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Ordered Mesoporous Carbons with Ia3d Symmetry Supported Pt Catalyst for Efficient Asymmetric Hydrogenation

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Abstract Pt nanoparticles supported on CMK-8 ordered mesoporous carbons (OMCs) with Ia3d symmetry after chirally modified with cinchonidine (CD) proved to be highly efficient for asymmetric hydrogenation of α-keto-esters. Up to 34,819 h^{-1} TOF with 75 % ee was furnished for the enantioselective hydrogenation of ethyl 2-oxo-4-phenylbutyrate with CD-modified Pt/CMK-8 catalyst. To the best of our knowledge, these results obtained with chirally modified Pt/CMK-8 catalyst are the best ones among those with Pt catalysts supported on carbon materials. It is suggested that both the physical structure features of CMK-8 OMCs and the chemical nature of Pt catalyst are beneficial for the asymmetric hydrogenation.

Keywords Asymmetric hydrogenation · Supported Pt catalyst · Ordered mesoporous carbons · Ethyl pyruvate · Ethyl 2-oxo-4-phenylbutyrate

1 Introduction

Enantioselective hydrogenation of α-functionalized ketones has received great attention in the past decades. Important information has been collected since the first report by Orito and co-workers [1–3] about the enantioselective hydrogenation of pyruvate esters on supported Pt catalysts after chirally modified with cinchona alkaloids. With the development of porous materials, FDU-14 mesopolymers [4], mesoporous alumina composites [5] and carbon nanotubes (CNTs) [6, 7], etc. have been used to support Pt nanoparticles for this reaction. Nevertheless, most of supported Pt catalysts showed inferior results to the commercial Pt/Al_2O_3 catalysts [1]. A few exceptions arose recently. The Pt nanoparticles confined in the mesoporous alumina composites Al_2O_3@SBA-15 and the Pt nanocatalyst encapsulated within CNTs showed superior performance in the enantioselective hydrogenation of α-ketoesters than the well-known Pt/Al_2O_3 under the same reaction conditions [5, 7].

Ordered mesoporous carbons (OMCs) have attracted much attention since their discovery due to periodic mesopores, uniform pore size, high surface areas, adequate pore volume and high thermal, chemical and mechanical stabilities [8, 9]. Among the OMCs families, CMK-3 OMCs with P6mm symmetry are widely known and used [10]. CMK-8 OMCs with Ia3d symmetry are another kind of OMCs synthesized using KIT-6 silica matrix with Ia3d symmetry as hard templates, sucrose as carbon source and sulfuric acid as carbonization catalyst using a nano-casting route [11, 12]. Since the synthesis of CMK-8 OMCs, they have been used as hard templates to synthesize nanostructured materials, such as SiCN, SiN_3, ordered mesoporous alumina and ordered mesoporous magnesium oxide, etc. [13–15]. Due to the structural features including three-dimensional cubic structure, large pore volume and wall thickness of the framework, CMK-8 OMCs have better adsorption characteristics compared with the CMK-3 analogues [16]. Hence, the mass transportation is anticipated easier if a reaction occurs with a CMK-8 OMCs-based catalyst.

Encouraged by our previous achievements in CMK-3 OMCs entrapped Pt nanoparticles, which showed remarkable performance in the enantioselective hydrogenation of ethyl pyruvate [17], we are motivated to investigate the

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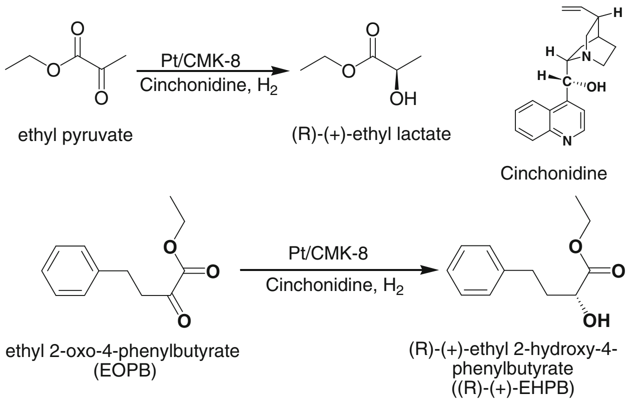

Scheme 1 Enantioselective hydrogenation of α-ketoesters on CD-modified Pt/CMK-8 catalysts

asymmetric hydrogenation of α-ketoesters with Pt/CMK-8 catalyst (Scheme 1). We expected Pt/CMK-8 catalyst after chirally modified with cinchonidine (CD) would show superior performance especially towards the asymmetric hydrogenation of ethyl 2-oxo-4-phenylbutyrate (EOPB) that bears a benzene ring with relatively large molecular size. To our delight, the CD-modified Pt/CMK-8 catalyst furnished a TOF over 34,000 h^{-1} with 75 % ee for the enantioselective hydrogenation of EOPB. To the best of our knowledge, these results are the best ones about the asymmetric hydrogenation of EOPB among those with the Pt catalysts supported on carbon materials until now.

2 Experimental

2.1 Catalyst Preparation and Characterization

The procedures for preparing Pt/CMK-8 catalyst are graphically illustrated in Fig. 1. The CMK-8 OMCs were synthesized using KIT-6 silica matrix with Ia3d symmetry as hard templates, sucrose as carbon source and sulfuric acid as carbonization catalyst using a nano-casting route according to Refs. [11, 12]. The Pt/CMK-8 catalysts with different Pt loadings were prepared mainly according to Ref. [4]: CMK-8 was impregnated with a solution containing H_2PtCl_6 and stirred for 4–6 h. Then the mixture was evaporated to remove excess solvent, followed by a drying at 353 K overnight. Subsequently, the catalyst precursor was reduced in an aqueous solution of sodium formate. According to diffusion medium of Pt precursor, the Pt/CMK-8 catalysts were denoted as Pt/CMK-8-W/E, where W represents water and E represents ethanol, respectively.

The X-ray diffraction (XRD) patterns of samples were collected on a Bruker D8 ADVANCE instrument using Cu-Kα radiation. The nitrogen sorption isotherms were measured at 77 K on a Quantachrome Autosorb-3B system after the samples were evacuated at 373 K for 10 h. The BET specific surface area was calculated using adsorption data in the relative pressure range from 0.05 to 0.35. The pore size distribution curves were calculated from the analysis of the adsorption branch of the isotherm using the BJH algorithm. The Raman spectrum of CMK-8 carbon was taken on a Renishaw inVia Raman spectroscopy excited using a 632.8 nm laser. The TEM images were taken on a Jeol JEM-2100 electromicroscopy with an acceleration voltage of 200 kV.

CO chemisorption of samples was measured at 308 K on a Quantachrome CHEMBET-3000 pulse chemisorption analyzer after the samples were pretreated in a 5 vol.% H_2/95 vol.% Ar flow at 673 K 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 8×10^{-20} m^2 and a stoichiometric factor of one, using nominal platinum concentrations. The Pt content of catalysts or the leached amount of Pt atoms into solution was measured or detected with a Thermo Elemental IRIS Intrepid II XSP inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The surface electronic state of Pt was examined using X-ray photoelectron spectroscopy (XPS) measurements with a Thermo Fisher Scientific ESCALAB 250 spectrometer with Al-Kα radiation (1486.6 eV) as incident beam with a monochromator

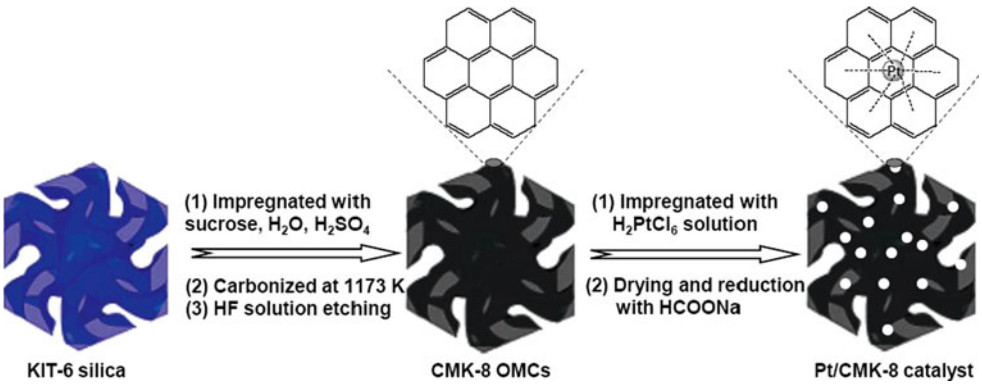

Fig. 1 Schematic illustration for preparation of Pt/CMK-8 catalyst

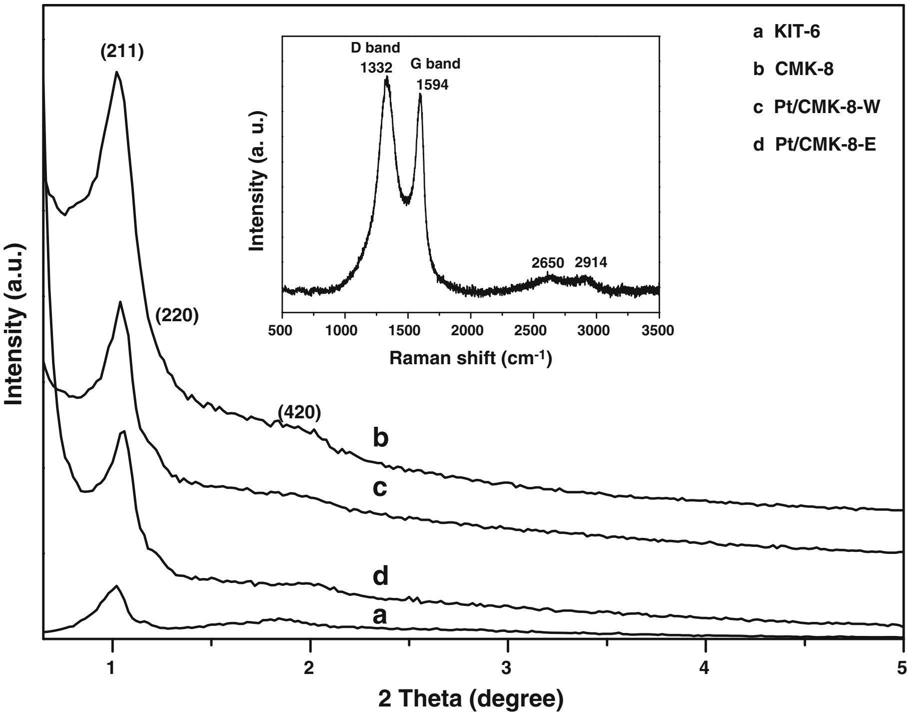

Fig. 2 Low-angle XRD patterns of Pt/CMK-8 catalysts and Raman spectrum of CMK-8 recorded with a 632.8 nm laser (*inset*)

2.2 Catalytic Tests

For a standard reaction, 0.1 g 5 wt% Pt/CMK-8 catalyst was pretreated in a hydrogen flow at 673 K for 2 h before use. The catalyst was then mixed with a certain amount of CD, 21.07 mmol ethyl pyruvate or 26.45 mmol EOPB, 20 ml acetic acid and transferred to a 100 ml autoclave with stirring. The hydrogenation reaction began at room temperature after hydrogen was introduced into the autoclave. The reaction was stopped after a period and then the products were analyzed by GC-FID (GC 2014, Shimadzu) equipped with a capillary chiral column (HP19091G-B213, Agilent). The optical yield was expressed as ee value: ee (%) = ([*R*] − [*S*])/([*R*] + [*S*]) × 100.

3 Results and Discussion

3.1 Catalyst Preparation and Characterization

The procedures for preparing CMK-8 supported Pt catalysts are graphically illustrated in Fig. 1. The well ordered mesoporous structure with Ia3d symmetry of CMK-8 OMCs was still maintained even after loaded with Pt nanoparticles, which was confirmed by the low-angle XRD patterns and nitrogen adsorption–desorption isotherms of Pt/CMK-8 catalysts (Figs. 2, 3). As listed in Table 1, the specific surface areas for Pt/CMK-8 catalysts ranged from 1,233 to 1,318 $m^2\ g^{-1}$. To obtain further information on the CMK-8 structure, Raman spectroscopy was carried out. Similar to that of CMK-3 OMCs [17], the Raman spectrum of CMK-8 OMCs was also dominated by the G and D bands at 1,594 and 1,332 cm^{-1} respectively, together with two broad and weak bands centered at 2,650 and 2,914 cm^{-1} (inset of Fig. 2). This indicates that the CMK-8 OMCs are also composed of disordered graphene and small amount of amorphous carbon.

The Pt particle size was firstly characterized using the wide-angle XRD (Fig. 4). All the samples did not show distinct diffraction peaks assignable to Pt crystalline planes, demonstrating that the Pt nanoparticles were uniformly dispersed and did not aggregate to form large particles. The TEM images in Fig. 5 also confirmed that the Pt particles were uniformly dispersed. The Pt particle size and dispersion were also calculated according to the CO chemisorption. Consistent with the wide-angle XRD and TEM characterizations, the mean Pt particle size for the Pt/CMK-8-W and Pt/CMK-8-E catalysts was 2.3 and 4.2 nm, respectively.

3.2 Enantioselective Hydrogenation of α-Ketoesters

Based on the findings in the enantioselective hydrogenation of α-ketoesters with Pt/CMK-3 catalysts [17], we firstly carried out the asymmetric hydrogenation of ethyl pyruvate with CD modified 5 wt% Pt/CMK-8 catalysts. As also listed in Table 1, 97.8 % conversion with 74.7 % ee of (*R*)-(+)-ethyl lactate was afforded with CD-modified 5 wt% Pt/CMK-8-W catalyst (Table 1, entry 2). With regard to the same reaction with 5 wt% Pt/CMK-8-E

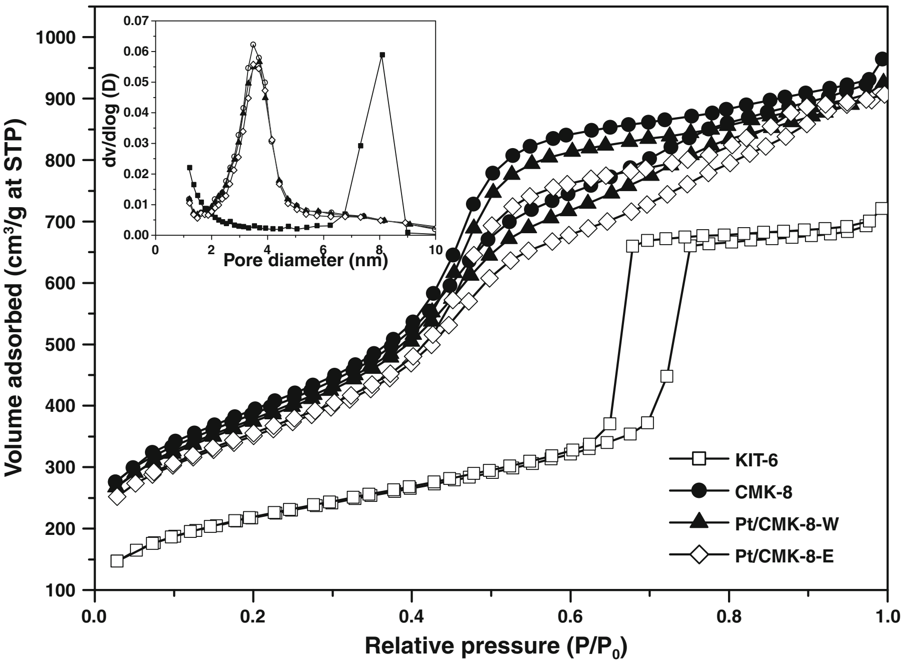

Fig. 3 N_2 sorption isotherms and pore size distribution of Pt/CMK-8 catalysts

Table 1 Relevant parameters of Pt/CMK-8 catalysts and the related samples and the results obtained on chirally modified Pt catalysts for the enantioselective hydrogenation of ethyl pyruvate

Entry	Catalyst	Pt content (wt%)	S_{BET} (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)	Pt diameter (nm)	Pt dispersion (%)	Conv. (%)	ee (%)
1	CMK-8	–	1364	3.5	1.50	–	–	0	0
2	5 wt% Pt/CMK-8-W	3.7	1318	3.7	1.43	2.3	48.8	97.8	74.7
3	5 wt% Pt/CMK-8-E	nm[c]	1233	3.5	1.40	4.2	27.5	67.5	53
4	5 wt% Pt/C[a]	4.0	892	3.8	1.07	10.3	11	16.8[b]	56.3
5	5 wt% Pt/Al_2O_3[a]	3.7	147	18.4	0.9	3.5	32.8	98.6[b]	92.6

Reaction conditions: Pt catalyst (0.026 mmol Pt), CD (0.034 mmol), ethyl pyruvate (21.07 mmol), acetic acid (20 ml), H_2 (4 MPa), 1,000 rpm, RT, 5 min and the main configuration of product is R

[a] Purchased from Alfa Aesar and pretreated in a hydrogen flow at 673 K for 2 h before use

[b] The results are quoted from Ref. [17]

[c] Not measured

catalyst, 67.5 % conversion with 53 % ee was achieved under the same conditions (Table 1, entry 3).

The activity of 5 wt% Pt/CMK-8-W catalyst for the enantioselective hydrogenation of ethyl pyruvate was higher than that of 5 wt% Pt/CMK-3-W catalyst, which had the similar Pt particle size and gave 81 % conversion with 82.2 % ee under the same conditions [17]. We also compared the performance of 5 wt% Pt/CMK-8 catalysts with that of the commercial 5 wt% Pt/Al_2O_3 and 5 wt% Pt/C catalysts in the asymmetric hydrogenation of ethyl pyruvate. Although the ee value obtained with 5 wt% Pt/CMK-8-W catalyst was slightly lower than that with 5 wt% Pt/Al_2O_3 catalyst, the conversions were comparable under the same conditions (Table 1, entry 5). Additionally, the 5 wt% Pt/CMK-8 catalysts were much more active than 5 wt% Pt/C catalyst, which afforded only 16.8 % conversion and 56.3 % ee (Table 1, entry 4). Hence, it is suggested that the large pore volume of CMK-8 OMCs is beneficial for the mass transfer.

In order to broaden the substrate scope, EOPB bearing a benzene ring with relatively large molecular size was taken as the other substrate. As listed in Table 2, the 5 wt% Pt/CMK-8-W catalyst furnished 93.4 % conversion and 75 % ee of (*R*)-(+)-EHPB under our conditions (Table 2, entry 1). The 5 wt% Pt/CMK-8-E catalyst gave 54.2 % conversion with 46.5 % ee (Table 2, entry 2). The commercial 5 wt% Pt/Al_2O_3 catalyst furnished 83.2 % conversion with 83.5 % ee (Table 2, entry 3). In terms of EOPB conversion under the same conditions, the 5 wt% Pt/CMK-8-W catalyst is even superior to the 5 wt% Pt/Al_2O_3

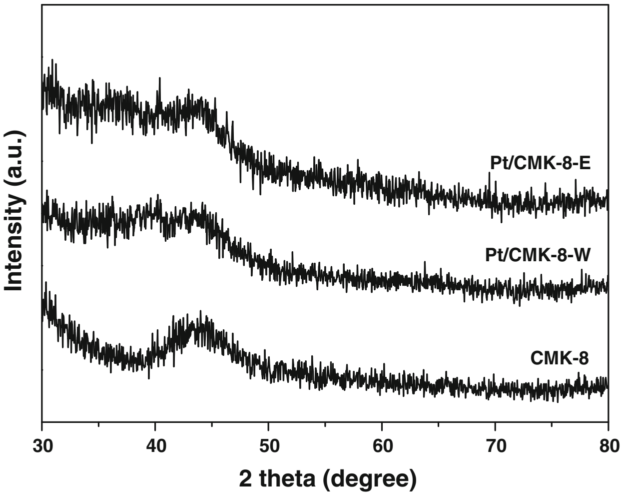

Fig. 4 Wide-angle XRD patterns of Pt/CMK-8 catalysts

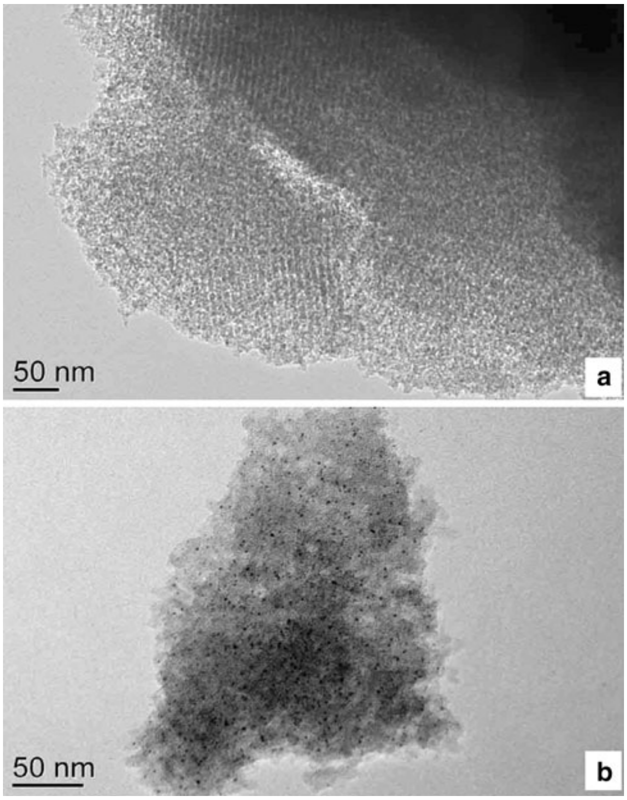

Fig. 5 TEM images of **a** Pt/CMK-8-W catalyst and **b** Pt/CMK-8-E catalyst

catalyst although the enantioselectivity is slightly lower. As for the commercial 5 wt% Pt/C catalyst, the lowest activity of 19.7 % conversion was obtained with 73.4 % ee (Table 2, entry 4).

Table 2 Reaction results obtained on chirally modified Pt/CMK-8 catalysts and related Pt catalysts for the chiral hydrogenation of EOPB

Entry	Catalyst	Pt particle size (nm)	Conv. (%)	ee (%)
1	5 wt% Pt/CMK-8-W	2.3	93.4	75
2	5 wt% Pt/CMK-8-E	4.2	54.2	46.5
3	5 wt% $Pt/Al_2O_3^a$	3.5	83.2	83.5
4	5 wt% Pt/C^a	10.3	19.7	73.4

Reaction conditions: Pt catalyst (0.026 mmol Pt); CD (0.034 mmol); EOPB (26.45 mmol); acetic acid (20 ml); H_2 (4 MPa); 1,000 rpm; RT; 5 min and the main configuration of product is R

[a] Purchased from Alfa Aesar and pretreated in a hydrogen flow at 673 K for 2 h before use

Table 3 Optimization of reaction parameters for the chiral hydrogenation of EOPB with chirally modified Pt/CMK-8-W catalysts

Entry	Pt loading (wt%)	CD amount (mmol)	Time (min)	Conv. (%)	ee (%)
1	5	0	5	3.8	0
2	5	0.017	5	92.2	74.5
3	5	0.051	5	75.6	75.4
4	5	0.034	2	41.2	75.5
5	3	0.034	5	39.6	70.0
6	10	0.034	5	94.0	75.5

Reaction conditions: Pt catalyst (0.026 mmol Pt); EOPB (26.45 mmol); acetic acid (20 ml); H_2 (4 MPa); 1,000 rpm; RT and the main configuration of product is R

To optimize the reaction parameters for the chiral hydrogenation of EOPB with Pt/CMK-8-W catalyst, a seires of experiments were carried out. The effect of Pt loading, reaction time and CD amount on the catalytic performance was investigated in detail. The 3 and 10 wt% Pt/CMK-8-W catalysts were prepared and investigated in the chiral hydrogenation of EOPB. The 3 wt% Pt/CMK-8-W catalyst gave 39.6 % EOPB conversion with 70 % ee value (Table 3, entry 5), while the 10 wt% Pt catalyst furnished 94 % conversion with 75.5 % ee value (Table 3, entry 6). The conversion and ee value were greatly increased when the Pt loading reached 5 wt% compared with those obtained with 3 wt% Pt/CMK-8-W catalyst. However, there was no obvious increase in both activity and enantioselectivity if the Pt loading was further increased from 5 to 10 wt%. The chiral hydrogenation of EOPB with 5 wt% Pt/CMK-8-W catalyst was also performed within 2 min. A 41.2 % conversion of EOPB with 75.5 % ee value was obtained (Table 3, entry 4). Additionally, the CD amount was also varied and as a result, 10 mg CD was the optimal dosage.

Among these catalysts, the 5 wt% Pt/CMK-8-W catalyst afforded the highest activity, resulting in a TOF of

34,819 h^{-1} based on the EOPB conversion within 2 min and the exact Pt content of 3.7 wt%. Of particular note is that the 5 wt% Pt/CMK-8-W catalyst is even more active than the Pt nanocatalyst confined within CNTs, which afforded higher than 20,000 h^{-1} TOF for the same reaction under the similar conditions [7]. The high activity of Pt/CMK-8-W catalyst might be mainly attributed to that the three-dimensional mesostructure with adequate pore volume is helpful for the asymmetric hydrogenation.

Although the ee value achieved with the 5 wt% Pt/CMK-8-W catalyst for the chiral hydrogenation of ethyl pyruavate and EOPB was a little lower, the catalytic activity of 5 wt% Pt/CMK-8-W catalyst was comparable with or even higher than the commercial 5 wt% Pt/Al_2O_3 catalyst. In order to identify how the Pt catalyst surface property affects the catalytic performance, the 5 wt% Pt/CMK-8-W catalyst was further characterized by XPS (Fig. 6). There are two Pt species for the 5 wt% Pt/CMK-8-W catalyst deduced from the deconvoluted Pt4f peaks (Fig. 6a). The one is Pt^{2+} species (the peaks of $4f_{7/2} = 73.4$ eV, $4f_{5/2} = 76.8$ eV), which is originated from re-oxidation of Pt when exposed to air. For the other Pt species, the Pt $4f_{7/2}$ and $4f_{5/2}$ peaks are observed at 72 and 75.3 eV and these values are shifted to higher binding energy compared with Pt^0 species (the peaks of $4f_{7/2} = 71.2$ eV, $4f_{5/2} = 74.5$ eV) [18]. This result indicates that electrons are donated from Pt to CMK-8 OMCs support and Pt exists as $Pt^{\delta+}$. Compared with the commercial Pt/alumina catalyst, which has $Pt^{\delta+}$ and Pt^0 species deduced from the diffuse reflectance infrared fourier transform spectroscopic studies using CO as a probe molecule, the dominant $Pt^{\delta+}$ species for the home-made Pt/CMK-8-W are beneficial for the activation of carbonyl groups, so that higher activity was achieved with Pt/CMK-8 catalyst [17, 19].

The XPS analysis of C1s region indicated that the CMK-8 OMCs are mainly composed of disordered graphene. For the sp^2-C, the C1s peak is observed at 284.7 eV. Besides the sp^2-C, there still exist sp^3-C (285 eV), oxygen containing C groups (286.1 and 288.8 eV). The results match well with the Raman characterization. This deduced that the high electron density of Pt/CMK-8 catalyst surface probably inhibits the adsorption of CD by quinoline moiety via the π interaction. As a result, slightly lower ee values were induced by CD-modified Pt/CMK-8 catalyst.

3.3 The Reusability of Pt/CMK-8 Catalyst

The reusability of Pt/CMK-8 catalyst is also an important matter to consider, so we also investigated the reusability of CD-modified Pt/CMK-8-W catalyst in detail. The Pt/CMK-8-W catalyst can be reused for almost 4 times for the enantioselective hydrogenation of ethyl pyruvate, although the conversion was gradually decreased with reaction runs. As a result, 97.8 % conversion was obtained with the fresh catalyst, whereas 82.8 % conversion of ethyl pyruvate was achieved in the fourth run (Fig. 7a). The enantioselectivity was maintained during the reuse since the fresh CD was added to each run.

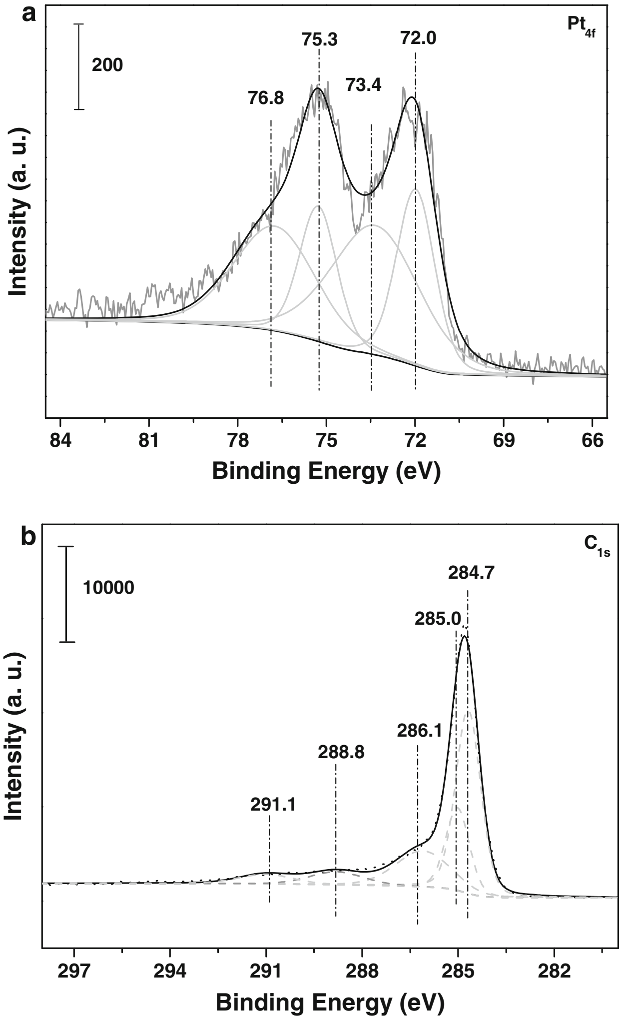

Fig. 6 XPS spectra for **a** Pt_{4f} and **b** C_{1s} regions of 5 wt% Pt/CMK-8-W catalyst

By comparison, the reusability of Pt/CMK-8-W catalyst towards the enantioselective hydrogenation of EOPB is a little poor although the enantioselectivity was maintained (Fig. 7b). The fresh catalyst gave 93.4 % conversion of EOPB, while the second run afforded 79 % conversion. The third and the fourth runs only gave 58.7 and 48 % conversion, respectively.

In order to make clear why EOPB conversion decreased dramatically during the reuse processes, the ICP-AES was carried out to detect the leached Pt atoms in the filtrate. As a result, about 7.8 % of Pt atoms were leached into the solution during the first run of EOPB hydrogenation, which is nearly eight times higher than that in the enantioselective hydrogenation of ethyl pyruvate with the same catalyst. We deduce that the d–π conjugation interaction between Pt

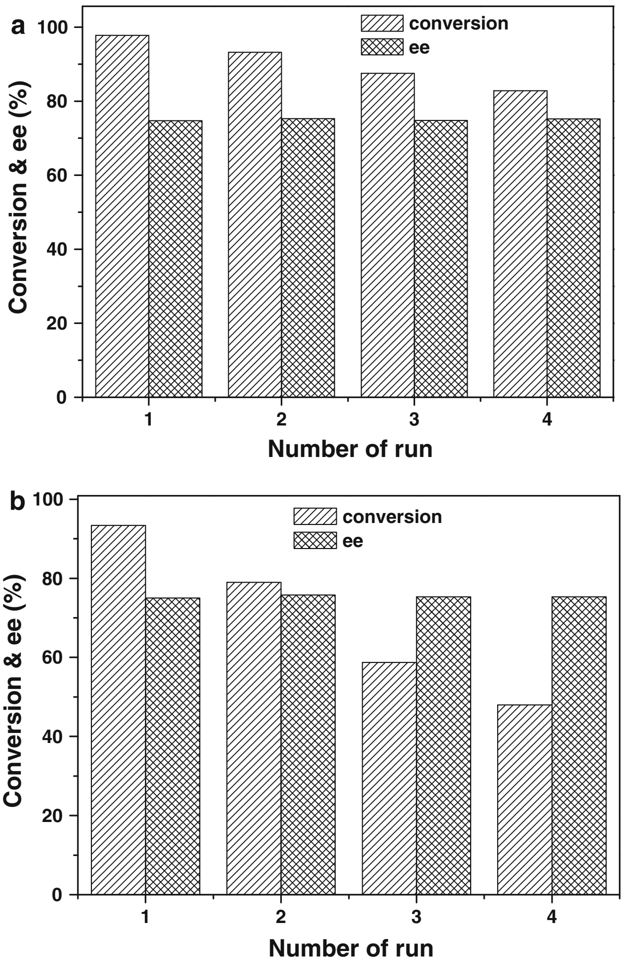

Fig. 7 Conversions and ee values versus number of run **a** in the asymmetric hydrogenation of ethyl pyruvate and **b** in the asymmetric hydrogenation of EOPB. The reaction conditions are same as Table 1, entry 2 and Table 2, entry 1, respectively

atoms and benzene ring of EOPB makes Pt atoms easier to dissolve in the solution. Since the leached Pt can not be ignored in this case, the separation and recovery of leached Pt should be paid much attention, particularly considering that the enantioselective reactions are mainly employed in Pharma industry. To the best of our knowledge, there are two main solutions about the leached Pt. The leached Pt can be recovered using an ion exchange resin scavenger such as DOWEX M-43 [20]. Alternatively, the leached Pt can be recovered as diammonium hexachloroplatinate by precipitation using ammonium chloride [21].

4 Conclusions

The CD-modified Pt/CMK-8 catalyst proved to be highly active and enantioselective for the chiral hydrogenation of ethyl pyruvate and EOPB under the mild conditions. The Pt/CMK-8 catalyst can also be reused for several times without significant loss of activity and enantioselectivity under the optimal conditions. Furthermore, the Pt/CMK-8 catalyst is much more active than the commercial Pt/C catalyst and even shows higher activity than the commercial Pt/Al_2O_3 catalyst in the chiral hydrogenation of EOPB. Of particular note is that the TOF higher than 34,000 h^{-1} and 75 % ee were achieved in the enantioselective hydrogenation of EOPB. To the best of our knowledge, these results with Pt/CMK-8 catalyst are the best ones among those obtained with Pt catalysts supported on carbon materials, including activated carbon, CNTs and OMCs.

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