Etherification from two different alcohols using molybdenum oxide supported on titania

Yoshihiro Kon*, Akira Yada, Takuya Nakashima, Shinji Tanaka, Tadahiro Fujitani
National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan

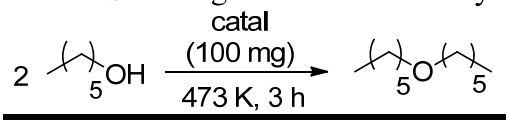
*E-mail: y-kon@aist.go.jp

Ethers are widely used as an intermediate to give specialty chemicals such as pharmaceutical, fragrance and cosmetic, and ether bond is found as an important building block in functional polymers to add ductility and toughness. [1] There are some reports about effective production of unsymmetrical ethers from alcohols using well-designed solid catalysts. [2-6] However, those catalysts are prepared by multi-step method of accurately controlled reaction conditions. It is still required to discover simple and easy handling solid catalyst that can achieve high-yield synthesis of unsymmetrical ether as well as symmetrical ether. In addition, the catalytic reaction under organic solvent- and halide-free conditions is also required to get the valuable ethers with excellent purity.

We surveyed the various kinds of metal oxides from the viewpoints of versatility and credibility as catalytic reaction and found that molybdenum oxide (MoO_n) as well as tungsten oxide (WO_3) showed good catalytic activity for etherification. Here we show the high yield synthesis of ethers from alcohols using MoO_n and WO_3 supported on titania catalysts without any halogenated compounds and organic solvents. Various kinds of metal oxides supported on titania were synthesized from their precursors and titania, a reference catalyst in Catalysis Society of Japan (CSJ).

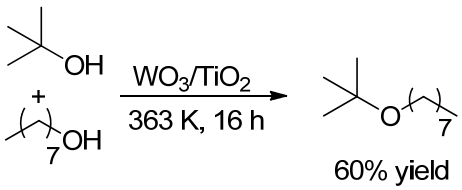
The screening of catalytic activities was conducted with 1-hexanol (2.0 mmol) and the catalyst (100 mg) at 200 °C for 3 h with vigorous stirring in batch reactor, and a part of the results are shown in Table 1. Etherification drastically proceeded at the case of using WO_3/TiO_2 and MoO_n/TiO_2 catalyst, and the reaction without any catalyst showed no reactivity. The reaction using copper oxide and vanadium oxide showed moderate conversion of 1-hexanol. The use of tungsten oxide and molybdenum oxide activated aliphatic alcohol. On the other hand, the yields of dihexyl ether were 41% and 11% for WO_3/TiO_2 and MoO_n/TiO_2, respectively. Dehydration of 1-hexanol occurred to give 1-hexene as side reaction from 1-hexanol with solid acid catalyst. Control of dehydration reaction is required to achieve the selective etherification.

Table 1. Screening of metal oxide catalysts



catal	conv. (%)
10wt% WO_3/TiO_2	94
10wt% $MoOn/TiO_2$	88
10wt% CuO/TiO_2	41
10wt% V_2O_5/TiO_2	44

WO_3/TiO_2 catalyst was applicable to the reaction of two different alcohols (Eq. 1). The reaction of *tert*-butyl alcohol (1 mmol) and 1-octanol (2 mmol) gave *tert*-butyl octyl ether in 60% yield at 90 °C for 16 h. The development of catalytic reaction toward selective etherification on the basis of these data will be shown the presentation of that day.



(1)

REFERENCES

[1] J. March, Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 4th ed., Wiley, New York, 1992, pp. 386-387.
[2] T. Mitsudome, T. Matsuno, S. Sueoka, T. Mizugaki, K. Jitsukawa and K. Kaneda, Green. Chem., 14 (2012) 610.
[3] H. Firouzabadi, N. Iranpoor, A. A. Jafari, J. Mol. Catal. A: Chem., 227 (2005) 97.
[4] A. Corma, M. Renz, Angew. Chem. Int. Ed., 46 (2007) 298.
[5] K. T. Venkateswara Rao, P. S. N. Rao, P. S. Sai Prasad, N. Lingaiah, Catal. Commun., 10 (2009) 1394.
[6] U. Filek, D. Mucha, M. Hunger, B. Sulikowski, Catal. Commun., 30 (2013) 19.