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Short Communication

Alumina incorporated with mesoporous carbon as a novel support of Pt catalyst for asymmetric hydrogenation



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ABSTRACT

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1. Introduction

Asymmetric catalysis plays an extremely important role in synthesizing chiral drugs, agrochemicals, food addictives and fragrances [1]. Enantioselective hydrogenation of activated ketones has featured considerably in the synthesis of important organic compounds and has attracted the attention of synthetic chemists [2]. Among these reactions, the asymmetric hydrogenation of α -ketoesters on the cinchona-modified supported Pt catalyst has initiated an avalanche of research in asymmetric heterogeneous catalysis [3–5].

Since the cinchona-platinum/support catalyst was firstly reported by Orito [3,6], a variety of researches have been done focused on the supports for platinum nanoparticles. In the beginning, Al_2O_3 [4,7–9], SiO₂ [10,11], zeolite [12], etc., were considered to be suitable supports. However, these materials supported Pt catalysts showed only mediocre performance, except cinchonidine(CD)-modified 5 wt% Pt/Al₂O₃ exhibited excellent enantioselectivity. With the development of periodic mesoporous materials, MCM-41 [13], FDU-type periodic mesoporous resols (PMRs) [14] and CMK-8 carbons [15] were adopted as supports for Pt nanoparticles in the heterogeneous asymmetric hydrogenation of α -ketoesters, obtaining medium to good enantiomeric excesses (ees).

Recently, Chen and co-workers [16] reported the usage of carbon nanotubes (CNTs) as support for Pt nanoparticles. The resulting catalyst was found to exhibit superior performance in the hydrogenation of α -ketoesters compared to the traditional Pt/Al₂O₃ system. However, the uncontrollable procedure of the catalyst preparation and costly CNTs

Mesoporous carbon incorporated with different alumina contents has been prepared by chelate-assisted coassembly method. These composites were used as supports for Pt particles, and the as-prepared catalysts were reduced at 873 K in hydrogen atmosphere. Our current study by using N₂ sorption, X-ray diffraction and transmission electron microscopy revealed that carbon incorporated with 10–15 wt% alumina was favorable for the high Pt dispersion and retained the mesostructure of carbon. Moreover, 15 wt% alumina-carbon composite supported Pt particles modified by cinchonidine afforded the highest (84.8%) enantiomeric excess and could be reused at least five times for the asymmetric hydrogenation of ethyl 2-oxo-4-phenylbutyrate in acetic acid.

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limited the application of the catalyst in industry. Meanwhile, Wang and co-workers [17] incorporated alumina with well-ordered hexagonal mesoporous silica structures (SBA-15) by a solvent-free solid-state grinding method. The Al₂O₃-SBA-15 composites were proved to be remarkable supports for Pt nanoparticles. And the resulting catalyst modified with CD was found to be effective in the chiral hydrogenation of ethyl pyruvate. In contrast, the performance of Al₂O₃-FDU-14 PMRs supported catalysts was in medium level and this was attributed to the weak interaction between Al₂O₃ and FDU-14 PMRs [18]. Interestingly, Böttcher and co-workers observed high enantioselectivity in the hydrogenation of ethyl pyruvate while using alumina-fused silica composites as supports for Pt nanoparticles, CD as modifier [19].

Sun and co-workers [20] demonstrated that guest precursors, such as $Fe(NO_3)_3$ and $Co(NO_3)_2$ could be incorporated with phenolic resol by a chelate-assisted co-assembly method. Followed by calcination, mesoporous carbon with embedded metal oxide nanoparticles was formed. Herein, chelate-assisted co-assembly method was used to prepare mesoporous carbon incorporated with highly dispersed uniform Al_2O_3 particles. These Al_2O_3 -carbon composites were used as supports for Pt particles and the catalytic properties of the resulting catalysts were studied in the asymmetric hydrogenation of ethyl 2-oxo-4-phenylbutyrate (EOPB).

2. Experimental section

2.1. Preparation of Pt catalysts

Soluble resol precursors were prepared according to the literature [20]. The preparation of Al_2O_3 -carbon composites and the Pt/ Al_2O_3 -carbon catalysts were depicted in Fig. 1. Typically, pluronic



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F127 (1.0 g) was dissolved in absolute ethanol (20 mL). The resol precursor solution (20 wt% in ethanol, 6 mL) was added and stirred for 10 min. Then a solution of Al(NO₃)₃·9H₂O (0.75 g) dissolved in ethanol (6 mL) was dropped slowly into the above mixture. Subsequently, acetyl acetone (acac) (0.61 mL) was added (the molar ratio of acac/Al is 3/1). The mixture was cast onto Petri dishes after further stirring for 40 min. After the evaporation of the solvent (6-10 h) at room temperature, the resulting sticky film was subjected to thermocuring at 373 K for 24 h. The obtained composite film was scrapped off and cut into pieces, followed by pyrolysis in tube furnace at 873 K for 3 h under N₂ atmosphere (the temperature ramp rate was 1 K/min). The resulting composite was ground into powders. A series of samples with different Al₂O₃-contents were synthesized and designated as xAl₂O₃-MC (MC is the abbreviation of mesoporous carbon, x refers to Al₂O₃ weight content (wt %) in the Al₂O₃–MC), which were denoted hereafter as xAM.

The 5 wt% Pt/xAM catalysts were prepared by impregnation method: xAM was impregnated with an aqueous solution of platinum precursor (H_2PtCl_6) and stirred for 5 h. Then the mixture was evaporated to remove excess water, followed by drying at 373 K for 12 h. The catalyst precursors were reduced at 873 K in a hydrogen atmosphere before use.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were obtained in a Panalytical X'Pert-Pro powder X-ray diffractometer using Cu K α radiation (40 kV, 40 mA). N₂ adsorption–desorption isotherms were recorded on a Micrometitics ASAP 2020M+C analyzer at 77 K. The BET method was adopted to calculate the special surface areas using adsorption data in a relative pressure range from 0.05 to 0.20. The pore size distributions were derived from the adsorption branches of isotherms using the BJH model. Transmission electronic microscopy (TEM) images were taken on a HITACHI H-7650 electronic microscope with an accelerating voltage of 100 kV. The exact Pt contents of the catalysts were measured with an Optima 7000 DV inductively coupled plasma optical emission spectroscopy (ICP-OES).

2.3. Catalytic tests

The catalytic properties of Pt/xAM catalysts for asymmetric hydrogenation of EOPB to (R)-(+)-ethyl 2-hydroxy-4-phenylbutyrate ((R)-(+)-EHPB) were evaluated in a 100-mL stainless-steel stirred pressure reactor at room temperature. Based on some precedents, about 10 wt% cinchonidine (CD, relative to the Pt supported catalyst) was the optimal concentration for the Pt/Al₂O₃ [21] and Pt/mesoporous carbon [22] in the asymmetric hydrogenation of EOPB. Herein, we used the same concentration of CD for the Pt/xAM catalysts. Typically, 0.1 g of catalyst, 10 mg of CD, 1 mL of EOPB, 25 mL of solvent, 5 MPa of H₂ and a stirring speed of 700 rpm were used for the reaction. The reaction was terminated after 1 h and then the products were analyzed by gas chromatography (Agilent 6890) equipped with capillary chiral column (CP-ChiraSil-DEX CB 25×0.25 Agilent). The pure (*R*)-(+)-EHPB was used as the marker, and external standard method was used for identifying the major product. The optical yield was expressed as ee value: ee (%) = ([*R*] – [*S*]) / ([*R*] + [*S*]) × 100.

After the reaction, the catalyst was separated and washed with fresh acetic acid. Fresh reactant, CD and acetic acid were added to the reactor together with the recovered catalyst to carry out the next cycle reaction.

3. Results and discussion

3.1. XRD

Fig. 2 exhibited the low-angle and wide-angle XRD patterns of the xAMs and Pt/xAMs. Low-angle XRD patterns of xAMs (Fig. 2a) showed a resolved diffraction peak at $2\theta = 0.6-1.0^\circ$, which could be indexed to the (110) reflection of a 2-D p6mm hexagonal mesostructure. Along with the increase in Al₂O₃ content from 5 to 25 wt%, the diffraction intensities decreased obviously, suggesting that excess incorporation of Al₂O₃ deteriorated the structure regularity of mesoporous carbon. That the very weak diffraction intensity at $2\theta = 1.0^{\circ}$ of MC attributed to the shrinkage and collapse of the mesopores after the removal of F127. In the wide-angle XRD patterns of xAMs (Fig. 2b), two weak and broad diffraction peaks centered at 22.5° and 43.5° characteristic of amorphous carbon appeared [23]. No distinct diffraction peaks assigned to the crystalline alumina phases were observed from all the curves, indicating that the alumina was of low crystallinity and highly dispersed in the mesoporous carbon. This probably attributed to the high melting point of $Al(acac)_x$ (468 K), which decomposed to Al₂O₃ during pyrolysis at 873 K [24]. Without the addition of acac, aluminum species in the resol could readily migrate, aggregate and grow during both thermosetting and pyrolysis treatment because of the low melting point of aluminum nitrate (346 K). As for the decreased intensity of (100) diffraction peak after Pt loading and reduction at high temperature of the catalyst (Fig. 2c), it could be attributed to three points: First, Pt loading led to pore-filling effects that reduce the scattering contrast between the pores and the framework [25]; Second, high temperature catalyst reduction somewhat destroyed the mesoporous



Fig. 1. Preparation of alumina-carbon composites and 5 wt % Pt/alumina-carbon catalysts.



Fig. 2. Low-angle and wide-angle XRD patterns of xAMs (a, b) and Pt/xAMs (c, d).

carbon framework, which could reduce the regularity of mesoporous; Third, the micropores generated by further carbonization of the composites after catalyst reduction also made a contribution to reduce the pores' regularity. The wide-angle XRD patterns of Pt/xAMs (Fig. 2d) displayed five resolved diffraction peaks, which could be assigned to the (111), (200), (220), (311) and (222) reflections of face-centered cubic metallic Pt (JCPDS card no. 04-0802). The intensities of diffraction peaks depended on the Al₂O₃ contents, namely, a certain amount inclusion of Al₂O₃ facilitated the dispersion of the Pt particles [17], whereas excess amount incorporation of Al₂O₃ resulted in the aggregation of Pt after high temperature reduction.

3.2. Special surface area and pore size

The textural properties of Pt/xAMs were summarized in Table 1. It was noted that with a rise of alumina content from 5 wt% to 15 wt%, the BET surface areas, the total volume and pore size of these catalysts increased slightly, while with a further increase in alumina from

Table 1 Relevant parameters of 15AM, 5 wt% Pt/xAMs $^{\rm a},$ Pt/Al_2O_3 and Pt/C.

Sample	$S_{\rm BET} \left(m^2/g \right)$	$V_{\rm t} ({\rm cm^3/g})$	$D_{\rm p}({\rm nm})$	$D_{\mathrm{Pt}}^{\mathbf{b}}(\mathrm{nm})$	Pt content ^c (wt %)
Pt/5AM	727	0.62	4.8	7.2	6.0
Pt/10AM	734	0.68	5.6	5.2	7.7
Pt/15AM	704	0.70	5.6	6.1	6.9
Pt/25AM	401	0.33	4.2	8.1	6.5
15AM	397	0.32	5.6	_	_
Pt/MC	526	0.28	<2	8.1	5.7
Pt/Al ₂ O ₃ d	193	0.42	6.8	3.1	3.8
Pt/C ^e	892	1.07	3.8	10.0	4.0

^a The Pt/xAM samples were reduced at 873 K for 2 h in a hydrogen atmosphere.

^b Average Pt sizes were estimated by the Scherrer equation from XRD patterns.

^c Exact Pt contents were measured by ICP-OES.

^d Prepared according to Ref. [24].

^e Purchased from Alfa Aesar and pretreated in a hydrogen flow at 673 K for 2 h.



15 wt% to 25 wt%, these pore parameters decreased. These results

implied that the presence of Al₂O₃ could limit the shrinkage of the

mesostructure of carbon during the high temperature reduction, and

pore-blocking occurred upon the incorporation of Al₂O₃ more than 15

wt%. N₂ adsorption-desorption isotherms of 15AM and Pt/15AM

(Fig. 3) showed representative type IV curves with pronounced H2

hysteresis loops, which attributed to the presence of well-developed

meso- and microporosity [20]. The pore size distribution curves (Fig. 3

inset) revealed the presence of relatively uniform mesopores in 15AM,

while pore parameters and special surface area became much larger

after Pt loaded and catalyst reduced (Table 1). This probably due to the generation of much more micropores by further carbonization of resol and the removal of trace amount of F127 when reduction at 873 K.

Fig. 3. $N_{\rm 2}$ sorption isotherms and corresponding pore size distributions (inset) of 15AM and Pt/15AM.



Fig. 4. TEM images of 15AM (a) and Pt/15AM (b).

3.3. TEM

TEM images of 15AM (Fig. 4a) showed stripe-like and hexagonally arranged pore morphology over large domains, indicating an ordered mesostructure with 2-D hexagonal pore symmetry. After Pt precursor loading and reduction at high temperature of the catalyst, the 2-D hexagonal pore morphology was not visible in the TEM images (Fig. 4b). These observations were further supported by low-angle XRD patterns (Fig. 2c). The non-visibility of the 2-D pore morphology was caused by pore-filled effect and the destruction of the ordered structure. The particle size distribution (Fig. 4b, inset) showed the most probable Pt particle size was 6.5 nm, which was consistent with the analysis of wide-angle XRD patterns (Fig. 2d and Table 1).

3.4. Asymmetric hydrogenation of EOPB

The results for asymmetric hydrogenation of EOPB on CD-modified Pt/xAM catalysts are listed in Table 2. It was noted that with an increase in Al₂O₃ amount from 5 wt% to 15 wt%, the conversion changed slightly, while the ee value increased obviously, and CD-modified Pt/15AM afforded the highest ee value of 84.8% (Table 2, Entry 1-3). The conversion was almost the same which may attribute to the similar surface area, pore size and Pt size of these catalysts. The alumina played an important role in determining the ee value could be interpreted as follows: first, the presence of alumina can stabilize the mesostructure of carbon and get relatively big pores, which facilitated the diffusion and adsorption on catalyst surface of chiral modifier; second, the introduction of alumina embedded into the mesopores of carbon host

Table 2

Reaction results of CD-modified Pt/xAMs for asymmetric hydrogenation of EOPB.^a

OEt	Pt/xAMs, Cinchonidine Solvent, H ₂	OH OEt	
EOPB		(<i>R</i>)-(+)-EHPB	Cinchonidine
Entry	Catalyst	Conv.%	ee%
1	Pt/5AM	97.6	74.2
2	Pt/10AM	97.4	80.7
3	Pt/15AM	97.0	84.8
4	Pt/25AM	93.1	80.0
5	Pt/MC	70.7	67.5
7	Pt/Al_2O_3	98.9	83.5
8	Pt/C	96.9	69.2

^a Reaction conditions: Pt catalyst (100 mg); CD (10 mg); EOPB (1 mL); acetic acid (25 mL); H_2 (5 MPa); RT; 700 rpm; 1 h and the main configuration of product is R.

generated $Pt^{\delta+}$ species, and the $Pt^{\delta+}$ species probably responsible for the enantioselection [17]; third, in acetic acid, alumina can form a kind of electrophilic alumina compound, $O^+(Al(OAC)_2)_3$ (oxonium ions), which may be in favor of the adsorption of CD and plays an important role in the development of chiral environment [26].

With a further increase in Al_2O_3 amount from 15 wt% to 25 wt%, both the conversion and the ee values decreased (Table 2, Entry 4). The decrease in the conversion attributed to the obvious decline of the BET surface area and slightly sintering of Pt particles. The change of the ee attributed to the decrease in the pore size, which might limit the diffusion of CD to Pt surface. As for the Pt/MC catalyst only afforded 70.7% conversion and 67.5% ee value (Table 2, Entry 5), it may be due to the serious destruction of mesostructure after high temperature reduction resulting in the coverage of some active sites. With regard to a bit higher ee value on Pt/15AM than on Pt/Al₂O₃, it may be caused by the larger Pt particles of Pt/15AM. These larger particles may give rise to more flat adsorption of CD on Pt surface and the flat adsorption of CD was considered to facilitate the reaction with enhanced enantioselectivity [27].

The reusability of the CD-modified Pt/15AM in the asymmetric hydrogenation of EOPB was also investigated. Fig. 5 showed the conversion and the ee values against the number of runs. It was noted that Pt/15AM could be reused for more than five times without any loss of enantioselectivity and activity. The slight increase in ee value after the first run may be due to the structural reorganization of mesoporous carbon composite. The superior stability of Pt/15AM mainly



Fig. 5. Reusability of Pt/15AM catalyst in the asymmetric hydrogenation of EOPB. The reaction conditions are same as Table 2, entry 3.

ascribed to the Pt nanoparticles could be stabilized by the π -donating interaction from the benzene rings of mesoporous carbon composite to Pt particles [22].

4. Conclusions

A series of alumina-carbon composites, with different alumina contents, were synthesized by chelate-assisted co-assembly approach, and these materials were used as supports for Pt particles. One-step high temperature (873 K) reduction method was applied to reduce the catalysts, and the supports containing 10–15 wt% alumina were favorable for the platinum dispersion and retaining the mesostructure of carbon. The CD-modified Pt/15AM showed remarkable catalytic performance for asymmetric hydrogenation of EOPB in acetic acid and afforded up to 84.8% ee value and a constant activity after 5th re-use, owing to the special surface properties of the composite. This novel Pt-supported catalyst was expected to show high activity and enantioselectivity for the catalytic hydrogenation of other compounds with carbonyl groups.

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