Chemoselective hydrogenation of nitro compounds over Ir-based hybrid clustering catalysts

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Chemoselective hydrogenation of nitroaromatics to form anilines especially in the presence of other reducible groups such as C=C is one of the important reactions in the production of fine chemicals. Since the catalytic activities of heterogeneous nanoparticle catalysts varies with the adjacent oxide species, forming a high density of metal/oxide interfaces is important to improve the selectivity.[1,2] We had previously reported a catalyst preparation method, namely hybrid clustering, for the efficient formation of metal/oxide interfacial active sites.[3] In this study, supported Ir-based catalysts were prepared by using hybrid clusters as precursors. The effect of the preparation method on the activity for 4-nitrostyrene hydrogenation is discussed in comparison with typical Ir based catalysts.

The hybrid clustering catalyst, Ir_4Mo_4/Al_2O_3, was prepared by using a hybrid cluster, $[(IrCp^*)_4Mo_4O_{16}]$ (Cp^* = η^5-C_5Me_5), as a precursor.[4] In the 4-nitrostyrene hydrogenation, Ir_4Mo_4/Al_2O_3 selectively reduced the nitro group to produce 4-aminostyrene (Figure 1a). In contrast, the coimpregnated catalyst, $Ir\text{-}Mo/Al_2O_3$, prepared from H_2IrCl_6 and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, reduced both nitro and vinyl groups nonselectively (Figure 1b). This suggests that the formation of the Ir/MoO_x interfaces is essential for the selective hydrogenation of nitro groups and that hybrid clustering is an efficient way to form a high density of such interfaces. The local structures and the formation mechanism of the Ir/MoO_x interfaces will be discussed based on X-ray absorption spectroscopy.

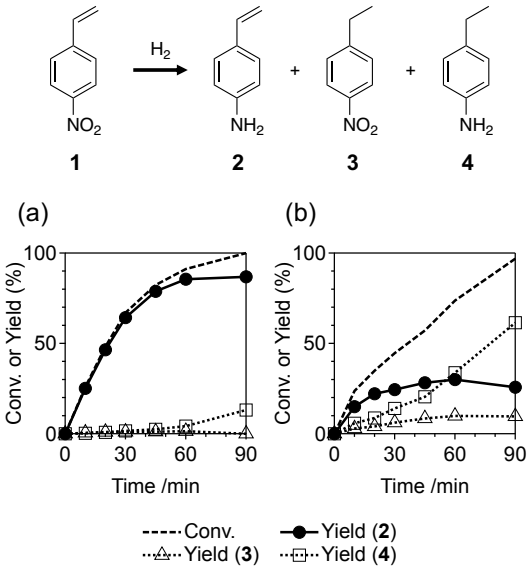

Figure 1. Time course of hydrogenation of 4-nitrostyrene (**1**) over (a) Ir_4Mo_4/Al_2O_3 and (b) $Ir\text{-}Mo/Al_2O_3$. Reaction conditions: **1** (0.1 mmol), H_2 (0.3 MPa), toluene (1 mL), catalyst (10 mg, Ir: 0.52 mol%), 303 K.

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