

Direct conversion of methane into methanol with O₂ over Cu-MOR

Sae Ha Lee and Eun Duck Park*

*Department of Chemical Engineering and
Department of Energy Systems Research, Ajou
University, Suwon, 16499, Korea*

*E-mail: edpark@ajou.ac.kr

Methane is an abundant energy source because it has the highest H/C ratio among hydrocarbons. It can also be a promising chemical feedstock as long as the stable C-H bond can be activated under mild conditions to lead a selective functionalization. Until now, lots of works have been done to functionalize methane under harsh conditions with strong oxidizing agents such as SO₃, H₂O₂, and N₂O. Even though high yields of methane oxygenates could be obtained, these approaches have their limitation because all these oxidants are more expensive than the final products. Therefore, it is the final and ideal goal to transform methane into valuable chemicals using O₂. The most serious problem is that the yield of valuable chemicals is very low because the valuable chemicals are just intermediates and labile for the following oxidation reactions with O₂. Therefore, separate steps are required to utilize O₂ directly to functionalize methane. Until now, Cu-based catalysts have been reported to be active to transform methane into methanol with O₂ [1-3]. In this study, we prepared Cu-mordenite catalyst with two different ion-exchange methods and applied them to methanol synthesis from methane and air.

Cu-mordenite catalysts were prepared either by an aqueous-phase ion-exchange (APIE) method or solid-state ion-exchange (SSIE) method. In the case of APIE method, an aqueous solution of Cu(NO₃)₂•H₂O (Junsei chem.) was contacted with H-mordenite (SiO₂/Al₂O₃ = 18, Zeolyst) at room temperature for 24 h. The slurry was filtered, washed several times with distilled water, dried in an oven at 120 °C, and then calcined in air at 400 °C. In the case of SSIE method, copper (II) acetylacetonate (Sigma Aldrich) was mixed with H-mordenite (SiO₂/Al₂O₃ = 18,

Zeolyst) in a mortar for 20 min. Then, it was calcined in a static air at 400 °C.

The reaction was carried out under an isothermal condition at 300 °C. The catalyst was first activated with air at atmospheric pressure and then contacted with high-purity methane at 37 bar. Finally, the catalyst was contacted with distilled water at room temperature and methanol can be extracted.

Methanol was quantitatively analyzed using gas chromatography with flame ionization detector. The catalysts were characterized using X-Ray Diffraction (XRD), Brunauer-Emmett-Teller (BET), Temperature-programmed reduction (TPR) and Inductively Coupled Plasma-Atomic emission spectroscopy (ICP-AES).

Table 1 shows that the methanol yield is strongly dependent on the ion-exchange method and Cu content. The APIE method seems to be more plausible than the SSIE method to obtain a higher methanol yield. Irrespective of ion-exchange method, about 3 wt% Cu seems to be optimum Cu content to achieve the highest methanol yield, which can be interpreted that the active Cu species can be formed favorably with this Cu content.

Table 1. Methanol yields over different Cu-mordenite catalysts

| Ion-exchange method | Cu wt% | Yield _{CH₃OH} (μmol g _{cat} ⁻¹) |
|---------------------|--------|--|
| APIE | 3.4 | 84.0 |
| APIE | 5.2 | 39.5 |
| SSIE | 1.0 | 6.4 |
| SSIE | 3.0 | 37.5 |
| SSIE | 10.0 | 2.2 |

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