Highly selective allylation from allyl alcohol using supported molybdenum oxide on titania catalyst

Yoshihiro Kon,[a, b]* **Akira Yada,**[a] **Tadahiro Fujitani,**[a] **Takuya Nakashima,**[a] **Yoichi Nakamura,**[a] **Toru Murayama,**[b, c] **Wataru Ueda**[b, d]*

[a] *Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, 305-8565, Japan*

**Corresponding author: Fax: +81-29-861-4441, E-mail: y-kon@aist.go.jp*

[b] *Institute of Catalysis, Hokkaido University, N21W10, Sapporo, 001-0021, Japan*

[c] *Research Center for Gold Chemistry, Tokyo Metropolitan University, 1-1-F203 Minami-Osawa, Hachioji, 192-0397, Japan*

[d] *Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, 3-27, Rokkakubashi, Yokohama, 221-8686, Japan*

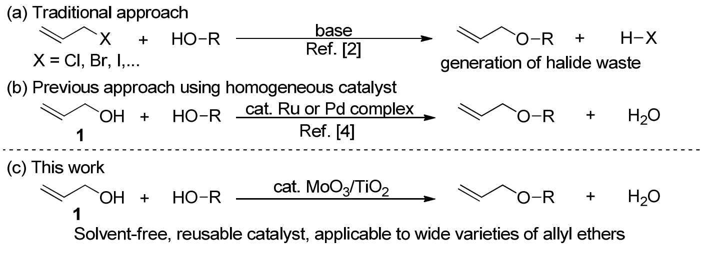
**Corresponding author: E-mail: uedaw@kanagawa-u.ac.jp*

Abstract: We demonstrate a versatile method to synthesize allyl ethers from allyl alcohol with various kinds of alcohols over 80% yields in the presence of reusable titania supported molybdenum oxide catalyst. The catalyst shows an excellent catalytic activity due to dispersed nature of molybdenum oxide on titania. According to a mechanistic study, the reaction seems to proceed through the formation of σ-allyl species from dehydration of the allyl alcohol, followed by a nucleophilic attack by another alcohol against the σ-allyl carbon to give allyl ethers.

Keywords: allyl ether, molybdenum oxide, allyl alcohol.

1. Introduction

Allyl ethers are known as a useful compounds for industry as well as laboratory and they can be utilized to a wide range of transformations such as alkylation and [3,3]-sigmatropic rearrangement.[1)] Conventionally, they have been produced from alcohol with allyl halide (Williamson synthesis).[2)] Recently, dehydration from allyl alcohol (**1**) with alcohols to produce allyl ethers should be selected as an ideal allyl ether synthesis without formation of waste halides.[3)] There are some high-yielding dehydrative allylation using homogeneous catalysts such as Pd and Ru complexes.[4)] Although they achieved useful dehydrative allylation, more sustainable method was required using a reusable heterogeneous catalyst with maintaining versatile applicability for various kinds of alcohols. To the best of our knowledge, there are no examples about effective synthetic methods producing various kinds of allyl ethers from **1** using solid catalyst (Scheme 1).[5)] Herein, we report heterogeneous molybdenum oxide catalyzed allylation from various kinds of alcohols with **1** under organic solvent-free conditions.



Scheme 1. Conventional method and this work.

2. Experimental

Preparation of catalyst: Catalysts of MoO_3 supported on TiO_2 (MoO_3/TiO_2) was prepared by an incipient-wetness impregnation method. For the preparation of 10 wt% MoO_3/TiO_2, 2.00 g of TiO_2 P25 was added to a diluted aqueous solution (1 mL) of $(NH_4)_6Mo_7O_{24}(H_2O)_4$ (245.3 mg, 0.2 mmol). After one hour, the impregnated catalysts were dried at 110 °C for 24 h and then calcined at 500 °C for 3 h. Catalytic reaction: A pressure-resistant glass tube equipped with a magnetic stirring bar was loaded with 10 wt% MoO_3/TiO_2 (100 mg) as catalyst, **1** (230 mg, 4.0 mmol), and 1-octanol (**2**) (133 mg, 1.0 mmol). The vessel was tightly sealed by a screw cap and the mixture was stirred (500 rpm) in an oil bath. Products were detected by GC analysis. The catalysts and catalytic reactions were analyzed using XRD, XRF, XPS, HAADF-STEM, NH_3-TPD.

3. Results and discussion

Conversion of **1** and **2** to give allyl octyl ether (**3**) was employed to check the catalytic activity of various metal oxides as shown in Figure 1. The reaction was optimized at the 140 °C outside temperature (inside temperature is 103 °C) for 3 h under the air atmosphere. The yields depended on the amount of loaded MoO_3, in the case of 1, 5, 10 and 20% of MoO_3 on titania, **3** was given in 4, 78, 84 and 79% yields, respectively. The reaction using WO_3 and ReO_3 instead of MoO_3 showed **3** in low yields. The use of SiO_2, Al_2O_3, ZrO_2, Nb_2O_5, and MgO instead of TiO_2 also showed low reactivity (Figure 1). Strong solid acid such as polymer bound *p*-toluenesulfonic acid and Nafion NR50 showed high conversion of **2**, but low selectivity to produce **3** in only 21% yield.

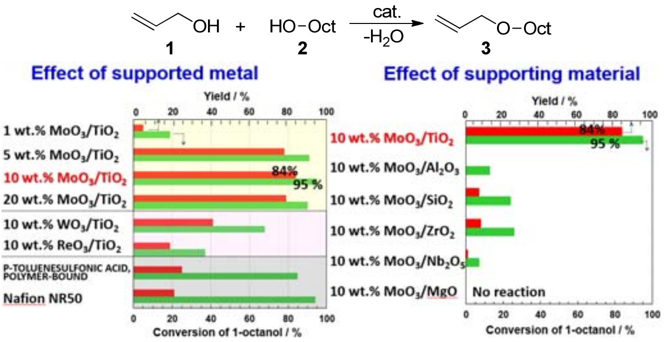


Figure 1. Allylation of **1** and **2** using various catalysts.

The catalytic reaction was suggested to carry out on the solid catalyst since the reaction was terminated when the catalyst was removed by hot filtration during the reaction. The spent catalyst was easily recovered by centrifugation, washed with MeCN and calcined at 500 °C for 3 h. No decrease of reactivity was observed at least five times of reuse for the reaction. MoO_3 dispersed nature on TiO_2 was observed by high-angle annular dark field scanning-mode transmission electron microscopy (HAADF-STEM) image and the data of STEM-EDS mapping of the spent catalyst after the reaction. X-ray photoelectron spectroscopy (XPS) showed the clear reductive change of Mo by measuring the Mo 3d profiles of the spent catalyst. The key step of the reaction seems to be the formation of σ-allyl species from dehydration of the allyl alcohol because the reaction of 2 with 1-propanol instead of 1 under optimized conditions did not form the estimated ether and bulky (3-methyl)-2-buten-1-ol did not give the corresponding ether, neither. The developed catalytic reaction was applicable to the allylation of various kinds of alcohols to give the corresponding ethers (Figure 2).

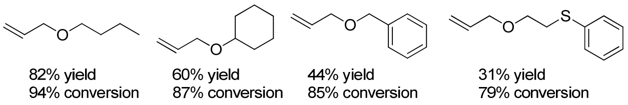


Figure 2. Allylation of various alcohols.

4. Conclusions

MoO_3/TiO_2 catalyst has been shown to facilitate the allylation of various kinds of alcohols to give the corresponding ethers in high yields. The reaction follows the sustainable manner due to production of water as only by-product. This is the first example to supply a useful method applicable to fine chemicals *via* σ-allyl coordinated Mo intermediate.

References

1. M. B. Smith, J. March, in *March's Advanced Organic Chemistry*, 6th ed., Wiley-Interscience, New York, **2007**, p. 641 (alkylation), 1668-1673 (rearrangement).
2. A. W. Williamson, *J. Chem. Soc.* **1852**, *4*, 229.
3. Dehydrative allylation is reported from 1920's using various kinds of acids as reagents, but the yields of allyl ethers are not so high, as examples, see; A. Mailhe, F. de Godon, *Bull. Soc. Chim. Fr*. **1920**, *4*, 328.
4. a) T. Satoh, M. Ikeda, M. Miura, M. Nomura, *J. Org. Chem*. **1997**, *62*, 4877; b) H. Saburi, S. Tanaka, M. Kitamura, *Angew. Chem. Int. Ed*. **2005**, *44*, 1730; *Angew. Chem*. **2005**, *117*, 1758.
5. a) K. T. Venkateswara Rao, P. S. N. Rao, P. S. Sai Prasad, N. Lingaiah, *Catal. Commun*. **2009**, 10, 1394; b) K. V. Katkar, S. D. Veer, K. G. Akamanchi, *Synth. Commun*. **2016**, 46, 1893; c) titanium cation exchanged montmorillonite catalyzed formation of unsymmetrical ethers from two kinds of alcohols was reported, see: T. Mitsudome, T. Matsuno, S. Sueoka, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Green Chem*. **2012**, 14, 610.