOR catalysts, respectively, but declined to the similar yield with the reference catalyst when increased to 2 wt.% Zn. The drop of methanol yield might be affected by the significant decrease of the BET surface area of 2.0Zn/CuMOR catalyst, leading to the loss of accessible active sites. The results strongly demonstrated that zinc addition via dry impregnation could improve the O<sub>2</sub> activation as it is probably due to the promotional effects of ZnO particles, which were more found in *y*Zn/CuMOR samples. According to the work of T. Yang et al. [15], they used a thermal pulse method and density functional theory simulation to investigate the transformation of absorbed O<sub>2</sub> at the ZnO surface. It was reported that O<sub>2</sub> molecule dissociates into two individual oxygen atoms by extracting electrons from ZnO surface layers when the temperature is above 170 °C. This conclusion may explain why the methanol yields were enhanced with the catalysts composing of ZnO species. In order to strengthen the promotional effect on O<sub>2</sub> activation, we further tested the catalytic activity of 1.0Zn/CuMOR at lower O<sub>2</sub> activation temperature of 400 and 250 °C, producing methanol for 2.9 and 1 µmol/g, respectively. It can be seen that at 400 °C the 1.0Zn/CuMOR was similarly

active with no drop of methanol yield, compared with the catalyst activated at 450 °C. This result clearly confirmed that zinc could improve the O<sub>2</sub> activation at a lower temperature but the appropriate temperature is still required to effectively activating Cu active species.

## Conclusion

The physical properties revealed that the structure of mordenite zeolite remained after Cu and Zn incorporation. The H<sub>2</sub>-TPR suggested the more creation of small ZnO particles in zinc-impregnated samples while these species less were found in zinc-exchanged samples. The catalytic test showed that zinc could act as an active center itself in the reaction without copper contain. For zinc-exchanged samples, zinc addition decreased the methanol yield at the beginning and gradually increased with further zinc concentration increase. Interestingly, zinc addition via dry impregnation increased the methanol yield as high as 63% with 1 wt.% of zinc content. Moreover, the 1 wt.% zinc-impregnated catalyst was then tested at lower O<sub>2</sub>-activation temperature of 400 and 250 °C. It was found that the methanol yields were similar at 400 °C and 65.5%-decreased at 250 °C, comparing to the catalyst activated at 450 °C. This result indicated that Zn incorporation significantly promoted the O<sub>2</sub> activation. The promotional effects of zinc addition could be attributed to itself catalytically active and promoting O<sub>2</sub> activation by small ZnO particles.

## Acknowledgements

The authors would like to thank the Silpakorn University Fund for Research and Creative Work (Faculty of Engineering and Industrial Technology).

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