

Some insights into the preparation of Pt/ γ -Al₂O₃ catalysts for the enantioselective hydrogenation of α -ketoesters

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Pt/ γ -Al₂O₃ catalysts were prepared by two different impregnation methods and characterized by XRD, TEM, and CO chemisorption. The Pt particle sizes ranged in 2.4–23.3 nm for these 5.0 wt% Pt/ γ -Al₂O₃ catalysts. The catalysts were also characterized by FT-IR spectroscopy using CO as a probe molecule before and after the chiral modification with cinchonidine. Two IR bands (2078 and 2060 cm⁻¹) due to CO linearly adsorbed on the Pt/ γ -Al₂O₃ catalyst, calcined at 500 °C before reduction in sodium formate solution were observed, whereas only one IR band at ~2070 cm⁻¹ was observed for other catalysts. A red shift of the IR band was observed after chiral modification of all the catalysts, except the one with the largest Pt particle size and lowest Pt dispersion. The catalytic performance of the cinchonidine-modified Pt/ γ -Al₂O₃ catalysts was tested for the enantioselective hydrogenations of ethyl pyruvate and ethyl 2-oxo-4-phenylbutyrate (EOPB). A 95% ee value was obtained for the ethyl pyruvate hydrogenation and about 83% ee was achieved for the enantioselective hydrogenation of EOPB under the optimized preparation and reaction conditions. It is deduced that the interaction of Pt with γ -Al₂O₃ is a crucial factor for obtaining high activity and that the adsorption abilities (adsorption of reactant, solvent and chiral modifier molecules) of the catalyst surface affect the catalytic performance significantly.

KEY WORDS: Pt/ γ -Al₂O₃; enantioselective hydrogenation; ethyl pyruvate; EOPB; FT-IR spectroscopy; CO adsorption; cinchonidine.

1. Introduction

Asymmetric catalysis has received great attention in the last decades because of its importance in synthesizing pharmaceuticals, flavors and fragrances [1]. Enantioselective hydrogenation of carbonyl compounds on solid surface is of particular importance because of its scientific significance and potential applications. Among various such reactions, the enantioselective hydrogenation of α -ketoesters catalyzed by supported platinum catalysts modified with cinchona alkaloids has been considered as one of the milestones of heterogeneous asymmetric catalysis [2], and extensive studies have been carried out on this system in the past decade or so [3–7].

Most of these studies were carried out on commercially available 5.0 wt% Pt/Al₂O₃ catalysts (e.g., E 4759 or JMC 5 R 94) [8] or on commercial 6.3 wt% Pt/SiO₂ catalysts (e.g., EUROPT-1) [9]. Under optimized reaction conditions, the best ee value achieved in the chiral hydrogenation of ethyl pyruvate catalyzed by Pt/ γ -Al₂O₃ catalysts (E 4759) was 97%. High ees and reaction rates can be obtained for the enantioselective hydrogenation of a variety of α -functionalized ketones using the commercial Pt/Al₂O₃ catalysts [7].

New types of catalysts such as platinum colloids [10] and Pt catalysts supported on other materials [11–13] have also been explored at around the same time.

Colloidal catalysts are of interest because the support effects can be eliminated, and there is a possibility to better control the morphology (size and shape) of metal particles compared to supported catalysts. However, colloids are not suitable catalysts for practical applications, although high ees have been reported [7]. A MCM-41 supported, cinchonidine-modified Pt catalyst afforded up to 64% ee in the enantioselective hydrogenation of ethyl pyruvate, but the reaction rate was low because of mass-transfer problems [11]. Moderate ees were obtained with Pt/HNaY [12] and Pt/clay catalysts [13].

In general, there is little doubt that for the supported Pt-cinchonidine catalysts the platinum dispersion has a strong influence on both activity and enantioselectivity for the ethyl pyruvate hydrogenation. High metal dispersions are detrimental for enantioselectivity [3,14]. Catalysts, with metal particle size < 2 nm, were reported to be less selective and showed lower turnover frequencies than those with larger particle sizes [3]. The enantioselectivity in the ethyl pyruvate hydrogenation increased with increasing platinum particle size [14].

The catalyst preparation and its effect on the morphology of Pt particles and reaction results have been extensively investigated in the past years. However, further understanding of the effects of catalyst preparation is still necessary. For this reason, our previous investigations [15–17] were focused on preparation methods aiming to control the size and distribution of Pt particles on γ -Al₂O₃. In this paper, we report the preparation, by two different impregnation methods,

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and the characterization of Pt/ γ -Al₂O₃ catalysts. The catalytic performance of the catalysts was studied in the enantioselective hydrogenations of ethyl pyruvate and ethyl-2-oxo-4-phenylbutyrate (EOPB) (Scheme 1). On the basis of the optimized catalyst preparation and reactions conditions, 95% ee was obtained for the enantioselective hydrogenation of ethyl pyruvate and about 83% ee was achieved for EOPB. This study shows that, to a great extent, the electronic properties and adsorption abilities (towards reactant, solvent and chiral modifier molecules) of the catalysts and the interactions of Pt with γ -Al₂O₃ affect the catalytic performance.

2. Experimental section

γ -Al₂O₃ (Belgium, 210 m²/g) was calcined at 500 °C for 2 h before use. Hydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆ · 6H₂O) and organic solvents were AR grade and used as received. Ethyl pyruvate was synthesized by the esterification of pyruvic acid with ethanol. Cinchonidine (Acros, minimum purity >98%) and EOPB (Aldrich, minimum purity >97%) were used as received.

2.1. Preparation of 5.0 wt% Pt/ γ -Al₂O₃ catalysts

Method I: γ -Al₂O₃ was impregnated with aqueous H₂PtCl₆ solution or with a mixture of water and isopropanol solution of H₂PtCl₆. After stirring for 4 h, instead of being dried or calcined at a high temperature, the mixture was directly reduced in a formaldehyde solution at 80 °C, keeping pH > 12 by the addition of aqueous sodium hydroxide (20 vol%). According to the amount of isopropanol added to the H₂PtCl₆ solution, Pt/ γ -Al₂O₃ catalysts prepared by this method were

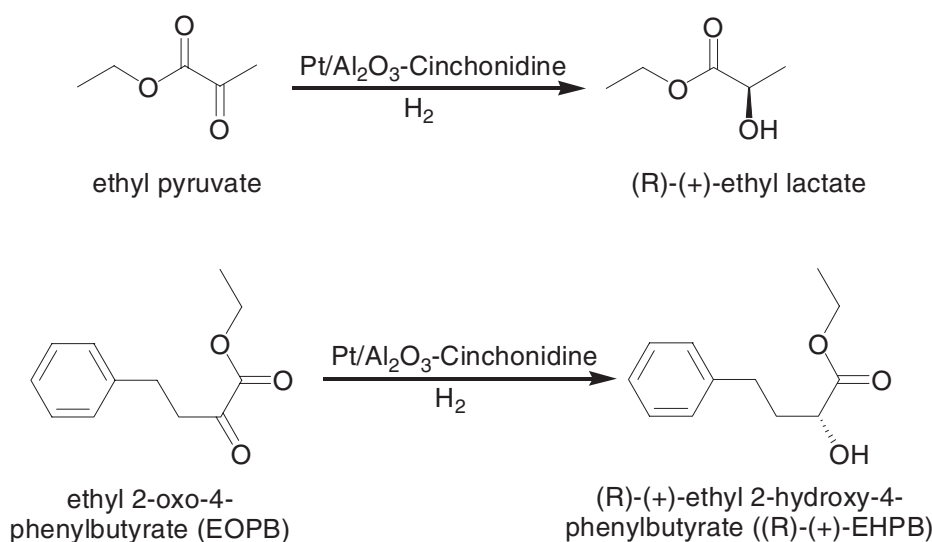
designated as catalysts M1-A, M1-B and M1-C (see table 1 for the specification).

Method II: In order to investigate the effects of Pt interaction with γ -Al₂O₃ on the catalytic performance, γ -Al₂O₃ was impregnated with aqueous H₂PtCl₆ solution and stirred for 4 h, followed by drying at 120 °C for 16 h. Then the catalyst precursor was calcined for 2 h at a chosen temperature. Finally, the precursor was reduced in a sodium formate solution at 90 °C. According to the calcination temperatures employed for the precursors, Pt/ γ -Al₂O₃ catalysts prepared by Method II were designated as catalysts M2-calcination temperature (see table 1 for the specification).

2.2. Characterization

Transmission electron microscope (TEM) images of the catalyst samples were taken on a JEM-2000EX electron microscope. X-ray diffraction (XRD) patterns were recorded by a Rigaku Rotaflex (Ru-200B) diffractometer (Cu K α , Rigaku Co.). The mean size of platinum particles and the degree of dispersion on γ -Al₂O₃ were determined by pulse titration of CO on a CHEMBET-3000 pulse chemisorption analyzer (Quanta Chrome Co.). The CO chemisorption of the samples was measured at 35 °C after the samples were pretreated in a hydrogen flow at 400 °C for 1 h. The degree of dispersion and the mean particle size (cubic model) were estimated from the measured CO uptake, assuming a cross-sectional area for a surface platinum atom of 8.0 × 10⁻²⁰ m² and a stoichiometric factor of one, using nominal platinum concentrations.

All infrared spectra were collected on a Fourier transform infrared spectrometer (Nicolet Nexus 470) with a resolution of 4 cm⁻¹ and 64 scans in the region of 4000–1000 cm⁻¹. The sample was pressed into a self-supporting wafer (ca. 15 mg/cm²) and put into a quartz



Scheme 1. Enantioselective hydrogenations of ethyl pyruvate and EOPB on cinchonidine-modified Pt/ γ -Al₂O₃ catalyst.

Table 1
Specifications of preparation procedures and relevant parameters of 5.0 wt% Pt/ γ -Al₂O₃ catalysts

Catalyst number	Preparation methods	Pt size (nm) ^a	Dispersion (%) ^a
M1-A	Method I (15 mL H ₂ O, without isopropanol)	3.9	29.2
M1-B	Method I (10 mL H ₂ O, 5 mL isopropanol)	5.5	20.5
M1-C	Method I (3 mL H ₂ O, 12 mL isopropanol)	23.3	4.9
M2-120	Method II (without calcination, Sodium formate)	6.1	18.5
M2-200	Method II (200 °C for 2 h, Sodium formate)	6.3	18.0
M2-350	Method II (350 °C for 2 h, Sodium formate)	3.1	36.8
M2-500	Method II (500 °C for 2 h, Sodium formate)	2.4	46.7

^aAverage Pt particles size and the degree of dispersion were determined by CO chemisorption.

IR cell with CaF₂ windows. It was then pretreated in a hydrogen flow at 400 °C for 2 h. Two different IR experiments were carried out as follows: (1) the as-pretreated sample was evacuated at room temperature for about 60 min, then 20 torr of CO was introduced. (2) The as-pretreated sample was purged with argon for 30 min and then immersed into a cinchonidine-dichloromethane solution (the concentration of cinchonidine was about 5.0×10^{-4} M) that had been flushed with hydrogen for more than 30 min. The sample was returned to the quartz IR cell again (special care was taken so that samples were not exposed to air during the transfer of the sample), evacuated at room temperature for about 60 min and then exposed to 20 torr of CO.

2.3. Test of cinchonidine-modified Pt/ γ -Al₂O₃ catalysts for the enantioselective hydrogenations of ethyl pyruvate and EOPB

All Pt/ γ -Al₂O₃ catalysts were pretreated in a hydrogen flow at 400 °C for 2 h before use. In a standard experiment, a pretreated Pt/ γ -Al₂O₃ catalyst, solvent, cinchonidine and ethyl pyruvate or EOPB were transferred into a 100 mL stainless autoclave. Then the hydrogenation reaction began at room temperature when hydrogen was introduced into the autoclave. The reaction was stopped according to the consumption of hydrogen. Conversion of ethyl pyruvate or EOPB and ee value of (*R*)-(+)-ethyl lactate or (*R*)-(+)-ethyl-2-hydroxyl-4-phenylbutyrate ((*R*)-(+)-EHPB) were analyzed by gas chromatography (6890N, Agilent Co.) using a chiral column (HP19091G-B213, 30 m × 0.32 mm × 0.25 μ m, Agilent Co.). The optical yield was expressed as the enantiomeric excess (ee) of (*R*)-(+)-ethyl lactate or (*R*)-(+)-EHPB:

$$ee(\%) = ([R] - [S]) / ([R] + [S]) \times 100$$

3. Results and discussion

3.1. Effect of preparation methods on average Pt particle sizes and CO adsorption

Table 1 gives the specifications of catalyst preparation procedures and the dispersions and average sizes of

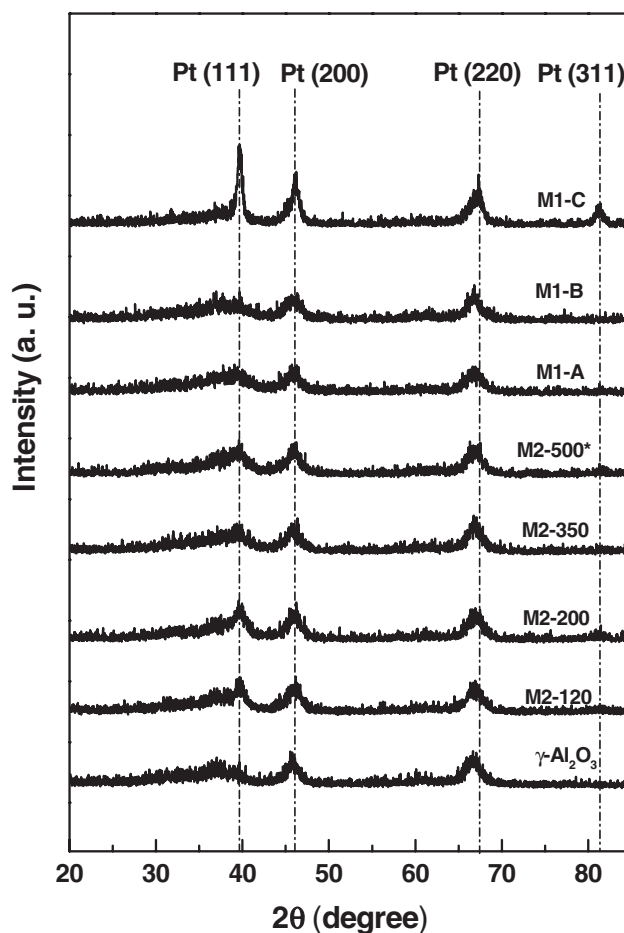


Figure 1. XRD patterns of 5.0 wt% Pt/ γ -Al₂O₃ catalysts prepared by Methods I and II. (M2-500 *represents the sample that had been used once and then dried at 120 °C.)

Pt particles measured by CO chemisorption. Figure 1 shows the XRD patterns of Pt/ γ -Al₂O₃ catalysts prepared by different methods.

The catalysts prepared by Method I: TEM images of catalysts M1-A and M1-C in figures 2 and 3 show that the average Pt particle size of catalyst M1-C is much larger than that of catalyst M1-A. The average Pt particle size of catalyst M1-C measured by CO chemisorption was 23.3 nm, while the average Pt particle sizes of catalysts M1-A and M1-B were 3.9 and 5.5 nm, respectively. This agrees well with the XRD and TEM results. The trend that the average size of Pt particles increases with increasing ratio of isopropanol/water demonstrates that the presence of isopropanol is not beneficial to the dispersion of Pt particles on γ -Al₂O₃. The presence of isopropanol decreases the hydrophilicity and adsorption ability of γ -Al₂O₃, resulting in the aggregation of Pt particles dispersed into isopropanol solution and the formation of large particles during reduction in an aqueous solution. This suggests that the size of Pt particles can be modulated by the addition of isopropanol.

Only one IR band at 2073 cm⁻¹ of CO linearly adsorbed on Pt/ γ -Al₂O₃ catalysts prepared by Method I before chiral modification was observed (figure 4). The IR absorbance of CO linearly adsorbed on catalyst M1-A was stronger than those on catalysts M1-B and M1-C, with that due to CO linearly adsorbed on catalyst M1-C the weakest. This can be explained in terms of the

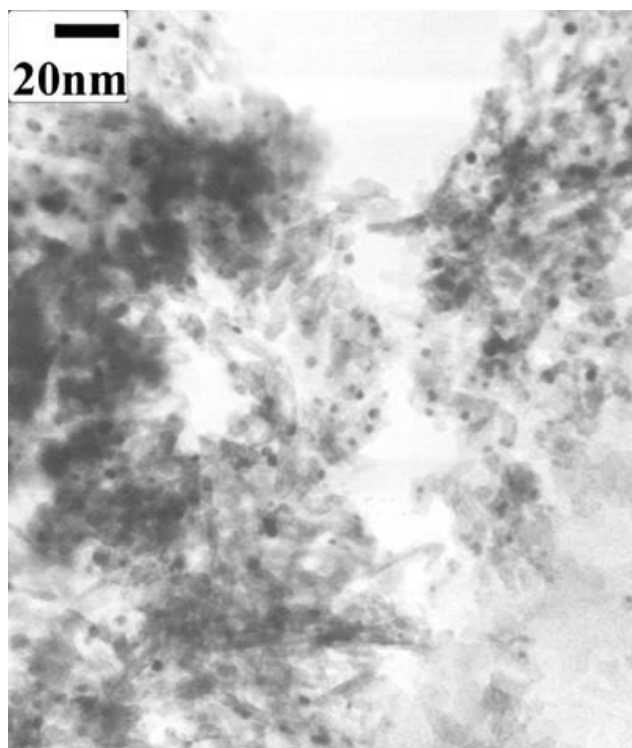


Figure 2. TEM image of catalyst M1-A.

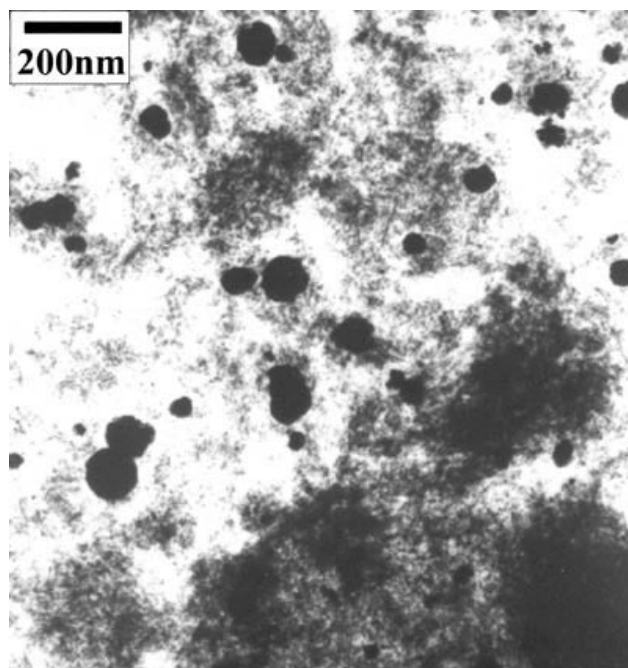


Figure 3. TEM image of catalyst M1-C.

exposed Pt atoms on the surface. The smaller the Pt particle size, the more Pt atoms are exposed, leading to more CO adsorption and hence stronger IR absorbance.

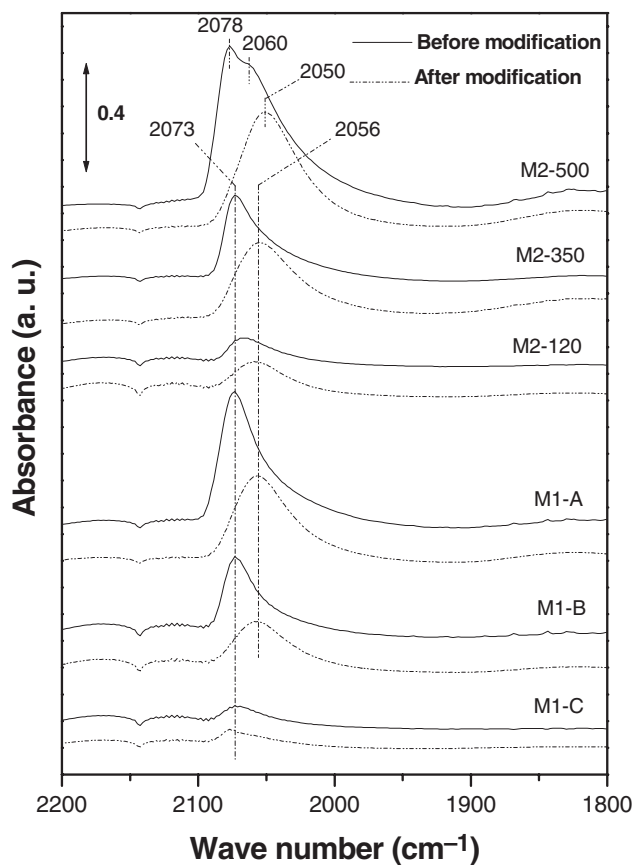


Figure 4. IR spectra of CO linearly adsorbed on Pt/ γ -Al₂O₃ catalysts before and after the chiral modification with cinchonidine.

After the chiral modification with cinchonidine, the IR band of CO linearly adsorbed on catalyst M1-A was shifted to 2056 cm⁻¹. For catalyst M1-B, the IR band of CO was shifted to 2058 cm⁻¹. However, no red shift of CO linearly adsorbed on catalyst M1-C was observed after chiral modification, and the IR absorbance of CO hardly decreased, indicating that the chiral modifier cinchonidine cannot be adsorbed on the surface of catalyst M1-C. The red shift of IR band of CO after chiral modification can be explained by the interaction of platinum with cinchonidine and the electron donation from cinchonidine to platinum surface. With an increasing amount of isopropanol added to the impregnation solution, the residual isopropanol on the surface possibly increases and the surface properties may change. The residual isopropanol can block the adsorption of cinchonidine, and the changed surface properties may not be beneficial to the adsorption of cinchonidine.

The catalysts prepared by Method II: Figures 5 and 6 show the TEM images of catalysts M2-120 and M2-500, which indicate that for catalyst M2-500 the average size of Pt particles was a little smaller, and the dispersion of Pt particles was more uniform than those of catalyst M2-120. In accordance with the TEM and XRD results, the average size of Pt particles for catalyst M2-500 measured by CO chemisorption (2.4 nm) was the smallest one among the catalysts prepared by Method II. The average sizes of Pt particles for catalysts M2-120, M2-200 and M2-350 were 6.1, 6.3, and 3.1 nm, respectively.

Increasing the calcination temperature of the catalyst precursor before reduction decreases the average size of Pt particles. This perhaps results from the interaction of platinum precursor with γ -Al₂O₃. When the catalyst precursor is calcined at a low temperature, the interaction between platinum precursor and γ -Al₂O₃ is weak. Thus, the Pt particles can easily gather to form large particles when the catalyst precursor is reduced in an aqueous solution. A strong interaction of platinum precursor with γ -Al₂O₃ is formed when the catalyst precursor is calcined at a high temperature. As a result, the Pt particles cannot aggregate together during reduction in an aqueous solution.

Two IR bands (2078 and 2060 cm⁻¹) of CO linearly adsorbed on catalyst M2-500 were observed, whereas for the other catalysts only one IR band (2073 cm⁻¹ for catalyst M2-350 and 2068 cm⁻¹ for catalyst M2-120 respectively) of linearly adsorbed CO was detected (figure 4). The IR band at 2078 cm⁻¹ is assigned to CO adsorbed on Pt atoms with somewhat positive charge, produced during calcination at 500 °C and resulting from a strong interaction between platinum and γ -Al₂O₃, while the IR band at around 2070 cm⁻¹ is assigned to CO adsorbed on Pt atoms [19].

After chiral modification, the IR band was shifted to 2050 cm⁻¹ for the catalyst M2-500, and to 2056 cm⁻¹ and 2058 cm⁻¹ for the catalysts M2-350 and M2-120 respectively. A red shift of CO linearly adsorbed on

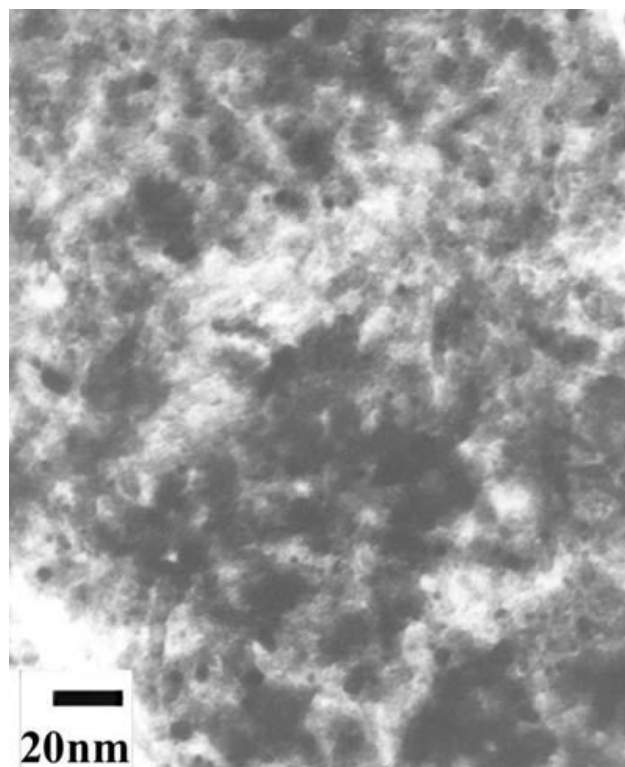


Figure 5. TEM image of catalyst M2-120.

Pt/ γ -Al₂O₃ catalysts prepared by Method II was observed after chiral modification. As discussed above, the different red shift of IR band of linearly adsorbed CO after chiral modification indicates that a different amount of cinchonidine is adsorbed on the catalyst

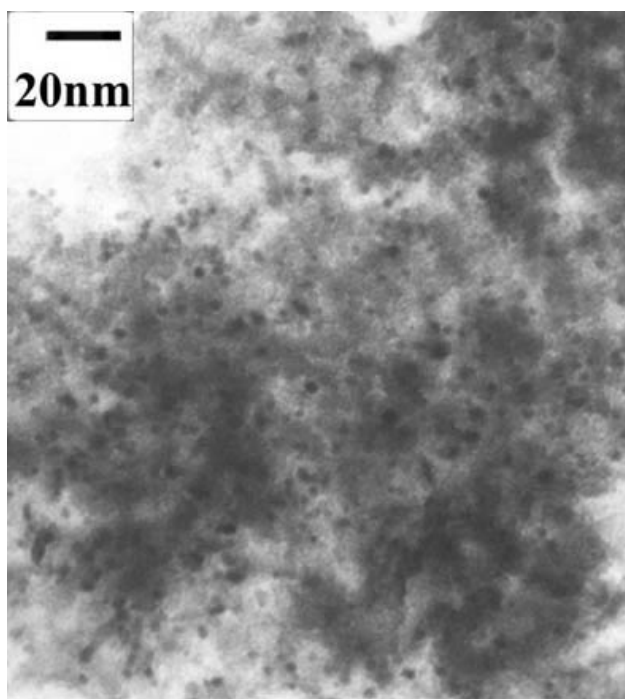


Figure 6. TEM image of catalyst M2-500.

Table 2

Conversions of EtPy (ethyl pyruvate) and ee values of (*R*)-(+)-ethyl lactate catalyzed by Pt/ γ -Al₂O₃ catalysts prepared by different methods

Entry	Catalyst	Catalyst (mg)	CD (mg) ^a	Solvent (mL)	Initial P _{H₂} (MPa)	EtPy (mL)	Reaction time (h)	Conversion (%)	ee (%)
1	M1-A	500	101	40 mL acetic acid	6.9	5.0	17.0	93.8	80.2
2	M1-B	492	102	40 mL acetic acid	6.5	5.0	18.0	88.3	75.4
3	M1-C	494	101	40 mL acetic acid	6.4	5.0	17.7	48.4	41.7
4	M2-120	496	101	40 mL acetic acid	7.5	5.0	0.2	99.0	90.5
5	M2-200	499	103	40 mL acetic acid	7.5	5.0	0.2	99.7	89.1
6	M2-350	500	103	40 mL acetic acid	7.6	5.0	0.2	99.3	91.1
7	M2-500	503	105	40 mL acetic acid	7.6	5.0	0.2	99.4	89.6
8	M2-350	253	53	20 mL acetic acid	7.5	5.0	0.2	99.8	94.8
9	M2-500	253	51	20 mL acetic acid	7.5	5.0	0.2	99.8	91.8
10	M2-350	116	24	12 mL ethanol	5.2	2.0	1.0	99.0	77.8

^aCD represents cinchonidine.

surface and then the interaction of cinchonidine with platinum is formed.

3.2. Effect of preparation methods on the enantioselective hydrogenation of ethyl pyruvate

Table 2 gives the conversions of ethyl pyruvate and the corresponding ee values of (*R*)-(+)-ethyl lactate catalyzed by the 5.0 wt% Pt/ γ -Al₂O₃ catalysts prepared by different methods. Under the optimized preparation and reaction conditions, the conversion of ethyl pyruvate reached about 100% and the ee value of (*R*)-(+)-ethyl lactate was nearly 95%.

For all the catalysts prepared by Method II, the conversions of ethyl pyruvate could reach almost 100% in 0.2 h. The ee values obtained for these catalysts were around 90%. It is very interesting that the ee value changed only slightly with the average size of Pt particles for the Pt/ γ -Al₂O₃ catalysts prepared by Method II (table 2, entries 4, 5, 6, and 7). The highest ee value of about 95% was obtained when acetic acid was used as a solvent for the catalyst M2-350, which was calcined at 350 °C for 2 h before reduction and which has an average Pt particle size of 3.1 nm (table 2, entry 8), while about 78% ee was achieved for the same catalyst when ethanol was used as a solvent (table 2, entry 10). Although the average sizes of Pt particles are different, it is the protonation of the quinuclidine N atom of cinchonidine by acetic acid and the interaction of the carboxylic acid with the reactant and the chiral modifier [20] that play a predominant role in determining the ee value of (*R*)-(+)-ethyl lactate; as a result, comparably high ee values are obtained when acetic acid is used as a solvent for the different Pt/ γ -Al₂O₃ catalysts prepared by Method II.

For the catalysts M1-A (3.9 nm), M1-B (5.5 nm) and M1-C (23.3 nm), conversions of ethyl pyruvate were 93.8, 88.3, and 48.4% respectively, while the corresponding ee values of (*R*)-(+)-ethyl lactate were 80.2, 75.4, and

41.7% after the reaction for more than 17 h (table 2, entries 1, 2, and 3). Evidently, the conversions and ee values decrease with the increase of average Pt particle size for the catalysts prepared by Method I and are much lower than those obtained for the Pt/ γ -Al₂O₃ catalysts prepared by Method II.

The poorer catalytic performance obtained for the catalysts prepared by Method I can be partly attributed to the weak interaction between Pt and γ -Al₂O₃. Since the catalyst precursors were neither dried nor calcined, the interaction of platinum with γ -Al₂O₃ for the M1 series catalysts is expected to be weak, resulting in poor ability to activate the reactant molecules. Another possible reason for this phenomenon is the possible change of the catalyst surface properties by the addition of isopropanol, which is not beneficial to the adsorption of the reactant, solvent and chiral modifier molecules. In addition, the residual isopropanol on the catalyst surface can block the adsorption of reactant, solvent and chiral modifier, resulting in low catalytic performance in the enantioselective hydrogenation of ethyl pyruvate. This can be verified from the IR spectra of linearly adsorbed CO on Pt/ γ -Al₂O₃ catalysts prepared by Method I before and after the chiral modification with cinchonidine.

3.3. Effect of preparation methods on enantioselective hydrogenation of EOPB

The results obtained under different preparation and reaction conditions for the enantioselective hydrogenation of EOPB are given in tables 3 and 4. The conversions of EOPB reached 91.6, 92.7, and 94.5% under the hydrogen pressure of 8.0 MPa for catalysts M2-120, M2-350, and M2-500, respectively, the corresponding ee values of (*R*)-(+)-EHPB being 71.0, 73.2, and 65.3% (table 3). For the Pt/ γ -Al₂O₃ catalysts prepared by Method II, the conversions and the ee values change with Pt particle size. While the conversion

Table 3

Conversions of EOPB and ee values of (*R*)-(+)-EHPB obtained on different Pt/ γ -Al₂O₃ catalysts modified with cinchonidine under the hydrogen pressure of 8.0 MPa

Entry	Catalyst	Pt (mg)	Conversion (%)	ee (%)
1	M2-120	5.37	91.6	71.0
2	M2-350	5.28	92.7	73.2
3	M2-500	5.19	94.5	65.3

Note: Reaction conditions: Solvent: 10 mL ethanol + 20 mL toluene; about 11.0 mg CD; 1 mL EOPB; Reaction temperature: 287 K; Reaction time: 1 h.

of EOPB increased with the decrease of Pt particle size, the highest ee value was achieved with catalyst M2-350, the one with a Pt particle size of 3.1 nm.

Table 4 gives the conversions of EOPB and the ee values of (*R*)-(+)-EHPB obtained in different solvents for catalysts M2-350 and M1-A. The hydrogenation reactions were almost complete in different solvents in 1 h for both catalysts, indicating that the solvents used in the enantioselective hydrogenation of EOPB cannot affect the surface properties of the catalysts significantly. However, for catalyst M2-350, the ee value of (*R*)-(+)-EHPB was increased by about 10% when ethanol was replaced by a mixture of ethanol and toluene (entries 1 and 2). About 82 and 79% ee were achieved for the same catalyst when acetic acid and dichloromethane were used respectively (entries 3 and 8). The ee value increased slightly when a mixture of acetic acid and toluene with an optimal ratio (V/V, 1/2) was used for catalyst M2-350 (entry 6). 80.4 and 75.8% ee were achieved for the EOPB hydrogenation on catalyst M1-A when acetic acid and dichloromethane were used as solvents respectively (entries 9 and 10).

That the solvent plays an important role in determining the ee value can be explained by the different interactions of solvents with the reactant and chiral

modifier occurring on the catalyst surface. That the ee increases considerably when toluene is used as a solvent can be interpreted in terms of toluene being strongly adsorbed on the naked platinum sites where the chiral modifiers are not present, thus reducing the probability of nonselective reactions [16].

3.4. Effect of preparation variables and reaction parameters on the enantioselective hydrogenations of ethyl pyruvate and EOPB

As mentioned above, 93.8% conversion and 80.2% ee were achieved for the enantioselective hydrogenation of ethyl pyruvate on catalyst M1-A after the reaction for 17 h (table 2, entry 1). In contrast, 99.3% conversion and 91.1% ee were obtained in 0.2 h for the same reaction on catalyst M2-350 (table 2, entry 6). Therefore, the catalytic performance of catalyst M1-A is much poorer than that of catalyst M2-350 in the ethyl pyruvate hydrogenation. However, for the enantioselective hydrogenation of EOPB with the catalyst M2-350, 98.4 and 99.3% conversions and 81.8 ee and 79.0% ee were obtained when acetic acid and dichloromethane were used as solvents respectively (table 4, entry 3 and 8), while 98.2 and 99.3% conversions and corresponding 80.4 ee and 75.8% ee were achieved for catalyst M1-A (table 4, entries 9 and 10). Clearly, the catalytic performances of these two catalysts are comparable in the enantioselective hydrogenation of EOPB.

As discussed separately for the enantioselective hydrogenations of ethyl pyruvate and EOPB, the ee values are influenced by Pt particle sizes, and the highest ee value is obtained for the Pt/ γ -Al₂O₃ catalysts with an optimal Pt particle size (3.1 nm) for both hydrogenation reactions. However, these phenomena cannot be simply interpreted in terms of the platinum dispersion. The major differences between the preparation Methods I and II is the calcination procedure and the addition of isopropanol, and this perhaps results in different

Table 4

Conversions of EOPB and ee values of (*R*)-(+)-EHPB obtained on different Pt/ γ -Al₂O₃ catalysts modified with cinchonidine in different solvents

Entry	Catalyst	Solvent	Conversion (%)	ee (%)
1	M2-350	30 mL ethanol	98.3	58.6
2	M2-350	10 mL ethanol + 20 mL toluene	99.4	69.0
3	M2-350	30 mL acetic acid	98.4	81.8
4	M2-350	30 mL acetic acid	98.1	82.3 ^a
5	M2-350	15 mL acetic acid + 15 mL toluene	98.0	81.4
6	M2-350	10 mL acetic acid + 20 mL toluene	98.0	83.0
7	M2-350	5 mL acetic acid + 25 mL toluene	98.2	82.0
8	M2-350	30 mL dichloromethane	99.3	79.0
9	M1-A	30 mL dichloromethane	99.3	75.8
10	M1-A	30 mL acetic acid	98.2	80.4

Note: Reaction conditions: 0.200 g Pt/ γ -Al₂O₃; 20.0 mg cinchonidine; Hydrogen Pressure: about 5.0 MPa; 1 mL EOPB; Reaction temperature: 287 K; Reaction time: 1 h.

^aHydrogen pressure: about 7.0 MPa; other reaction parameters were the same as mentioned above.

interactions of platinum with the support and the different adsorption abilities. It can be deduced that the interaction between platinum and γ -Al₂O₃ is very important for a high activity and that an optimal adsorption ability (adsorption of reactant, solvent and chiral modifier) of the catalyst surface is advantageous to achieving high enantioselectivity.

The differences between the enantioselective hydrogenations of ethyl pyruvate and EOPB may be caused by the different reaction pathways and kinetics of these two reactions. The enantioselective hydrogenation of EOPB is probably less structure-sensitive than the asymmetric hydrogenation of ethyl pyruvate, and the latter reaction is influenced more significantly by surface properties including electronic properties and adsorption abilities, which are determined by different preparation methods.

4. Conclusions

Pt/ γ -Al₂O₃ catalysts with Pt particle sizes in the range of 2.4–23.3 nm were prepared by two different impregnation methods. The average size of Pt particles decreases with increasing calcination temperature of the catalyst precursor, as a result of increased interaction of Pt with γ -Al₂O₃. The surface property of the platinum on γ -Al₂O₃ was characterized by IR spectroscopy using CO as the probe molecule. Owing to the interaction of platinum precursor with γ -Al₂O₃, induced particularly after the calcination at high temperatures, the Pt/ γ -Al₂O₃ catalysts prepared by impregnation, calcination and reduction in a sodium formate solution exhibit higher activities for both the enantioselective hydrogenations of ethyl pyruvate and EOPB. The Pt/ γ -Al₂O₃ catalysts, prepared by impregnation in a solution containing isopropanol without drying or calcination, do not show high catalytic performance in the enantioselective hydrogenation of ethyl pyruvate possibly because the surface properties after the addition of isopropanol are not beneficial to the adsorption of reactant, solvent and chiral modifier, or because the residual isopropanol blocks the adsorption of reactant, solvent and chiral modifier.

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