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High Selective Hydrogenation of Acetophenone Catalyzed by Alumina Supported Platinum Nanoclusters

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Abstract: A new preparation and reduction method of γ-Al_2O_3 supported and PVP stabilized platinum nanoclusters was studied. The catalyst exhibited very high activity and selectivity for acetophenone hydrogenation in isopropanol-KOH solution at 25~60°C and P_{H2}=1~5 MPa.

Keywords: Platinum nanoclusters, acetophenone, hydrogenation.

Hydrogenation of acetophenone in homogeneous catalysis had a lot of reports[1, 2], but its application was limited owing to the difficulty of catalyst separation from products. Therefore the study of immobilized catalyst was an interesting project[3, 4]. The catalyst of γ-Al_2O_3 supported platinum nanoclusters had high activity in hydrogenation of ethyl pyruvate[5], when it was reduced by hydrogen at high temperature. However, its catalytic activity was very low in the hydrogenation of acetophenone[6]. We studied a new preparation and reduction method of alumina supported and PVP (polyvinylpyrrolidone) stabilized platinum nanoclusters under the mild conditions. The catalyst exhibited very high activity and selectivity of 100% for DL-1-phenylethanol in acetophenone hydrogenation.

Platinum nanoclusters were prepared by $H_2PtCl_6 \cdot nH_2O$ (0.288 mmol) and PVP (MW=10000, 2.900 mmol) in a mixed solvent (80 mL) of ethanol, isopropanol and distilled water (ethanol : isopropanol : water = 2 : 5 : 1) in a flask. The solution was refluxed for 0.5 h to give a dark brown sol, and then it was supported on γ -Al_2O_3 (40-100 mesh). The catalyst was dried under vacuum and its platinum content was 3%. The hydrogenation of acetophenone was carried out in an autoclave with a glass liner and magnetic stirrer. After the catalyst (10 mg), acetophenone (1.75 mL) and solvent (3 mL) were added, the autoclave was flushed with hydrogen for several times and then hydrogen was introduced to desired pressure. The products were determined on GC960 with FID and capillary column β-DEX^{TM} 120 (30 m × 0.25 mm) at 120ºC. The components were identified by authentic samples on GC and IR and the product 1-phenylethanol was racemic.

The effect of solvent on the reaction was studied at 60ºC, P_{H2}=5 Mpa. The results

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showed that ethanol and isopropanol were excellent solvent in acetophenone hydrogenation, the conversions were 76~77% at substrate: Pt=575:1 (mole ratio) for 6h. If KOH was added into ethanol or isopropanol solution (KOH concentration=0.04 mol/L), the conversions could reach 95% and 100%, respectively. When the molar ratio of substrate: Pt: KOH increased from 10000:1:26 to 10000:1:78, the conversion rose from 13.6% to 99.6% for 3h. If the ratio increased further to 10000:1:104, the conversion decreased to 95.8%.

The catalyst could also exhibited high activity at 25ºC, P_{H2}=5 Mpa, when the mole ratio of substrate: Pt: KOH = 575: 1: 13, the conversions of acetophenone were 72% (1h), 97% (2h) and 100% (3h). If hydrogen pressure reduced to 1 Mpa and 3 Mpa, the conversions at 60ºC for 1h were 68% and 99%, respectively. The activity and selectivity of the catalyst did not change after 5 recycles. This showed that the stability of the catalyst was excellent.

In order to investigate hydrogen source in the hydrogenation product DL-1-phenylethanol, we designed two experiments. One was carried out at 60ºC, P_{H2} or P_{N2}=0.1 Mpa and KOH concentration=0.04 mol/L, the conversions of acetophenone were 1.7% in nitrogen and 68.2% in hydrogen, respectively. Another was carried out in ethanol or isopropanol solution at 60ºC, P_{H2}=5 Mpa and KOH concentration =0.04 mol/L, the conversions were 94.7% and 99.9%, respectively. The results indicated clearly that hydrogen in the product DL-1-phenylethanol came from activated hydrogen molecule rather than hydrogen transfer reagent isopropanol. The fact that acetone was not found in the product also supported the above mentioned suggestion.

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