

The Effect of Oxidants on Methanol Production for Direct Oxidation of Methane over Cu-MOR

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The direct conversion of methane into methanol has been a challenge that modern chemists have pursued because of its tremendous potential [1]. Copper exchanged zeolites can produce methanol from methane at temperatures below 200 °C by its distinctive copper-oxo active sites [2]. The geometric and electronic structures of active sites have been broadly studied, and active sites are known to consist of di- or tri-copper sites for selective oxidation of methane [3,4]. The oxidants, oxygen (O₂) and nitrous oxide (N₂O), have been used for formation of the active sites by providing oxygen source to zeolite framework in activation process. Although spectroscopic analysis revealed that same active sites are formed regardless of used oxidants [5], the effect of oxidants on methanol production has not been identified yet.

In this study, we report that O₂ and N₂O activation resulted in difference in methanol production, and N₂O activation contributes to improvement in methanol production at elevated temperatures. The N₂O-activated Cu-MOR showed an increasing tendency of methanol production with increases in the activation temperature, whereas O₂-activated Cu-MOR showed a volcano-type plot over a range of temperatures. The maximum methanol production for N₂O activation was 97 μmol g⁻¹, which is 1.5 times higher than that for O₂ activation (69 μmol g⁻¹). Copper species during N₂O or O₂ activation was

analyzed by UV-vis-NIR spectroscopy and X-ray absorption near edge spectroscopy (XANES). It revealed that N₂O activation process entailed continuous augmentation of active Cu^{II} species as temperature increases. In contrast, the Cu^I species were observed in the XANES spectrum of O₂ activated Cu-MOR at 450 °C (Fig. 1). O₂ activation entailed retardation of forming active sites and kept in inactive Cu^I states presumably due to an O-O cleavage of the intermediate site.

This mechanistic difference between N₂O and O₂ activation result in the favorable formation of an active copper sites during N₂O activation at elevated temperatures as a result of the lower negative change in entropy.

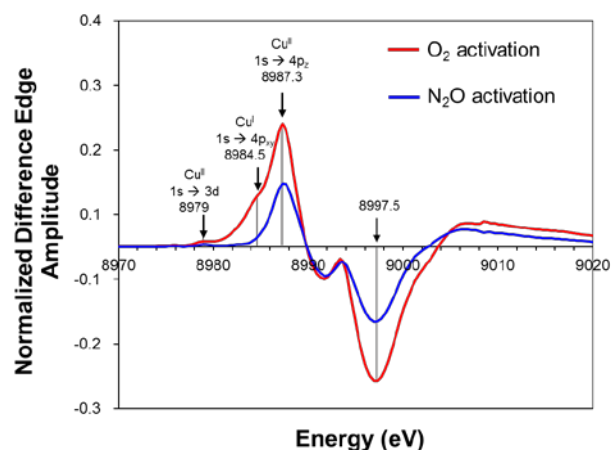


Fig.1 X-ray absorption near edge spectra (XANES) of Cu-MOR activated by O₂ at 450 °C (red) and N₂O at 600 °C (blue) subtracted by bare Cu-MOR.

REFERENCES

- [1] A. I. Olivos-Suarez, À. Szécsényi, E. J. M. Hensen, J. Ruiz-Martinez, E. A. Pidko, and J. Gascon, *ACS Catal.*, 6 (2016) 2965.
- [2] M. H. Groothaert, P. J. Smeets, B. F. Sels, P. A. Jacobs and R. A. Schoonheydt, *J. Am. Chem. Soc.*, 127 (2005) 1394.
- [3] T. Sheppard, C. D. Hamill, a Goguet, D. W. Rooney and J. M. Thompson, *Chem. Commun.*, 50 (2014) 11053.
- [4] G. Li, P. Vassilev, M. Sanchez-Sanchez, J. A. Lercher, E. J. M. Hensen and E. A. Pidko, *J. Catal.*, 338 (2016) 305.
- [5] P. Vanelderen, B. E. R. Snyder, M. L. Tsai, R. G. Hadt, J. Vancauwenbergh, O. Coussens, R. A. Schoonheydt, B. F. Sels and E. I. Solomon, *J. Am. Chem. Soc.*, 137 (2015) 6383.