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Size effects of supported Pt nanoparticles were entirely different for benzylic alcohols aerobic oxidation and hydrogenation reduction of nitroaromatics

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ARTICLE TYPE

Distinctive size effects of Pt nanoparticles immobilized on Fe_3O_4 (a) PPy used as an efficient recyclable catalyst for benzylic alcohols aerobic oxidation and hydrogenation reduction of nitroaromatics

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 Fe_3O_4 @PPy composite microspheres have been synthesized using Fe_3O_4 microspheres as a chemical template under an ultrasonic treatment process. Pt nanoparticles (NPs) were immobilized onto Fe_3O_4 @PPy by using ethylene glycol (EG) and NaBH₄ as reducing agent. The information of the

- ¹⁰ morphologies, sizes, and dispersion of Pt NPs of the as-prepared catalysts was verified by TEM, XRD, FTIR and XPS. As expected, the chemical reduction methods remarkably affected the size of Pt NPs (~2.5nm and ~5.5nm, respectively) and the prepared catalysts exhibited high catalytic activities as well as awsome stabilities for aerobic oxidation of benzylic alcohols and hydrogenation reduction of nitroaromatics. It was highlighted that size effects for the catalytic properties of the two reactions were
- ¹⁵ found to be quite different. Fe₃O₄@PPy-Pt (2.5nm) afforded a higher conversion for benzylic alcohols aerobic oxidation, while the selectivities toward benzaldehyde over these two catalysts were similar. However, they showed almost same catalytic performance for hydrogenation reduction of a majority of nitroaromatics. What's more, Fe₃O₄@PPy-Pt (5.5nm) gave better activities of several nitroaromatics which were relatively difficult to be hydrotreated under the same conditions. In addition, the EG reduced ²⁰ Fe₃O₄@PPy-Pt catalyst exhibited slightly poorer stability than the NaBH₄ reduced Fe₃O₄@PPy-Pt
- 10 re²O₄(*W*PPy-Pi catalyst exhibited signify poorer stability than the NaBH₄ reduced re³O₄(*W*PPy-Pi catalyst in the recycle tests, which might due to the agglomeration of small Pt NPs.

Introduction

The function of a heterogeneous catalyst with supported active component is determined by the complicated interplay of many ²⁵ factors. The size of the active component is one of the most important factors in controlling the catalytic performance in many systems¹. Nanosized particles of noble metals as active components have attracted much interest in recent years because of their size-dependent catalytic properties². Among noble ³⁰ metals, Pt NPs, with good resistance to corrosion and chemical attack³, play a major role in many applications such as electrocatalysis⁴, photocatalysis⁵, biosensors⁶ and other

- heterogeneous catalysis⁷. It is expected that, the size of Pt NPs may affect the electronic structure and the coordination structure ³⁵ of the active site, and thus may influence the activation of
- reactant molecules and the active species, leading to differences in activity and/or selectivity⁸. Therefore, the deep understanding of the size effect of supported Pt NPs in various kinds of reactions would be very helpful for the rational design of highly 40 efficient catalysts.
- However, Pt is not common and cheap enough for widespread application. So it is a big challenge to improve the efficiency, save resource and increase recycle rate. In recent years, there has been an increasing trend toward the use of magnetically
- ⁴⁵ retrievable materials in a variety of areas⁹. Fe₃O₄ as a superior magnetic material, has been used in efficient green chemical

synthesis and biomedical sciences¹⁰. Moreover, interest in preparation of shell coated magnetic Fe₃O₄ microparticles is increasing dramatically. So far, different kinds of shell have been ⁵⁰ reported to coat magnetic Fe₃O₄ microparticles¹¹. Our team also has reported many works about synthesis and application of coreshell Fe₃O₄ supported nanoparticle catalysts^{7b, 12}. The catalyst with magnetic particle core allows it to be facilely recovered and reused using an external magnet. And the shell coating Fe₃O₄ solution effect, thus, avoiding metal NPs splitting from the support during the catalytic reaction.

In previous report, reduction method or reducing agent of platinum mainly include photodeposition, radiation-induced, 60 ethylene glycol, ethanol, sodium borohydride, hydrogen, sodium phosphinate, argon plasma and so on¹³. And size effects of supported Pt NPs have been used in nanoparticles-electrocalytic oxidation reaction. In this work, Fe₃O₄@PPy composite immobilize different sizes of Pt NPs using ethylene glycol and 65 sodium borohydride as classical reducing agent. And the information of the morphologies, sizes, and dispersion of Pt NPs for the as-prepared catalysts is investigated. Meanwhile, the size effects of Pt NPs are tested in aerobic oxidation of benzylic alcohols and hydrogenation reduction of nitroaromatics. It is 70 conceivable that catalytic activities of the two completely opposite reactions would give a relevant conclusion about sizes

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effects of the supported Pt NPs catalysts. To our best knowledge, size effects of Pt NPs supported on magnetic core-shell material for different kinds of reaction have not been reported.

Experimental

5 Materials

Iron (III) chloride hydrate, sodium acetate, Poly-N-vinylpyrrolle-2-one (PVP, K-30), ethylene glycol, pyrrole, potassium chloroplatinite, hexachloroplatinic acid, ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Various reaction 10 reagents, such as 4-mthylbenzyl alcohol, 4-chlorobenzyl alcohol, 4-methoxybenzyl alcohol, 4-nitrobenzyl alcohol, 4bromonitrobenzene, 4-nitroanisole, 4-methylnitrobenzene, 2, 5dichloronitrobenzene, 1-nitronaphthalene and 4chloromethylnitrobenzene, were purchased from Alfa Aesar. All 15 chemicals were of analytical grade and used as received without further purification. Deionized water was used throughout the experiments

Preparations of Fe₃O₄@PPy-Pt catalysts

Fe₃O₄ microparticles were synthesized with the solvothermal ²⁰ method according to our previous Work^{7b}. Firstly, 1.5 g FeCl₃·6H₂O, 1.0 g PVP and 2.0 g NaAc were added into 200 mL ethylene glycol. The mixture was stirred violently for 2 hours to make all materials dissolve completely. Then the mixture was transferred to a Teflon-lined stainless steel autoclave and sealed ²⁵ to heat at 200 °C for 8 h. The precipitated black product was collected from the solution by an external magnet and washed

- with deionized water and ethanol several times. Finally, the black product was dried in a vacuum for 24 h at 60°C. Typically^{12c}, Fe₃O₄ microparticles (0.30 g) were dispersed in 70
- ³⁰ mL H₂O under sonication, and then pyrrole (4 mL) in ethanol (15 mL) and HCl solution (15 mL, 6 M) were added into the above solution in turn under sonication for 1 h. Finally, the black product was collected with the help of a magnet, washed with deionized water and ethanol repeatedly to remove the residual ³⁵ pyrrole monomers and HCl acid, and then dried in a vacuum at
- 60° C for 12 h to get magnetic Fe₃O₄@PPy composite. Syntheses of Fe₃O₄@PPy-Pt(EG). An aqueous solution of Fe₃O₄@PPy (100 mg) in deionized water (100 mL) was
- ultrasonicated for 1 h to form a uniform suspension. ⁴⁰ Subsequently, K₂PtCl₄-EG (0.005 M, 10 mL) solution was added to the suspension and sonicated for 2 h. The pH of the solution was adjusted to 10 using potassium hydroxide-EG (KOH-EG) solution (0.1 M), and then the solution was stirred under argon at
- solution (0.1 M), and then the solution was suffed under argon at 130°C for 3h. The precipitated black product was collected from 45 the solution by an external magnet and washed with deionized water and ethanol. The step was repeated several times before drying in vacuum at 60°C for 24h.

Syntheses of $Fe_3O_4@PPy-Pt(NaBH_4)$. An aqueous solution of $Fe_3O_4@PPy$ (100 mg) in deionized water (100 mL) was

- $_{\rm 50}$ ultrasonicated for 1 h to form a uniform suspension. Then, an aqueous solution of $\rm H_2PtCl_6$ (0.01 M, 5.6 mL) was added into the suspension under stirring and the mixture was stirred for 30 min at room temperature. Subsequently, the NaBH_4 solution (0.01 M, 50 mL) was delivered by drops into the above suspension under
- ss continuous stirring. After reacting for 3 h at room temperature, the precipitated black product was collected from the solution by

an external magnet and washed with deionized water and ethanol several times and finally dried in a vacuum at 60° C for 12 h.

Characterizations of Fe₃O₄@PPy-Pt catalyst

- ⁶⁰ These magnetic micro-materials were characterized inductively coupled plasma (ICP), powder X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), fourier transform-infrared (FT-IR) and vibrating sample magnetometry (VSM). XRD measurements ⁶⁵ were performed on a Rigaku D/max-2400diffractometer using Cu–Ka radiation as the X-ray source in the 2θ range of 5–80°. The size and morphology of the magnetic microparticles were observed by a Tecnai G2 F30 transmission electron microscopy and samples were obtained by placing a drop of a colloidal ⁷⁰ solution onto a copper grid and evaporating the solvent in air at room temperature. Pt content of the catalyst was measured by ICP on IRIS Advantage analyzer. Magnetic measurements of Fe₃O₄@PPy-Pt were investigated with a Quantum Design VSM at room temperature in an applied magnetic field sweeping from Other Res.
- 75 8 to 8 kOe. XPS was recorded on a PHI-5702 instrument and the C1s line at 284.8 eV was used as the binding energy reference.

Typical procedure for aerobic oxidation of benzylic alcohols

In a typical process, benzylic alcohols and Pt of Fe₃O₄@PPy-Pt with a mole ratio of 50 were dissolved in 5 mL deionized water. ⁸⁰ Then the reactions were carried out under oxygen atmosphere with electro-magnetic stirring at 40°C for a certain time. After the reaction, the aqueous phase was extracted five times with diethyl ether. Then the combined organic extracts were dried over MgSO₄ and analyzed by characterizing the reaction mixture using ⁸⁵ Gas Chromatograph-Mass Spectrometer (GC-MS).

Typical procedure for hydrogenation reduction of nitroaromatics

In a typical process, nitroaromatics and Pt of Fe₃O₄@PPy-Pt with a mole ratio of 200 were dissolved in 5 mL ethanol. Then the ⁹⁰ reactions were carried out under hydrogen atmosphere with electro-magnetic stirring conditions at room temperature for a certain time. The reaction was monitored and analyzed by characterizing the reaction mixture using GC-MS.

Results and Discussion

95 Preparation and characterizations of Fe₃O₄@PPy composite and Fe₃O₄@PPy-Pt catalyst



Scheme 1 Preparation process of catalysts

The process of preparation of the Fe₃O₄@PPy-Pt catalyst is ¹⁰⁰ schematically described in Scheme 1. Fe₃O₄ microparticles were synthesized with the solvothermal method according to our previous Work^{7b}. Secondly, in the strong acidic solution, the Fe³⁺ released from Fe₃O₄ microspheres and the polymerization of pyrrole monomers occurred, thus a layer of polypyrrole was

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coated on the surface of $Fe_3O_4^{12c}$. Thirdly, under magnetic stirrers, K₂PtCl₄ and H₂PtCl₆ were reduced onto the surface of polypyrrole by EG and NaBH₄ to obtain Fe₃O₄@PPy-Pt catalysts.



Fig. 1 TEM images of (a) Fe₃O₄, (b) Fe₃O₄@PPy

Fig. 1a shows the typical TEM image of Fe₃O₄ microspheres prepared by the versatile solvothermal reaction. As can be seen from the image, the average diameter of the as-synthesized spherical particles was about 400 nm. The TEM image in Fig. 1b 10 showed that a continuous layer of PPy could be observed on the outer shell of the Fe₃O₄ microsphere cores and the thickness was about 35 nm. The resultant Fe₃O₄@PPy composites had good dispersibility and spherical morphology.



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The XRD pattern of Fe₃O₄ (Fig. 2a) and Fe₃O₄@PPy (Fig. 2b) showed characteristic peaks of magnetite microparticles and the sharp. The main peaks of the Fe₃O₄@PPy composite were similar to the Fe_3O_4 , exhibiting that the coating process under acidic 20 conditions did not affect the structure of Fe₃O₄. Both of the two patterns showed strong peaks which confirmed the products were well-crystallized and detected diffraction peaks in every pattern could be indexed as cubic Fe₃O₄ (JCPDS card No. 82-1533). A broad peak was observed at $2\theta = 10^{\circ} - 25^{\circ}$, which suggested ²⁵ newly generating a layer of PPy¹⁴.



Fig. 3 FT-IR patterns of (a) Fe₃O₄, (b) Fe₃O₄@PPy

The compositions of Fe₃O₄@PPy composite microsphere were confirmed by FT-IR (Fig. 3). As was also shown in the picture, in ³⁰ the low-frequency region, the peak at 586.3 cm⁻¹ (Fig. 3a), 582.5 cm⁻¹ (Fig. 3b) corresponded to the stretching vibration peak of Fe-O. From the spectrogram, the peaks around at 1562 cm⁻¹ (C=C stretching vibrations), 1209 cm⁻¹ (C-N stretching vibrations), and 931 cm⁻¹ (C-H stretching vibrations) revealed the presence of 35 PPv.



Fe₃O₄@PPy-Pt(NaBH₄); particle size distribution of (c) Fe₃O₄@PPy-Pt(EG) and (f) Fe₃O₄@PPy-Pt(NaBH₄)

The morphologies, the sizes, and the dispersion of Pt NPs deposited on Fe₃O₄@PPy had been investigated by TEM (Fig. 4). As exhibited in Fig. 4d, e and f, the Pt NPs reduced by NaBH₄ were randomly dispersed on Fe₃O₄@PPy with a wide size New Journal of Chemistry Accepted Manuscrip

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distribution affording an average diameter of about 5.5 nm (Fig 4f). On the other hand, the Pt NPs got by using EG as reducing agent, which were observed with a narrow size distribution with a average diameter of about 2.5 nm (Fig 4c), were equably attached ⁵ on the surface of Fe₃O₄@PPy (Fig. 4a, b). However, it possessed a more inferior crystal structure than that of the Pt/NaBH₄ (HRTEM in the inset image in Fig. 4b, e), which indicated NaBH₄ was a better reducing agent to forming perfect crystal structure of Pt NPs. Therefore, it was significant to control the ¹⁰ reducing agents and reducing conditions for the design of the



Fig. 5 XPS spectra for (a) Fe₃O₄@PPy-Pt(EG) and (b) Fe₃O₄@PPy-Pt(EG) showing Pd 3d_{5/2} and Pd 3d_{3/2} binding energies.

- ¹⁵ The XPS elemental survey scan of the surface of the Fe₃O₄@PPy-Pt(EG) was showed in Fig. 5a. Peaks corresponding to iron, oxygen, nitrogen, palladium and carbon were clearly observed. To ascertain the oxidation state of the Pt, XPS studies was carried out. The XPS analysis of the Pt (0) catalyst showed in ²⁰ Fig. 5b. As expected, the spectrum of the Pt 4f region confirmed
- the presence of Pt (0) with peak binding energy of 71.2 and 75.2 eV, which were assigned to Pt $4f_{5/2}$ and Pt $4f_{7/2}$, respectively.



Fig. 6 VSM of (a) Fe_3O_4 , (b) Fe_3O_4 @PPy, (c) Fe_3O_4 @PPy-Pt(EG) and (d) Fe_3O_4 @PPy-Pt(NaBH₄)

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Since the ability of recoverability was important for this catalyst, magnetic measurements were performed using a VSM at room temperature. As shown in Fig. 6, Fe₃O₄@PPy (Fig. 6b), Fe₃O₄@PPy-Pt(EG) (Fig. 6c) and Fe₃O₄@PPy-Pt(NaBH₄) (Fig. ³⁰ 6d) showed small reduction of the saturation magnetization. This slightly reduction of the saturation magnetization for the material loaded solid was expected. The measured saturation magnetizations were 36.0 emug⁻¹ for Fe₃O₄@PPy-Pt(EG) (Fig. 6c) and 34.4 emug⁻¹ for Fe₃O₄@PPy-Pt(NaBH₄) (Fig. 6d). The

³⁵ decrease of the saturation magnetization suggested the presence of platinum nanoparticles on the surface of the magnetic support. Even with this reduction in the saturation magnetization, the catalyst could still be efficiently separated from solution with an external magnet as shown in the inset image in Fig. 6.

40 Catalyst testing for the aerobic oxidation of benzylic alcohols and hydrogenation reduction of nitroaromatics

For compare of the catalytic activity of the two Fe₃O₄@PPy-Pt catalysts, the benzylic alcohols aerobic oxidation and hydrogenation reduction of nitroaromatics were carried out under $_{45}$ atmospheric pressure of O₂/H₂ as model reactions.

Table 1 Aerobic oxidation of various benzylic alcohols in water						
R	OH Cat (2 mol % of Pt) H ₂ O; O ₂ (1 atm; 40°C	R	о н	+	Он	
		Λ		i	3	
Entry	Substrate	Catalyst	Time (h)	A Yield (%)	B Yield (%)	
1		Pt/EG ^a	8	81	13	
2		Pt/NaBH4 ^b	8	72	10	
3		Pt/EG	8	75	12 ^c	
4	\wedge \wedge	Pt/NaBH ₄	8	70	10^{d}	
5	ОН	Pt/CNT- plasma	2	18 ^e		
6	-	Pt/CNT- IMP	2	13	3^{f}	
7		nPt@hC ^g	24	46		
8		Pt/AC ^h	24	44		
9		Pt/EG	6	93	4	
10	\land	Pt/NaBH ₄	6	85	4	
11	ОН	PS-PtNPs ⁱ	10	80	16	
12		Pt/C^{j}	10	60	10	
13		$K_2PtCl_4{}^k$	10	0	0	
14	ОН	Pt/EG	6	96	<1	
15	MeO	Pt/NaBH ₄	6	87	<1	
16	ОН	Pt/EG	10	82	15	
17	CI CI	Pt/NaBH ₄	10	77	12	
18	ОН	Pt/EG	12	74	9	
19	0 ₂ N	Pt/NaBH ₄	12	59	7	

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^a Fe₃O₄@PPy-Pt(EG); ^bFe₃O₄@PPy-Pt(NaBH₄); ^{c, d} Yield after 5 runs; ^{e,f}[ref 13f] conversion of benzyl alcohol. Reaction conditions: alcohol 1

 $_5$ mmol, deionized water 50 ml, catalyst 4mg (0.001 mmol Pt), O₂ flow rate 25 ml/min, T=75 °C, t=2 h; $^{\rm g.h}$ [ref 15a] Reaction conditions: catalyst 0.1 mol% of Pt, O₂ balloon, T=60 °C, t=24 h; $^{\rm i, j., k}$ [ref 15b] Reaction conditions: alcohol 0.5 mmol, deionized water 1 ml, catalyst 2.0 mol% of Pt, O₂ balloon, T=30 °C, t=10 h;

- ¹⁰ Table 1 listed the catalytic performances of Fe₃O₄@PPy-Pt(EG) and Fe₃O₄@PPy-Pt(NaBH₄) in aerobic oxidation of benzyl alcohol in aqueous solution. The reactions with Fe₃O₄@PPy-Pt(EG) took place at 40°C for 8 h in the absence of base to gave a mixture of benzaldehyde and benzoic acid in 81% and 13%
- ¹⁵ yields, respectively (Table 1, entry 1). In contrast, Fe₃O₄@PPy-Pt(NaBH₄) exhibited slightly lower catalytic activity, probably due to their large particle size (entry 2). To further address this issue, alcohol substrates with different electron densities were introduced as probes to examine the catalytic activities of
- ²⁰ Fe₃O₄@PPy-Pt(EG) and Fe₃O₄@PPy-Pt(NaBH₄), and the results were shown in Table 1 (entry 9-19). When the aerobic oxidation was performed with para-substituted benzyl alcohols, the electron-donating group facilitated the reaction. Compared to benzyl alcohol, 4-mthylbenzyl alcohol, 4-chlorobenzyl alcohol

25 and 4-methoxybenzyl alcohol showed a higher conversion, while 4-nitrobenzyl alcohol showed a lower conversion over both Fe₃O₄@PPy-Pt(EG) and Fe₃O₄@PPy-Pt(NaBH₄) catalysts. Both catalysts showed higher catalytic activity for substituted aromatic alcohols containing electron-donating group (-CH₃, -OCH₃ and -30 Cl) than those containing electro-withdrawing group (-NO₂), implying that the electronic effects and intrinsic properties of Pt NPs over these two catalysts were the same^{13f}. On the other hand, while the conversions over Fe₃O₄@PPy-Pt(EG) were constantly higher than Fe₃O₄@PPy-Pt(NaBH₄) for different aromatic 35 alcohols, the selectivities toward benzaldehyde over these two catalysts were similar. This illustrated the EG reduced small Pt NPs was only beneficial to improve the conversion of benzylic alcohols aerobic oxidation not the selectivity of benzaldehyde. In addition, both Fe₃O₄@PPy-Pt(EG) and Fe₃O₄@PPy-Pt(NaBH₄) 40 exhibited better catalytic properties than those already reported as shown in Table 1, entry 5-8, 11-13.13f, 15

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Table 2 Hydrogenation	reduction	of various	nitroaromat	ics in ethanol

	Cat (0.	5 mol % of Pt)		NH
	Ethanol	; H ₂ (1 atm); R.T.	R	
Entry	Substrate	Catalyst	Time (min)	Yield (%)
1		Pt/EG ^a	40	>99
2		Pt/NaBH4 ^b	40	>99
3		Pt/EG	40	92.5°
4		Pt/NaBH ₄	40	95.1 ^d
3		Pt/EG	40	98.7
4		Pt/NaBH ₄	40	98.2
5	Br-NO ₂	Pt/EG	40	98.4
6		Pt/NaBH ₄	40	98.0
7		Pt/EG	40	97.7
8		Pt/NaBH ₄	40	97.5
9		Pt/EG	40	>99
10	HONO2	Pt/NaBH ₄	40	>99
11		Pt/EG	40	95.2
12	H3CC	Pt/NaBH ₄	40	95.6
13 14		Pt/EG	60 120	85.5 88.6
15	H ₂ N NO ₂	Pt/NaBH ₄	60	88.8
16 17	NO ₂	Pt/EG	90 180	90.3 92.9
18		Pt/NaBH ₄	90	95.5
19		Pt/EG	240	67.3
20		Pt/NaBH	480 240	/1.6
21	_cı	1 U 1 (1 DI 14	240	18.4
23		Pt/EG	480	20.7
24		Pt/NaBH ₄	240	37.2

^a Fe₃O₄@PPy-Pt(EG); ^b Fe₃O₄@PPy-Pt(NaBH₄); ^{c, d} Yield after 5 runs

In order to give a relevant conclusion about sizes effects of the ⁵ supported Pt NPs catalysts, the catalytic activities were also tested for the hydrogenation of a variety of nitroaromatics to their corresponding products. The reactions were carried out in ethanol at room temperature and under 1 atm pressure of H₂. Detailed observations of all the reactions were given in Table 2. In contrast ¹⁰ to aerobic oxidation reactions, catalytic properties of

- Fe_3O_4 @PPy-Pt(EG) and Fe_3O_4 @PPy-Pt(NaBH₄) for hydrogenation of most nitroaromatics were almost the same (entry 1, 2, 5-12), being very active for the hydrogenation reaction under such mild conditions and affording over 95% yield
- ¹⁵ of aminobenzene. It was worth noting that Fe₃O₄@PPy-Pt(NaBH₄) gave better activities to several nitroaromatics which were relatively difficult to be hydrotreated under the same conditions (entry 13-24). Interestingly, along with the increase of

the difficulty of the hydrogenation reaction, the gap between the ²⁰ yields got by the two catalysts was widening in the same reaction time. For instance, the yield of 2, 5-dichloroaniline catalyzed by Fe₃O₄@PPy-Pt(NaBH₄) achieved 37.2% (entry 24) — more than twice the yield by Fe₃O₄@PPy-Pt(EG) (entry 22). And even if the reactions time catalyzed by Fe₃O₄@PPy-Pt(EG) had been ²⁵ doubled, the yields of phenylamines were still lower than yields catalyzed by Fe₃O₄@PPy-Pt(NaBH₄), indicating these hydrogenation reactions had achieved the final stages of reactions in the corresponding time. This might be due to the better crystal structure of NaBH₄ reduced Pt NPs, which probably be in favour ³⁰ of improving catalytic activities.



Fig. 7 TEM images of (a) Fe₃O₄@PPy-Pt(EG) and (c) Fe₃O₄@PPy-Pt(NaBH₄); HRTEM images of (b) Fe₃O₄@PPy-Pt(EG) and (d) Fe₃O₄@PPy-Pt(NaBH₄) after 5 runs of nitroaromatics hydrogenation

35 The recycling experiment of the catalyst was further investigated because the recyclability of the heterogeneous catalyst was one of the most important issues for practical applications. Both catalysts could be recycled 5 times for the two reactions, while less than 10% loss of conversion after recycle reactions was 40 observed (Table 1. entry 3, 4 and Table 2. entry 3, 4). Interestingly, after 5 times recycle reactions, Fe₃O₄@PPy-Pt(NaBH₄) showed a lesser loss of activities for both aerobic oxidation of benzylic alcohols and hydrogenation reduction of nitroaromatics than Fe₃O₄@PPy-Pt(EG). Therefore, the EG $_{45}$ reduced Fe₃O₄@PPy-Pt catalyst exhibited slightly poorer stability than the NaBH₄ reduced Fe₃O₄@PPy-Pt catalyst in the recycle tests, which might due to the agglomeration of small Pt NPs. In order to certify this assumption, TEM and HRTEM were used to observe the morphology of Pt NPs after 5 runs of nitroaromatics 50 hydrogenation, as shown in Fig. 7. Compared with Pt NPs of $Fe_3O_4(a)PPy-Pt(NaBH_4)$ before the reactions (Fig. 4d, e), it could be concluded that Pt NPs of Fe₃O₄@PPy-Pt(NaBH₄) after 5 runs had no obvious change in running process, except that its crystal structure was unable to be easily observed (Fig. 7c, d). However, 55 Pt NPs of Fe₃O₄@PPy-Pt(EG) after 5 runs exhibited an apparent

⁵⁵ Pt NPs of Fe_3O_4 @PPy-Pt(EG) after 5 runs exhibited an apparent agglomeration of Pt NPs (Fig. 7a, b), compared with Pt NPs of Fe_3O_4 @PPy-Pt(EG) before the reactions (Fig. 4a, b).

Conclusion

In conclusion, we used NaBH₄ and EG as classical reducing agent to successfully prepare highly dispersed different diameters of Pt nanoparticles supported on PPy-coated Fe₃O₄. As expected, ⁵ the chemical reduction methods remarkably affected the size of Pt nanoparticles — about 5.5nm and 2.5nm, respectively. The

- prepared catalysts exhibited high catalytic activity and good stability for aerobic oxidation of benzylic alcohols and hydrogenation reduction of nitroaromatics. It was highlighted that 10 Fe₃O₄@PPy-Pt(EG) afforded a higher conversion for benzylic
- alcohols aerobic oxidation, while the selectivity toward benzaldehyde over these two catalysts was similar. However, catalytic performances for hydrogenation reduction of a majority of nitroaromatics of two catalysts were almost the same. More
- ¹⁵ interesting, Fe₃O₄@PPy-Pt(NaBH₄) gave better activities of several nitroaromatics which were relatively difficult to be hydrotreated under the same conditions. Furthermore, both catalysts could be recycled 5 times for the two reactions, while less than 10% loss of conversion after recycle reactions is
- ²⁰ observed. And because of the agglomeration of small Pt nanoparticles, the EG reduced Fe₃O₄@PPy-Pt catalyst exhibited slightly poorer stability than the NaBH₄ reduced Fe₃O₄@PPy-Pt catalyst in the recycle tests. Our work demonstrated the important role of reducing agents for immobilizing Pt nanoparticles. It also
- ²⁵ could be obtained that size effects might be quietly different for different kinds of reactions. Sometimes, superior crystal structure was probably more meaningful than smaller size diameter for a certain kind of reaction. It is surely that preparing smaller metal nanoparticles with prefect crystal structure and avoiding ³⁰ interaction agglomeration can greatly improve catalytic activities.

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