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Microscopic Characterization of Pt-ZnO catalysts with Cl additive

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Selective catalytic hydrogenation of α,β-unsaturated aldehyde using a heterogeneous catalytic system is of great interest since it could replace the metal hydrides and reduce the waste production. The challenge is the selective hydrogenation of carbonyl bonds without affecting the olefinic bonds, which is thermodynamically more favored, unaffected. Monometallic catalysts supported on non-reducible support usually lead to formation of saturated aldehyde. In order to achieve high selectivity towards unsaturated alcohol, promoter, bimetallic catalysts or reducible supports must be used to modify the catalysts [1, 2]. Recently, Pt particles supported on ZnO were found to exhibit a high performance in selective hydrogenation of crotonaldehyde to crotyl alcohol [3, 4]. By using a metallic precursor containing chlorine, the selectivity of the catalysts can be further improved. This is attributed to the residual chloride [3-5]. In this abstract, we report the structural investigation of Pt-ZnO with Cl additive catalyst by transmission electron microscopy (TEM).

Samples containing 1% and 5% Pt supported on ZnO are prepared by impregnation of commercial ZnO by H_2PtCl_6, followed by calcination under air (760 Torr) at 673 K and reduction under H_2 at 673 K for 4 hours. Both catalysts show high selectivity (80-90%) towards crotyl alcohol. The powder samples were dispersed in ethanol and placed onto copper grids covered with holey carbon film for TEM observation in a Philips CM200 FEG microscope.

The two samples show similar morphology and microstructures. The selected area diffraction pattern (Fig. 1) indicates the samples are well crystallized. Most of the diffraction rings can be attributed to hexagonal ZnO (zincite). In addition, some weak intensities (indicated by arrows in Fig. 1) corresponding to the 111 and 200 diffractions of tetragonal PtZn are present. Some HRTEM images from the ZnO support show stacking faults along its [001] direction. Their influence on the catalytic activity is not clear. The HRTEM images from the particles indicate the existence of both Pt and PtZn alloy, as shown in Figs. 2a and 2b respectively. The lattice fringes in Fig. 2a correspond to a interplanar spacing of 1.96 Å which can be attributed to Pt 200 reflection. In Fig. 2b, the particle can be determined as PtZn on its [101] zone axis.

To detect the chlorine distribution in the samples, energy dispersive X-ray spectroscopy (EDX) is used. Electron beam is converged into small size to probe the local concentration of chlorine. Chlorine is not evenly distributed in the sample. The Cl-rich region is usually accompanied with amorphous or multi-crystalline morphology of the support, as seen in Fig. 3. The typical Cl concentration in such region measured by EDX is below 1 atomic%. In addition, in the HRTEM image shown in Fig. 3, lattice fringes with interplanar spacing of about 3.6 Å possibly arising from metal chloride.

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In summary, we confirm the alloy formation in the reduced Pt-ZnO catalysts. It may increase the selectivity of unsaturated alcohol by introducing changes in electronic structure, favoring the adsorption of carbonyl bonds. Extra chlorine may play an important role as a promoter by changing morphology of the support and the formation of metal chloride. The detailed mechanism needs further investigations.

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6. The work is performed in the framework of the European Laboratory for Catalysis and Surface Science (ELCASS).

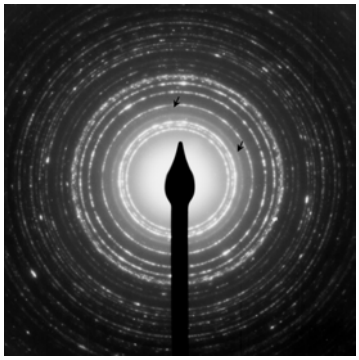

Fig. 1 Representative diffraction pattern from Pt-ZnO catalysts.

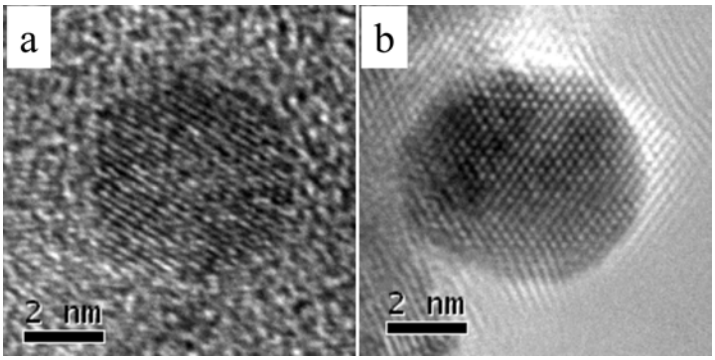

Fig. 2 HRTEM images of (a) Pt and (b) PtZn particles

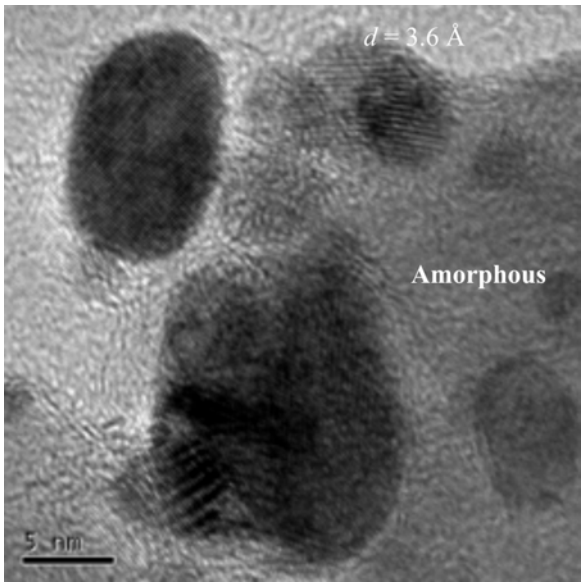

Fig. 3 HRTEM image of Cl-rich region for the 1% Pt-ZnO catalyst.

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