

Comparing the Sorption and Catalytic Performances of Porous Isostructural V-MIL-47-X (X = -CH₃, -Cl, -Br, -OH) Metal-Organic Frameworks

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Metal-organic frameworks have attracted a great deal of interest 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] Recently, we have demonstrated[2] the remarkable catalytic performance of the coordinatively saturated V-based MIL-47 in cyclohexene epoxidation using TBHP/decane as the oxidant. In order to verify the effect of functionalization on the catalytic properties of parent MIL-47, we have now introduced four different functionalities (X = -CH₃, -Cl, -Br and -OH) into the terephthalate linker.

The compounds have been synthesized in a rapid (30 min) microwave irradiation route under hydrothermal conditions (150-170 °C). Thermogravimetric analyses show high thermal stability (250-300 °C). The as-synthesized solids were calcined under dynamic vacuum for overnight to remove the free linkers from the pores and achieve significant microporosity (type-I isotherms, Fig. 1a; S_{BET} : 305-657 m² g⁻¹). The catalysts have been further characterized by DRIFT, elemental analysis and X-ray powder diffractometry. Employing TBHP/decane as the oxidant, catalytic tests exhibit moderate yields (35-39%, Fig. 1b) of the cyclohexene epoxide for all the catalysts with good regenerability.

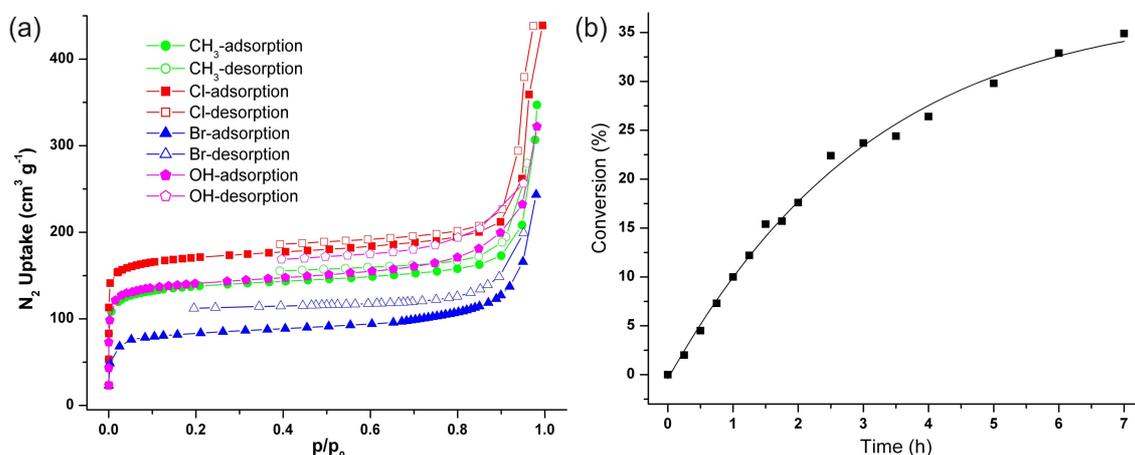


Fig. 1. (a) N₂ sorption analysis, and (b) time conversion plot of cyclohexene oxide for MIL-47-CH₃.

- [1] Corma, A., Garcia, H. and Llabres i Xamena, F. H., *Chem. Rev.* B. 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.* (2011), doi:10.1016/j.jcat.2011.09.014.