High-density immobilization of molybdenum complex on BPy-PMO and its catalysis for epoxidation of olefins

Yoshifumi Maegawa,[a] Satoshi Ishikawa,[b] Minoru Waki,[a] Shinji Inagaki[a],*
[a] *Toyota Central R&D Labs., Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan*
[b] *Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama, 221-8686, Japan*
**Corresponding author: fax +81-561-63-6507, E-mail address inagaki@mosk.tytlabs.co.jp*

Abstract: High-density immobilization of metal complex catalysts on the solid support is important for applications to flow-through reaction systems. Here, we succeeded in immobilization of MoO_2Cl_2 complex on a silanol-free bipyridine-periodic mesoporous organosilica (**BPy-PMO-TMS**) at high density without a significant loss of activity. The obtained **Mo-BPy-PMO-TMS** exhibited efficient catalysis for epoxidation of cyclooctene with *tert*-butylhydroperoxide. The catalytic activity was never dropped even at the high density of MoO_2Cl_2 complex up to 0.62 mmol Mo/g in catalyst. In contrast, a conventional solid support showed significant drop of activity with increase in the loading amount of MoO_2Cl_2 complex.

Keywords: Periodic mesoporous organosilica, Solid chelating ligand, Epoxidation.

1. Introduction

For efficient flow-through reaction, high-density immobilization of metal complex catalysts on a solid support is desirable because the contact time for column reactor is short. However, conventional solid supports have a limitation of high-density loading of metal complexes due to the poor ligand ability and the ununiform surface structure causing the deactivation of the immobilized metal complex catalysts. We recently reported a bipyridine-bridged periodic mesoporous organosilica (**BPy-PMO**), which has an ordered mesopores (3.8 nm) and extremely high density of BPy ligands on the pore surface (3.18 mmol BPy/g in the material) [1]. Unlike the conventional solid supports, BPy-PMO can immobilize a large amount of metal complex on the pore surface without a loss of the catalytic activity because of the well-defined pore surface structure and large pore size allowing the smooth diffusion of reactant and product molecules. Here, we report the high-density immobilization of MoO_2Cl_2 complex on the pore surface of silanol-free BPy-PMO (**BPy-PMO-TMS**) and its catalysis for epoxidation of cyclooctene with *tert*-butylhydroperoxide (TBHP) (Figure 1). The relation between catalytic activity and loading amount of Mo on the support was investigated for **BPy-PMO-TMS** and compared to that of a polystyrene-supported bipyridine (**BPy-Polymer**) as a conventional solid support.

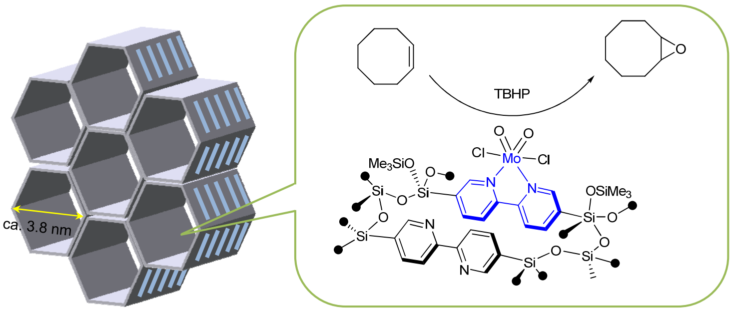

Figure 1. Epoxydation of cyclooctene with *tert*-butylhydroperoxide (TBHP) catalyzed by Mo-BPy-PMO-TMS catalyst.

2. Experimental

The coordination ability of Mo complex on **BPy-PMO-TMS** and **BPy-Polymer** was investigated by reacting **BPy-PMO-TMS** or **BPy-Polymer** with different amounts of MoO_2Cl_2 in acetonitrile. The loading amount of Mo in **Mo-BPy-PMO-TMS** and **Mo-BPy-Polymer** was measured by ICP analysis (Figure 2a). The obtained Mo catalysts were characterized by physicochemical techniques such as FT-IR and Raman spectroscopies, powder X-ray diffraction, nitrogen adsorption/desorption isotherm measurements, and X-ray absorption fine structure (XAFS) analysis. **Mo-BPy-PMO-TMS** (0.14 ~ 0.62 mmol Mo/g) and **Mo-BPy-**

Polymer (0.09 ~ 0.23 mmol Mo/g) were evaluated for epoxidation of cyclooctene with TBHP in decane/toluene at 75 °C for 8 h.

3. Results and discussion

The loading amount of Mo complex on **BPy-PMO-TMS** could be controlled by varying the concentration of MoO_2Cl_2 in acetonitrile (Figure 2b). The maximum loading amount of Mo in **Mo-BPy-PMO-TMS** was 0.72 mmol Mo/g. This means that the 37% of the surface bipyridine ligands in the **BPy-PMO-TMS** were coordinated with MoO_2Cl_2 (Figure 2c) However, **Mo-BPy-Polymer**, which has greatest bipyridine loading amount (~2.0 mmol BPy/g) among commercially available solid supports, showed low coordination ability (Figure 2b). The maximum loading amount of Mo was only 0.23 mmol Mo/g.

Mo-BPy-PMO-TMS and **Mo-BPy-Polymer** showed catalytic activity for epoxidation of cyclooctene to give 1,2-epoxycyclooctane at 75 °C. The turnover frequency (TOF) per Mo of **Mo-BPy-PMO-TMS** (0.14 mmol Mo/g) was almost comparable to that of **Mo-BPy-Polymer** (0.09 mmol Mo/g) at low loading amount of Mo. However, TOF of **Mo-BPy-PMO-TMS** was never dropped even at the high density of Mo complex up to 0.62 mmol Mo/g while **Mo-BPy-Polymer** showed significant drop of activity with increase in the loading amount of Mo (Figure 2d). This is attributed that the MoO_2Cl_2 complexes on BPy-PMO-TMS are well-isolated on the bipyridine layers sandwiched between two TMS layers even at high density (Figure 2c). These results indicate that BPy-PMO-TMS is a unique chelating support that can accept a high density of MoO_2Cl_2-bipyridine complex on the pore surface without a loss of activity.

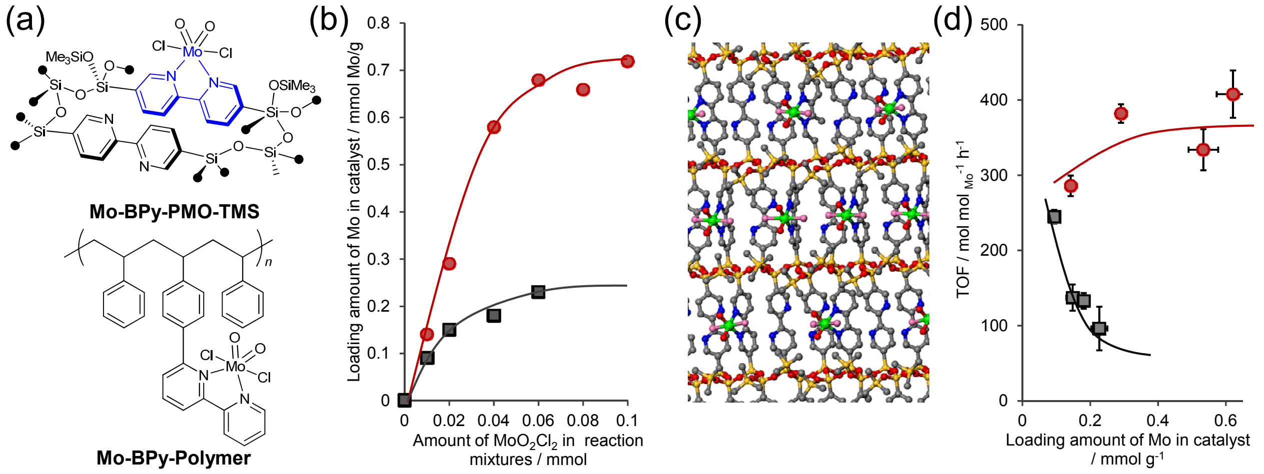

Figure 2. (a) Chemical structure of **Mo-BPy-PMO-TMS** and **Mo-BPy-Polymer**. (b) Coordination ability of MoO_2Cl_2 on **Mo-BPy-PMO-TMS** (●) and **Mo-BPy-Polymer** (■). (c) CG image for pore surface of **Mo-BPy-PMO-TMS** (0.62 mmol Mo/g). Approximately 35% of bipyridine ligands on the pore surface were coordinated with MoO_2Cl_2. Mo: green, Cl: pink, O: red, Si: orange, C: gray, N: blue, H: omitted. (d) TOF value per Mo in **Mo-BPy-PMO-TMS** (●) and **Mo-BPy-Polymer** (■).

4. Conclusion

The Mo complexes could be formed on up to 37% of the BPy ligands exposed on the pore surface without a loss of catalytic activity. The high loading and relatively small loss in catalytic activity indicate that this supported catalyst has the potential for application to a flow-through reactor that requires a solid catalyst containing a large number of active centers and a small loss of activity.

References

1. M. Waki, Y. Maegawa, K. Hara, Y. Goto, S. Shirai, Y. Yamada, N. Mizoshita, T. Tani, W. J. Chun, S. Muratsugu, M. Tada, A. Fukuoka, S. Inagaki, J. Am. Chem. Soc. 136 (2014) 4003.