

Activities of Low Leaching Metal-Organic Framework Catalysts MIL-47-X₂ (X = -CH₃, -CF₃, -F, -Br, -CO₂H) in Cyclohexene Oxidation

Shyam Biswas and Pascal Van Der Voort; Department of Inorganic and Physical Chemistry, COMOC: Center for Ordered Materials, Organometallics and Catalysis Ghent University

Metal-organic frameworks (MOFs) have attracted tremendous interest recently due to their applications in gas storage/separation and catalysis. However, catalytic investigations using MOFs as catalysts are still in their infancy and the catalytic reaction mechanisms in MOFs are still poorly understood.[1] Using TBHP/decane as the oxidant, we have recently demonstrated the remarkable catalytic activity of the coordinatively saturated vanadium-based MOF MIL-47 (Fig. 1a) in cyclohexene oxidation with low leaching.[2] The mono-substituted MIL-47-X catalysts (X = -F, -Cl, -Br, -CH₃, -NH₂ and -OH) exhibited moderate yield of cyclohexene oxide with severe leaching of vanadium.[3] Herein, we illustrate that the leaching of vanadium in cyclohexene oxidation can be significantly lowered when bi-substituted MIL-47-X₂ (X = -CH₃, -CF₃, -F, -Br, -CO₂H) catalysts are used.

The compounds have been synthesized in a rapid microwave-assisted hydrothermal route. The as-synthesized solids were calcined under dynamic vacuum for overnight to remove the free linkers from the pores to achieve considerable microporosity. The catalysts have been further characterized by DRIFT, elemental analysis and X-ray powder diffractometry. Employing TBHP/decane as the oxidant, catalytic tests display moderate yield (Fig. 1b) of the cyclohexene oxide for all the catalysts with good regenerability.

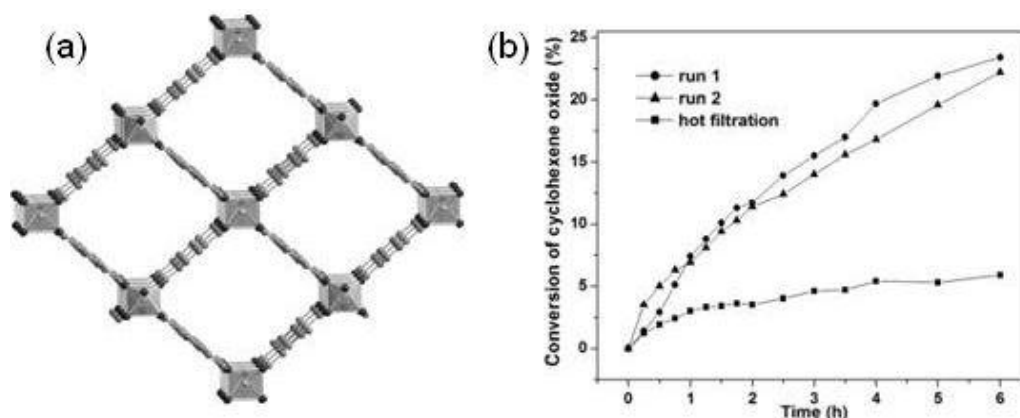


Fig. 1. (a) Structure of MIL-47. (b) Time conversion plot of cyclohexene oxide for MIL-47-(CH₃)₂.

[1] Corma, A., Garcia, H. and Llabres i Xamena, F. H., *Chem. Rev.* 110 (2010) 4606.

[2] Leus, K., Vandichel, M., Liu, Y.-Y., Muylaert, I., Musschoot, J., Pyl, S., Vrielinck, H., Callens, F., Marin, G. B., Detavernier, C., Wiper, P. V., Khimyak, Y. Z., Waroquier, M., Van Speybroeck, V. and Van Der Voort, P., *J. Catal.* (2012), 285, 196.

[3] Vandichel, M., Biswas, S., Leus, K., Paier, J., Sauer, J., Van Der Voort, P., Waroquier, M. and Van Speybroeck, V., manuscript in preparation.