

Design of Cerium Promoted Cu/SiO₂ Catalysts for Selective Hydrogenation of Dimethyl Oxalate to Ethanol

Peipei Ai, Minghui Tan, Noritatsu Tsubaki*
Department of Applied Chemistry, School of Engineering, University of Toyama, Toyama, Japan

*E-mail: tsubaki@eng.u-toyama.ac.jp

Ethanol, as a form of alcohol that is combustible and can power engines easily, has been pushed to the center stage of clean and renewable energy [1]. Due to the expensive biological process and shrinking oil resource [2, 3], the efficient production of ethanol from syngas (the mixture of CO and H₂) with dimethyl oxalate (DMO) as the intermediate has gained increasing attention in recent years [4]. Considerable studies showed that silica-supported Cu catalysts were promising candidates for DMO hydrogenation to ethanol [5]. However, several problems of existing Cu/SiO₂ catalysts remain unsolved, such as insufficient catalytic activity and stability. To overcome these disadvantages, one of the most convenient and feasible means is introduction of an appropriate catalyst promoter.

Motivated by the above considerations, in this contribution, a series of cerium promoted Cu/SiO₂ (xCe-Cu/SiO₂) catalysts were prepared by urea-assisted gelation approach. The catalytic activity and stability of xCe-Cu/SiO₂ catalysts were investigated for the selective hydrogenation of DMO to ethanol. The physicochemical properties of the synthesized catalysts were analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscope (TEM), N₂ physisorption, N₂O chemisorption, H₂ temperature-programmed reduction (H₂-TPR), H₂ temperature-programmed desorption (H₂-TPD), X-ray photoelectron spectroscopy (XPS), etc. The XRD and N₂O chemisorption results indicated that addition of Ce promoter to Cu/SiO₂ catalyst remarkably increased the dispersion of metallic Cu and retarded the sintering of small-sized Cu species. The strong interaction between Ce promoter and Cu species substantially changed the reducible nature of cerium promoted Cu/SiO₂ catalysts and made

the Cu²⁺ species on catalysts easy to be reduced, which was revealed by H₂-TPR (Fig. 1). In addition, the activation ability of H₂ species was significantly improved in the cerium promoted Cu/SiO₂ catalysts, as evidenced from H₂-TPD studies. Among the synthesized catalysts, the 1Ce-Cu/SiO₂ catalyst with 1.0 wt% Ce loading exhibited the highest catalytic activity and stability (Fig. 2). The combined effect of the above-mentioned positive changes was presumably responsible for the improved catalytic performance of 1Ce-Cu/SiO₂ catalyst.

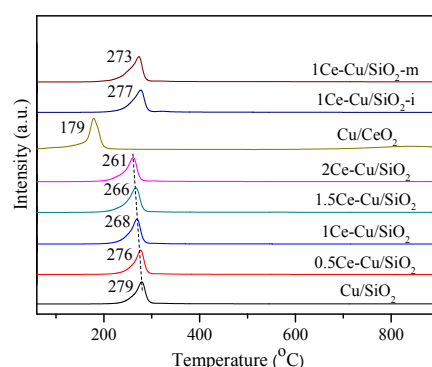


Fig.1 H₂-TPR profiles of different catalysts.

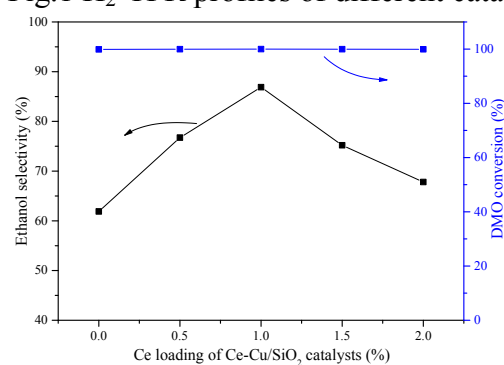


Fig.2 The correlation of catalytic activity with xCe-Cu/SiO₂ catalysts.

REFERENCES

- [1] V. Subramani and S. K. Gangwal, *Energy Fuels*, 22 (2008) 814-839.
- [2] U. N. Maiti, W. J. Lee, J. M. Lee, Y. Oh, J. Y. Kim, J. E. Kim, J. Shim, T. H. Han and S. O. Kim, *Adv. Mater.*, 26 (2014) 40-67.
- [3] Y. Zhang, J. Zhang and D. S. Su, *ChemSusChem*, 7 (2014) 1240-1250.
- [4] A. E. Farrell, R. J. Plevin, B. T. Turner, A. D. Jones, M. O'hare and D. M. Kammen, *Science*, 311 (2006) 506-508.
- [5] P. Ai, M. Tan, Y. Ishikuro, Y. Hosoi, G. Yang, Y. Yoneyama and N. Tsubaki, *ChemCatChem*, 2017.