Heterogeneous Enantioselective Hydrogenation of Ethyl Pyruvate on Chirally Modified Nanocatalyst 5.0 wt.% Pt/γ-Al_2O_3

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Introduction

Asymmetric synthesis has been focused on since two decades ago, due to its importance in synthesizing the flavors, fragrances, pharmaceuticals, and so on. Enantioselective hydrogenation of α-ketoesters and related compounds on a solid surface is of great scientific interests after Orito first reported in 1978 the enantioselective hydrogenation of α-ketoesters catalyzed by a cinchona alkaloid modified supported platinum catalyst [1].

Most of the researches were carried out on a commercial 5.0 wt.% Pt/γ-Al_2O_3 catalyst (in the references, they were named as Engelhard 4759 or JMC 5 R 94) [2] or on a commercial 6.3 wt.% Pt/silica catalyst (EUROPT-1) [3]. However, there are so many researchers who are devoting themselves to exploring new types of catalysts such as platinum clusters [4] or others [5-7]. In our previous researches [8-10], we are looking for suitable preparation methods by which we can freely design or control the size distribution and the average size of the catalyst. To avoid the wash out of Pt particles from the support surface when the catalyst precursors are being reduced in aqueous solution, we have tried several methods. Finally we find a novel impregnation method to prepare 5.0 wt. % Pt/γ-Al_2O_3 with nanoscale particle size. Here we report the preparation of Pt/γ-Al_2O_3 catalysts by different impregnation methods and their catalytic performance in enantioselective hydrogenation of ethyl pyruvate to obtain (R)-(+)-ethyl lactate.

Experimental

γ-Al_2O_3 (Belgium, 210 m^2/g) was calcined at 500 ^{o}C for 2 h before use.Hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) was purchased from Shenyang Institute of Mineral and Smelting.5.0 wt. % Pt/γ-Al_2O_3 was prepared by impregnating the support γ-Al_2O_3 (2.109 g) with H_2PtCl_6 aqueous solution (30ml, 3.7 mg Pt/ml) and stirring for 4 h, followed by slowly drying at 120 ^{o}C for 16 h. Then the catalyst precursor was calcined at different temperature for 2 h. At last the precursors were reduced in Na(HCOO) solution at 90^{o}C.

Results and Discussion

Fig. 1 gives the TEM photograph of $7^{\#}$ catalyst, which was calcined at 500^{o}C for 2 h. The Pt particle size is about 2-3 nm, which agrees well with the results of CO chemisorptions (Table 1). Pt/γ-Al_2O_3 catalyst is found to be very enantioselective in asymmetric hydrogenation of ethyl pyruvate. The preparation method combines the conventional impregnation method with calcination of catalyst precursor at an optimal temperature before reduction. It is very necessary for the 5.0% wt. % $Pt/\gamma\text{-}Al_2O_3$ catalyst precursors to be calcined at a higher temperature to obtain a suitable particle size because the strong interactions between the support and the catalyst precursor can be formed during the calcination process; on the other hand, too small particle size can't be helpful for the adsorption of chiral modifier through its quinoline ring in the enantioselective hydrogenation. The highest e.e. value of about 95% was obtained on the 5.0% wt. % $Pt/\gamma\text{-}Al_2O_3$ catalyst having an average particle size of 3.1 nm after calcined at 350 °C for 2 h before reduced in Na(HCOO) aqueous solution under the optimised reaction conditions (Table 1).

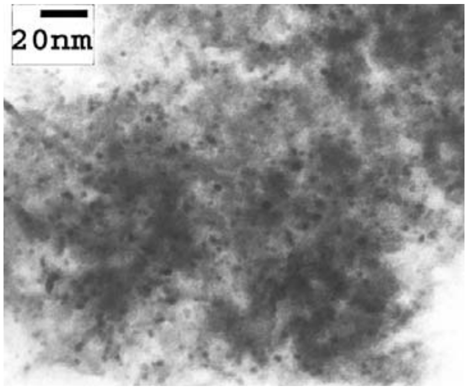

Fig. 1 TEM photographs of $7^{\#}$

Table 1 Results of enantioselective hydrogenation of ethyl pyruvate [a] and some relevant parameters

Entry	Preparation methods	Avg. particle size (nm) [b]	Dispersion (%) [b]	Conv. (%)	E.e. (%)
$3^{\#}$	Without calcinations, Na(HCOO)	6.1	18.53	99.0	90.5
$8^{\#}$	200 °C for 2h, Na(HCOO)	6.3	17.96	99.7	89.1
$2^{\#}$	350 °C for 2h, Na(HCOO)	3.1	36.84	99.3	91.1
				99.8	94.8[c]
$7^{\#}$	500 °C for 2h, Na(HCOO)	2.4	46.68	99.4	89.6
				99.8	91.8[c]

Reaction conditions are as follows: 0.500 g 5.0 wt.% $Pt/\gamma\text{-}Al_2O_3$, 0.100 g cinchonidine, 40 ml acetic acid, 5 ml ethyl pyruvate; (b) Determined by CO chemisorption; (c) 0.250 g 5.0 wt.% $Pt/\gamma\text{-}Al_2O_3$, 0.050 g cinchonidine, 20 ml acetic acid, 5 ml ethyl pyruvate.

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