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Effective and Reusable Pt Catalysts Supported on Periodic Mesoporous Resols for Chiral Hydrogenation

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Abstract Platinum nanoparticles supported on periodic mesoporous resols by simple impregnation serve as effective, robust and remarkably reusable catalysts after chirally modified with cinchonidine for the asymmetric hydrogenation of ethyl pyruvate, affording up to 62% enantiomeric excess (ee) and a constant activity after 25th re-use. They can also catalyze the reaction in an environmentally benign manner by using water as a solvent.

Keywords Periodic mesoporous resols · Pt/FDU-15 · Enantioselective hydrogenation · Ethyl pyruvate

1 Introduction

Enantioselective hydrogenation of α-functionalized ketones catalyzed by supported platinum catalysts modified with cinchona alkaloids and related modifiers has been considered as one of the milestones of heterogeneous asymmetric catalysis, and extensive studies have been carried out on this system in the past decades [1–6]. Most of these studies focused on commercially available 5.0 wt.% Pt/Al_2O_3 catalysts [7–16], e.g. E 4759 from Engelhard or JMC 5 R 94 from Johnson Matthey, or 6.3 wt.% Pt/SiO_2 catalysts [17, 18], e.g. EUROPT-1. New types of catalysts such as platinum colloids [19] and Pt particles supported on inorganic materials other than Al_2O_3 and SiO_2 have also been explored at around the same time. Moderate to good enantiomeric excesses (ees) were obtained with Pt/MCM-41 [20–22], Pt/HNaY [23], Pt/clay [24, 25], Pt/LDH [26], and Pt/SWNTs catalysts [27].

Due to use of the expensive noble metal catalysts and to enhance productivity, the continuous operation in a fixed-bed reactor for the asymmetric hydrogenation of α-functionalized ketones has received much attention in recent years [1, 28–32]. Continuous feeding of minute amounts of chiral modifier can maintain the ee of product [29, 31]. Even though time-required charging, discharging and catalyst handling are needed, the recycling of Pt/Al_2O_3 catalyst was realized using a batch reactor [33–35]. In ethanol, the catalyst can be reused for at least thrice without distinct decrease in ee values and conversions, but decrease in activity [33]. In toluene medium, “an increase in ee on reuse” of 10–20% was observed under the mild experimental conditions depending on the reaction conditions [34]. However, when the reaction was performed in acetic acid, the relatively inferior reusability of Pt/Al_2O_3 catalyst was observed [34, 35].

Organic polymers have also attracted much more attention in recent years due to their specific physical and chemical properties and thus their application for product separation, catalyst recycing and so on [36, 37]. FDU-type periodic mesoporous resols (PMRs), is a class of newly developed advanced materials possessing tunable mesostructures, textural properties of mesoporous materials and the merits of organic polymers [38, 39]. These materials, with three-connected benzene ring framework, large surface area and uniform pore size, can be derived from resols precursor (phenol/formaldehyde) via a solvent evaporation induced self-assembly (EISA) [38], or through a simple dilute aqueous strategy under a basic condition from the

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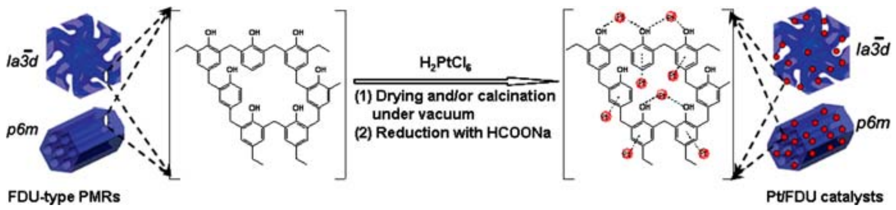
Scheme 1 Preparation of FDU-type PMRs supported Pt catalysts



organic–organic self-assembly of triblock copolymer with resols [39]. They are stable even under the acidic and basic conditions [39, 40]. They maybe exhibit unique hydrophobic affinity towards organic reactants or solvents, quite different from their silica-based inorganic analogues. In addition, the noble metal nanoparticles may be stabilized inside the mesopores via the interaction between the metal particles and aromatic moiety [41], as a result, the catalyst is expected to show promising stability and remarkable reusability potentially in acetic acid.

Since the FDU-type PMRs was firstly reported [38, 39], the application of FDU-type PMRs in catalysis has been rarely reported up to now [40]. The present work is aimed at its application as a support to accommodate and stabilize Pt nanoparticles for the enantioselective hydrogenation of ethyl pyruvate (Scheme 1).

2 Experimental

2.1 Catalyst Preparation and Characterization

We synthesized FDU-14, 15 PMRs with *Ia*3*d* and *p*6*m* symmetry, respectively, and they showed the similarity in serving as a support in the chiral hydrogenation of ethyl pyruvate. Here we adopted Pt/FDU-15 as an example.

FDU-15 was synthesized according to reference [39]. Pt/FDU-15 catalysts were prepared mainly according to references [30, 35]: FDU-15 was impregnated with an aqueous solution of platinum precursor (H_2PtCl_6) and stirred for 4–6 h. Then the mixture was evaporated to remove the excess water, followed by a drying at 80 °C overnight. One portion was directly reduced in an aqueous solution of sodium formate, while the other portion of catalyst precursor was calcined under vacuum at 350 °C for 2 h before the same reduction. Pt/FDU-15 catalysts with 5.0 wt.% Pt loading were designated as Catalysts FDU-Pt and FDU-Pt-350, while the latter represents the sample previously calcined at 350 °C under vacuum before reduction.

The X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE instrument using Cu-Kα radiation. The nitrogen adsorption–desorption isotherms were measured at 77 K on a Quantachrome Autosorb-3B system, after the samples were evacuated for 10 h at 373 K. The BET specific surface area was calculated using adsorption data in the relative pressure range from 0.04 to 0.3. The pore size distribution curves were calculated from the analysis of the adsorption branch of the isotherm using the BJH algorithm. The TEM images were taken on an FEI (company) Tecnai G2 Spirit at an acceleration voltage of 120 kV. Thermogravimetric analysis (TGA) of samples was performed in N_2 atmosphere from 293 K to 773 K with a heating rate of 10 K min^{-1} using a METTLER TOLEDO TGA/SDTA851^e apparatus. CO chemisorption of samples was measured at 40 °C on a CHEMBET-3000 pulse chemisorption analyzer (Quantachrome Co.) after the samples were pretreated in a hydrogen flow at 300 °C for 2 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} m^2 and a stoichiometric factor of one, using nominal platinum concentrations.

2.2 Catalytic Performance

About 0.1 g of catalyst was pretreated in a 40 mL/min hydrogen flow at 300 °C for 2 h before use. The catalyst was then mixed with 0.01 g cinchonidine, 2 mL ethyl pyruvate, 20 mL solvent and transferred to a 100 mL autoclave. The hydrogenation reaction began at ambient temperature after 4.0 MPa of hydrogen was introduced into the autoclave. The reaction was stopped after 30 min or 1 h and the products were analyzed by GC (6890N, Agilent Co.) equipped with a capillary chiral column (HP19091G-B213, 30 m × 0.32 mm × 0.25 μm, Agilent Co.). The optical yield was expressed as the ee of (R)-(+)-ethyl lactate:

$$\mathrm{Ee}\ (\%) = ([\mathrm{R}] - [\mathrm{S}])/([\mathrm{R}] + [\mathrm{S}]) \times 100.$$

After the each run, the catalyst was centrifugated and washed with fresh solvents. Fresh reactant, solvent and cinchonidine were then charged to the autoclave together with the recovered catalyst to carry out the next run reaction.

3 Results and Discussion

3.1 Catalyst Preparation and Characterization

The well-ordered mesoporous structure of FDU-15 PMRs was still maintained even after loaded with Pt, which was

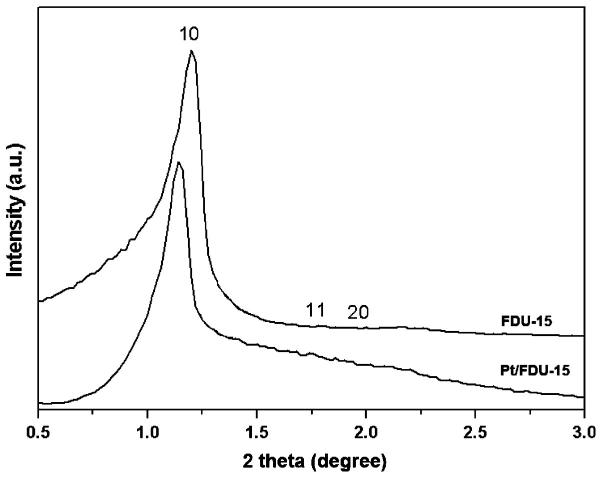


Fig. 1 Low-angle XRD patterns of FDU-15 PMRs before and after loaded with Pt nanoparticles

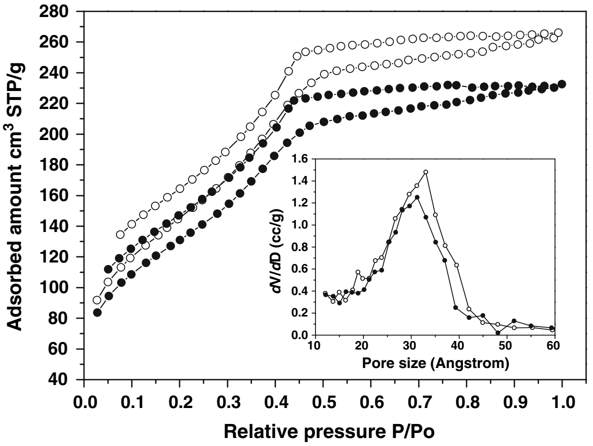


Fig. 2 N_2 adsorption–desorption isotherms and pore size distribution (inset) of FDU-15 PMRs before (-○-) and after (-●-) loaded with Pt nanoparticles. The specific surface area from 534 m^2/g to 478 m^2/g and pore size from 3.3 nm to 3.1 nm decreased reasonably due to the Pt particles occluded in the pores

confirmed by the low-angle XRD patterns and N_2 adsorption–desorption isotherms of FDU-15 PMRs (Figs. 1 and 2). Figure 3 shows the TEM images of Pt/FDU-15 catalysts. The Pt nanoparticles for Catalyst FDU-Pt were uniformly dispersed inside the FDU-15 mesopores and the average Pt particle size was around 3 nm with the dispersion of 33.5%.

However, a previous calcination resulted in the aggregation of platinum precursor, so that Catalyst FDU-Pt-350 had an average Pt particle size of 5.0 nm according to CO chemisorption result. It seemed that the thermal treatment at high temperature caused an aggregation of Pt particles, which made the mesopores of FDU-15 partially broken.

This trend is obviously different from the observation for Pt/γ-Al_2O_3 catalysts, on which the Pt particles decreased with increasing the calcination temperatures under aerobic conditions due to the metal-support interaction [30]. In order to interprete this observation, the TGA of Catalyst FDU-Pt precursor was performed in a nitrogen atmosphere. The TGA results indicated that the H_2PtCl_6 precursor on FDU-15 PMRs has been decomposed to form Pt^0 after losing chloride ions during the calcination, while the chloride ions are considered to inhibit the growth of platinum particles [42]. As a result, Catalyst FDU-Pt-350 had a larger partice size than Catalyst FDU-Pt.

3.2 Catalytic Performance of Pt/FDU-15 Catalysts

Table 1 lists the conversions and ee values obtained with various Pt/FDU-15 catalysts in-situ modified with cinchonidine in different solvents for the enantioselective hydrogenation of ethyl pyruvate. Catalyst FDU-Pt gave slightly higher convesions than those obtained with Catalyst FDU-Pt-350, while the ee values achieved from these two catalysts were comparable in the same solvents (entries 1 and 2, 3 and 5, 7 and 9). When the reaction was performed in acetic acid, higher ee value was achieved in

Fig. 3 TEM images of Pt/FDU-15 catalysts

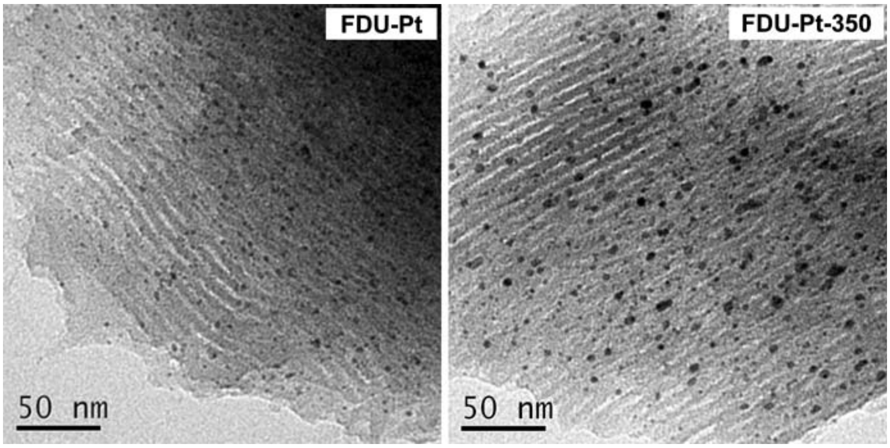
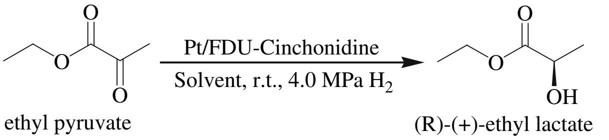


Table 1 Conversions of ethyl pyruvate and ee values of (R)-(+)-ethyl lactate obtained on different Pt/FDU-15 catalysts modified with cinchonidine in different solvents[a]



Entry	Catalyst	Solvent	Conv. (%)[b]	ee (%)[b]
1	FDU-Pt-350	EtOH	88	29
2	FDU-Pt	EtOH	94	29
3	FDU-Pt-350	AcOH	98	53
4[c]	FDU-Pt-350	AcOH	72	62
5	FDU-Pt	AcOH	100	55
6[c]	FDU-Pt	AcOH	99	54
7	FDU-Pt-350	H_2O	100	38
8[c]	FDU-Pt-350	H_2O	73	38
9	FDU-Pt	H_2O	100	38
10[c]	FDU-Pt	H_2O	95	37

[a] Reaction conditions: 0.1 g catalyst; 0.01 g cinchonidine; 2 mL ethyl pyruvate; 20 mL solvent; 4.0 MPa H_2; r. t.; 1 h; 900 rpm

[b] Determined by GC and the dominant configuration of product is R

[c] Reaction time, 0.5 h

comparison to ethanol (entries 3–6). In particular, Catalyst FDU-Pt-350 gave a highest value of 62% ee (entry 4). These phenomena can be explained by the Pt particle size effect and solvent effect well addressed before elsewhere [1–6, 43, 44].

It is worth notifying that the conversions obtained in water (entries 7–10) were very comparable with those achieved in other solvents, even when the reactions were conducted for a shorter period (entries 4, 6, 8 and 10), furnishing moderate ee values. The TOF of Catalyst FDU-Pt reached 3908 mol mol^{-1} h^{-1} in water (entry 10), demonstrating that the enantioselective hydrogenation of ethyl pyruvate on Pt/FDU-15 catalysts can be performed actively in an environmentally benign manner. However, for the same reaction run on cinchona alkaloids modified Pt/γ-Al_2O_3 catalysts, the activity and ee value were both lower in water because of high dielectric constant and high polarity of water and thus poor solubility of cinchona alkaloid in it [44].

The surprising water effect on the catalytic performance we noticed here can be interpreted in terms of the limited solubility of ethyl pyruvate, but good solubility of the product ethyl lactate in water, whereas FDU-15 PMRs are soaked well with ethyl pyruvate layer. Thus, the concentration of ethyl pyruvate on the catayst surface is much higher than that in water, while the product diffuses quickly from the catalyst surface into water once it is formed. The phase-transfer of product from the catalyst surface to solvent would accelerate the reaction as a result of the reaction equilibrium shifting. Moreover, the high hydrophobicity of PMRs with pure organic framework may also contribute to the high activity in water.

The reusability of Pt/FDU-15 catalyst was also investigated. Figure 4 shows conversions and ee values against the number of runs-on Catalyst FDU-Pt in acetic acid within 0.5 h. The catalyst was re-used for more than 25 times without distinct loss of activity. Since fresh cinchonidine was added to each reaction system, the enantioselectivity was maintained almost the same upon 25 times multiple re-use (50–56% ee).

Compared with Pt/FDU-15 catalysts, Pt/γ-alumina catalysts showed much more inferior reusability, which can only be re-used at best three times under the similar reaction conditions [35]. This is probably caused by the peptization of the γ-alumina support in acetic acid to some extent during re-use, resulting in embedded Pt active species in alumina fragments and thus a poor reusability [45]. As for Pt/FDU-15 PMRs, the mesoporous structure of FDU-15 PMRs can be retained very well even if under the acidic or basic conditions because of an organic polymer backbone [39, 40]. Furthermore, the Pt nanoparticles were

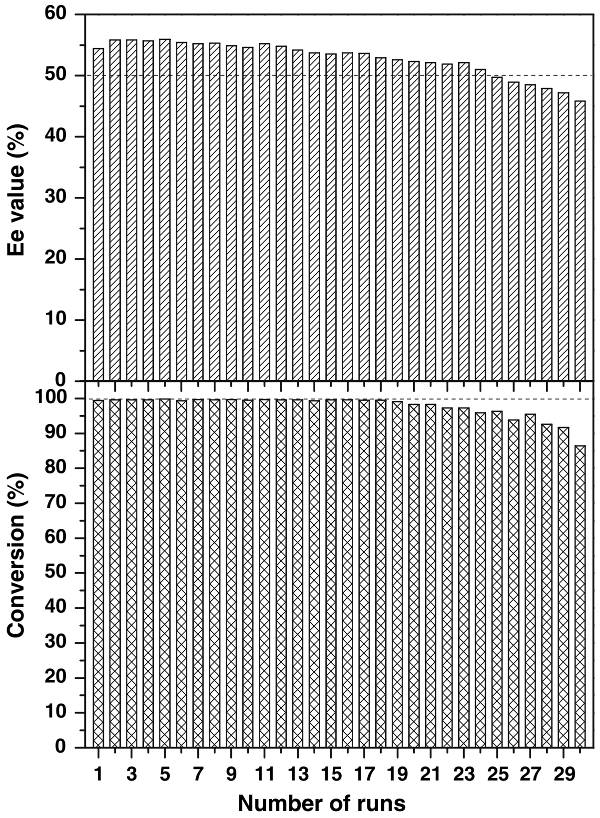


Fig. 4 Conversions and ee values against number of runs in asymmetric hydrogenation of ethyl pyruvate. Reaction conditions: same as Table 1, Entry 6

probably stabilized by the π-donating interaction from the benzene rings of FDU-15 PMRs to Pt particles [41].

4 Conclusion

In conclusion, our results show that Pt/FDU-type PMRs catalysts are effective, robust and remarkably reusable catalysts for enantioselective hydrogenation of ethyl pyruvate under the mild conditions, affording up to 62% ee. They can also catalyze the reaction in an environmentally benign manner by using water as a solvent. The most remarkable feature of Pt/FDU-15 is that it can be reused for more than 25 times without distinct deactivation. This kind of catalyst may provide a potential alternative for the hydrogenation of other compounds containing carbonyl groups.

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