

Effect of Carbon Supports on RuRe Bimetallic Catalysts for Effective Hydrodeoxygenation of Lignin Pyrolysis Oils

Kyung Bin Jung^{1,2}, Chul-Ho Jun², Dong Jin Suh¹, Jungho Jae^{1,*}

¹Korea Institute of Science and Technology, Seoul, Republic of Korea

²Yonsei University, Seoul, Korea

*E-mail: jjae@kist.re.kr

The hydrodeoxygenation (HDO) of biomass pyrolysis oils is an effective method for improving the pyrolysis oil quality by selectively removing oxygen. In this regard, research into the development of highly active and stable catalysts for the HDO of pyrolysis oils has rapidly expanded in the last decade. Due to the diversity of molecules contained in the pyrolysis oils, lignin-derived phenols (e.g., guaiacol) were commonly used as a pyrolysis oil model compound. The HDO of guaiacol has been studied with a range of catalysts, including noble metals (Pt, Pd, Rh), transition metals (Ni, Fe), and metal sulfides (NiMoS) [1]. Although monometallic catalysts showed some HDO activity, the use of metal-acid bifunctional catalysts (e.g., Pt/H-Beta) or bimetallic catalyst (e.g., Pd-Fe, Ni-Fe) was reported to remarkably enhance the deoxygenation of phenolic compounds due to the synergy between metal (for hydrogenation) and acid sites (dehydration) [1, 2].

In a previous report, we showed that Re promotion of Ru/C catalysts significantly enhance the rate of C-O hydrogenolysis of guaiacol [3]. The high activity of RuRe/C catalysts was explained by the formation of acid sites from rhenium oxide species, while Ru provides metal sites for hydrogenation. In this study, we investigate how the physicochemical properties of carbon supports affect the structure and HDO activity of bimetallic particles using three very different carbon supports, i.e., activated carbon (C), carbon black (VC), multi-walled carbon nanotube (MWCNT).

The RuRe/C catalysts with a Re/Ru atomic ratio of 0.5 were prepared by successive

impregnation using RuCl₃ and NH₄ReO₄ as metal precursors. The reactions were performed in a 150 mL autoclave reactor at 200 °C with 20 bar H₂ for 1 h.

The catalysis results showed that the deoxygenation activity of RuRe/MWCNT and RuRe/VC are remarkably higher than that of RuRe/C (Fig. 1). The STEM-EDS analysis revealed that RuRe/MWCNT had larger particle sizes (4.5 ~ 7 nm) with Re rich surface than RuRe/C (1 ~ 2 nm). The average Ru : Re EDS ratios of RuRe/MWCNT and RuRe/C were 1 : 0.4 and 1 : 0.2, respectively, even though their overall compositions determined by ICP were similar (1 : 0.5). The XPS analysis also revealed the differences in the oxidation state of Re among the catalysts. The ratio of Re⁴⁺ to Re⁶⁺ were highest on the MWCNT followed by VC and C supports, which was correlated with the HDO activity trend. The efficient HDO of lignin pyrolysis oils and other phenolic compounds were also demonstrated using RuRe/MWCNT.

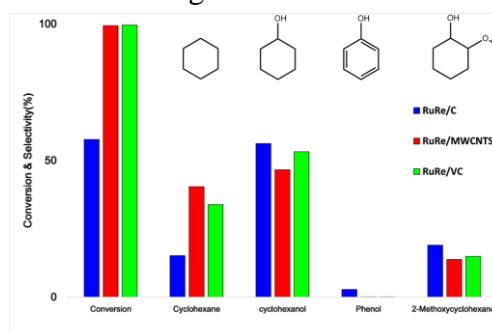


Fig. 1. Catalytic activity of various carbon supported RuRe catalysts for HDO of guaiacol.

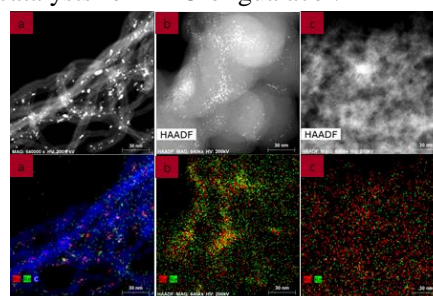


Fig. 2. STEM-EDS images of RuRe/MWCNT (a), RuRe/VC (b), and RuRe/C (c).

REFERENCES

- [1] M. Saidi, F. Samimi, D. Karimipourfard, T. Nimmanwudipong, B.C. Gates, M.R. Rahimpour, Energy Environ. Sci. 7 (2014) 103.
- [2] J. Sun, A.M. Karim, H. Zhang, L. Kovarik, X.S. Li, A.J. Hensley, J.-S. McEwen, Y. Wang, J. Catal. 306 (2013) 47.
- [3] M. Kim, J.-M. Ha, K.-Y. Lee, J. Jae, Catal. Commun. 86 (2016) 113.