

Abstract

Hydrogenation reactions belong to the most important reactions in the chemical industry. They are needed for crude oil processing, production of pharmaceutical, polymers, chemical specialties, etc. Supported noble metal catalysts are commonly used industrial catalysts due to their high activity and selectivity. However, the high cost of production and recovery of noble metal catalysts is one of the disadvantages of their use. The application of transition metal catalysts containing Cu, Fe or Zn presents a more environmentally friendly alternative to currently used catalysts. In this work, we studied the catalytic activity of metal@zeolite composite catalysts containing CuFe and CuZn bimetallic nanoparticles, prepared by reductive demetallation in hydrogenation of $-\text{NO}_2$, $-\text{C}\equiv\text{C}-$, $-\text{C}=\text{C}-$ and $-\text{C}=\text{O}$ groups. Reductive demetallation is a novel method for the synthesis of bimetallic nanoparticles encapsulated inside zeolite pores.

The catalytic activity of the metal@zeolite composites prepared by reductive demetallation was compared with analogues synthesised by impregnation and ion exchange in the hydrogenation of *p*-nitrotoluene, 3-ethynylanisole and cinnamaldehyde. Metal@zeolite catalysts synthesised by reductive demetallation were active in the hydrogenation of all the cited groups: $-\text{NO}_2$, $-\text{C}\equiv\text{C}-$, $-\text{C}=\text{C}-$ and $-\text{C}=\text{O}$. In the hydrogenation of *p*-nitrotoluene, the highest conversion was provided by CuZn@VET (56 % after 6 h). Reductively demetallated catalysts also provided higher selectivity than Pd based reference catalysts in the hydrogenation of $-\text{C}\equiv\text{C}-$ into $-\text{C}=\text{C}-$ using 3-ethynylanisole as the substrate. CuZn@MFI prepared by reductive demetallation gave the highest conversion of 3-ethynylanisole (30 % after 3) and its selectivity toward 3-vinylanisole containing $-\text{C}=\text{C}-$ was 93 % at 15% conversion. In the hydrogenation of cinnamaldehyde, the metal@zeolite composites provided selectivity advantages in a system of competing hydrogenations (containing $-\text{C}=\text{C}-$ and $-\text{C}=\text{O}$) as well. Reductively demetallated CuFe@MFI provided the highest conversion of cinnamaldehyde (98 % after 70 h) and slightly favoured hydrogenation the carbonyl group. On the other hand, Pd/Al₂O₃SiO₂ reference preferred to hydrogenate the $-\text{C}=\text{C}-$.