

Pt/MCM-41 Catalysts for the Selective Oxidation of 2-Propanol by Molecular Oxygen in Supercritical Carbon Dioxide

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The selective oxidation of alcohols to aldehydes or ketones is an important transformation for the production of fine chemicals. Supported noble metal catalysts have long been known to catalyze this conversion with oxygen or air as the oxidant at mild conditions. But due to rapid deactivation, these catalysts have often not been further considered for industrial applications. Recently, the deactivation of noble metal catalysts was shown to be significantly reduced when the oxidation is carried out in supercritical carbon dioxide (scCO₂). While in most of the studies on selective alcohol oxidations in scCO₂ so far noble metals on supports with less defined (macro)pores were used, we report here on the application of Pt supported on ordered mesoporous silica, i.e., MCM-41. The results with these catalysts are compared to those obtained with a macroporous silica gel at comparable platinum loadings and dispersions.

The catalysts were prepared by incipient wetness impregnation of either siliceous MCM-41 or silica gel (SiO₂) with [Pt(NH₃)₄]Cl₂. Different metal dispersions were obtained by treatment of the impregnated supports at various temperatures in air followed by reduction in hydrogen at 280 °C. In addition, platinum was introduced by adding [Pt(NH₃)₄]Cl₂ to a synthesis gel of the MCM-41-type material. Generally, higher Pt dispersions as assessed by hydrogen chemisorption were found on MCM-41 with respect to SiO₂ at constant Pt loading and otherwise the same preparation conditions.

In the conversion of 2-propanol with oxygen to acetone and water in scCO₂ (100 °C, 140 bar, batch reactor), the mass of Pt introduced with the catalyst was kept constant. Consequently, higher reaction rates and product yields were found for catalysts with higher Pt dispersions. However, considerably higher reactions rates resulted for the MCM-41-supported catalysts, even if compared to the silica gel based catalysts at the same Pt loading and dispersion. Moreover, the activity loss of the Pt/MCM-41 upon re-use was significantly less than that of a commercial carbon supported Pt catalyst. These results clearly demonstrate the superior performance of the catalysts with the ordered mesoporous MCM-41 as compared to those with macroporous silica gel as the support. They may be explained in terms of improved accessibility and/or stabilization of the metal particles within the pores of the mesoporous host. Interestingly, the results from the conversion in scCO₂ were different from those in liquid water where the initial reaction rate depends on the available Pt surface only.