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Controlled immobilization of Keggin-type heteropoly acids on the surface of silica encapsulated γ -Fe₂O₃ nanoparticles and investigation of catalytic activity in the oxidative esterification of arylaldehydes with methanol

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ABSTRACT

Preparation, leaching and solid acidity measurements of $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ supported on silica-encapsulated γ -Fe₂O₃ nanoparticles were performed. The impregnating solvent and calcination temperature were optimized using various techniques. Catalytic activity of samples was examined by carrying out oxidative esterification of benzaldehyde with methanol under the same conditions. The acidity of the catalysts that was determined by NH₃-temperature-programmed desorption technique and chemisorption of pyridine. The best catalyst was characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy and laser particle size analyzer. Finally, a mild, simple and clean procedure was presented for the one-pot oxidative esterification of arylaldehydes with methanol using magnetically recoverable nanocatalyst and hydrogen peroxide as a green oxidant.

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1. Introduction

The development of new strategies for the recycling of catalysts is a task of great economic and environmental importance in chemical and pharmaceutical industries. Immobilization of homogeneous catalysts on various insoluble supports (especially porous materials with high surface areas) can lead to simplify catalyst recycling via filtration or centrifugation. However, a substantial decrease in the activity of the immobilized catalyst is frequently observed due to the loss of the catalyst in the separation processes and/or diffusion factors [1]. At present, nanoparticles (NPs) are attractive candidates as solid supports for the immobilization of well-defined homogeneous catalysts [2]. Because of the nanometer dimensions of NPs, such catalysts have better reaction kinetics as compared to the traditional heterogeneous catalysts on mesoporous solid supports. Additionally, due to their large surface area, which can carry a high payload of catalytically active species, these supported catalysts exhibit very high activity under mild conditions.

In NPs-based heterogeneous catalysis, the use of silica coated magnetic NPs can be of additional values: the magnetic nature of these particles allows for facile recovery and recycling of catalysts. Thus far, various catalytic species, including organometallic [3–5] and organic catalysts [6,7] and biocatalysts [8–10], were

immobilized on the modified surface of magnetic NPs. Following this line of research, we have previously reported interesting results in the immobilization of heteropoly acids (HPAs) with Keggin anion structure [11]. In our work, the primary motivation was to create the novel magnetically recoverable nanocatalyst by immobilization of Keggin-structured $H_3PW_{12}O_{40}$ (PW) on silica-coated magnetic NPs. This synthesized catalyst possesses both magnetic separation and strong acidic sites. Moreover, the nano scale support materials have the high surface area. Consequently, NPs could have higher catalyst loading capacity and higher dispersion than many conventional support matrices, leading to an improved catalytic activity and high leaching stability of HPA species even in polar reaction media.

However, the effects of various processing parameters, including the concentration of impregnating solutions, the solvent used, calcination temperature and the type of HPA have remained a challenge. Literature survey showed that the above-mentioned parameters are major factors contributing to the catalytic activity of HPA immobilized on conventional solid supports [12–14]. Nevertheless, there has been scant investigation of HPA catalyst supported on magnetic NPs [15–20] and to the best of our knowledge, the detailed studies of the effective parameters on catalyst preparation have not been well developed.

Keeping in mind these statements, herein, we propose a simple method for the synthesis of magnetically recoverable HPA-based catalyst that relies on our pervious paper, but with an examination and subsequently careful choice of processing parameters.

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The synthesis of silica coated magnetic NPs, covering a wide range of compositions and tunable sizes, has made substantial progress, especially over the past decade [21,22]. Most of these researches focused on the generation of uniform particles, often of distinct size, shape, and structure, with little consideration of the expensive precursors used to prepare them or the cost of processes to produce them. On the other hand, for the large-scale application in industry, an important consideration will be to prepare NPs economically using relatively low-grade reagents under aerobic conditions. So, a simple ferric oxide, γ -Fe₂O₃, was chosen as the magnetic material for its low price, air stability and non-toxicity. It was prepared simply through chemical coprecipitation [23], and subsequently was coated with silica shell by the ordinary Stöber process [24] without expensive systems. After the surface coating by silica, magnetic solid (designed as Fe@Si) was used as support for immobilization of HPA. Preparation conditions including the impregnating solvent used, calcination temperature and the type of HPA have been optimized. Ultimately, the efficiencies of obtained catalysts were evaluated in oxidative esterification of benzaldehyde with methanol as the test reaction. The ever-increasing concern for the catalytic oxidative esterification of aldehydes as an interesting and potentially valuable alternative transformation [25-29] and the wide application of aromatic esters in pharmaceuticals, agrochemicals, and food additives [30-32] encouraged us to evaluate the scope and generality of the catalytic system by using various substituted benzaldehyde. To the best of our knowledge, the application of magnetically recoverable HPA-based catalyst in the oxidative esterification of arylaldehydes has not yet been studied

2. Experimental

2.1. Catalyst preparation

FeCl₂·4H₂O (99%) and FeCl₃·6H₂O (99%), concentrated ammonium hydroxide (25%), tetraethyl orthosilicate (TEOS, 98%), PW (>99%), H₄SiW₁₂O₄₀ (SiW, >99%), H₃PMo₁₂O₄₀ (PMo, >99%) and other reagents and solvents used in this work were obtained from Merck, Aldrich or Fluka and used without further purification.

Magnetic γ -Fe₂O₃ NPs were prepared through the chemical co-precipitation method [23]. FeCl₂·4H₂O (2.0 g) and FeCl₃·6H₂O (5.4 g) were dissolved in water (20 mL) separately. These solutions were being mixed together under vigorous stirring (1200 rpm). A concentrated NH₄OH solution (25% w/w) was then added to the stirring mixture at room temperature to maintain the pH between 11 and 12. The resulting black dispersion was continuously stirred (1200 rpm, 1 h) at room temperature and then heated to reflux for 1 h to yield a brown dispersion. The γ -Fe₂O₃ NPs were then purified by a four times repeated centrifugation (3000–6000 rpm, 20 min), decantation and redispersion cycle until a stable brown magnetic dispersion was obtained.

Coating of a layer of silica on the surface of the γ -Fe₂O₃ NPs was achieved by mixing a dispersion of the purified NPs (8.5% w/w, 20 mL) obtained previously with ethanol (80 mL) for 1 h at 40 °C. A concentrated ammonia solution (15 mL) was added and the resulting mixture stirred at 40 °C (800 rpm, 30 min). Subsequently, TEOS (1.0 mL) was charged to the reaction mixture and the mixture continuously stirred at 40 °C (800 rpm, 24 h). The Fe@Si NPs were collected using a permanent magnet, followed by washing three times with ethanol, diethyl ether and drying in a vacuum for 24 h [33].

In order to study the effect of preparation conditions on leaching stability, acidity and activity of supported HPA catalysts, a series of samples were prepared using different impregnating solvents (water, MeOH and MeCN), calcination temperatures (100, 150, 200, 250 and 300 °C) and HPA types (PW, SiW and PMo).

All supported HPA catalysts were generally prepared by impregnating 1.0 g of Fe@Si with an aqueous or organic solution of HPA (1.2 g in 50 mL of solvent) with stirring at about 60 °C for 24–72 h. The catalyst was dried using a rotary evaporator. Further calcination of the catalyst was carried out at corresponding temperature in air for 2 h.

2.2. Catalyst characterization

The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30 and S-4160) with gold coating. Transmission electron microscopy (TEM) image was obtained using a TEM microscope (Philips CM 120 KV, The Netherlands). The size distribution of the samples was obtained using a laser particle size analyzer (HPPS 5001, Malvern, UK). X-ray diffraction (XRD) measurements were performed using a Bruker axs Company, D8 ADVANCE diffractometer (Germany). Fourier transform infrared (FTIR) spectra were recorded with KBr pellets using a FT-IR spectrometer ALPHA. UV-vis spectra were obtained with an Agilent (8453) UV-vis diode-array spectrometer using quartz cells of 1 cm optical path. The tungsten (W) content in the catalyst was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Spectro Ciros CCD spectrometer. NH₃-temperature programmed desorption (NH₃-TPD) measurements were carried out with 200 mg samples on a Micromeritics 2900 TPD/TPR apparatus with a thermal conductivity detector (TCD).

The equilibrium adsorption of the support with different PW solutions was performed by contacting 1.0 g of support with 50 mL of solution, at 60 °C, under constant stirring during 72 h. At regular intervals, the samples of this mixture were taken for their UV–vis analyses.

To check the leaching stability of the catalysts, 0.02 g of each catalyst was stirred in 5 mL methanol for 1 h. UV–vis spectra of the diluted solutions were recorded after removal of solid. The content of HPA in solution was determined with the aid of calibration curves.

The surface acidity of the catalysts was determined by chemisorption of pyridine [34]. 1.0g of solid was suspended in hexane (100 mL). The suspension was titrated with a 0.1 M solution of pyridine in hexane. Equilibrium concentration of pyridine in hexane solution between each addition was measured by UV-vis spectroscopy based on the fact that pyridine molecule has an absorbance at λ_{max} = 251 nm. For each measurement, 1 mL of solution was separated (1 mL of hexane was added into suspension in order to maintain a constant volume). Then the absorption value of this separated solution was measured, and the equilibrium concentration of pyridine can be calculated using calibration curves, considering the diluted factor. Since the amount of pyridine added was known, the amount of base adsorbed by the solid was calculated by difference.

Time dependent UV adsorption measurements were performed. It was observed that the absorbance was constant for standing times above 15 min. Therefore, the experiments were performed in the time scale of 15 min between each addition of pyridine. All the measurements were repeated at least three times and the reported values are average of the individual runs.

2.3. Catalytic experiments

The oxidative esterification was carried out as follows: catalyst (25 mg), aldehyde (1 mmol) and alcohol (4 mL) were magnetically stirred in the reaction flask. H_2O_2 (6 mmol) was progressively added to the reaction mixture using a syringe. The completion of reaction was monitored by thin layer chromatography (TLC). At



Fig. 1. Time profiles for adsorption of PW on Fe@Si in different solvent.

the end of the reaction, the catalyst was separated from the product solution using an external magnet, followed by decantation of reaction mixture. The solvent was evaporated to generate the crude product. The crude products were purified by column chromatography on silica gel using hexane/ethyl acetate 4:1 as eluent.

The remaining catalyst was washed with diethyl ether to remove the residual product, dried under vacuum and reused in a subsequent reaction. More than 95% of the catalyst could usually be recovered from each run.

3. Results and discussion

3.1. Immobilization characteristics

The presence of the Keggin anion on support surface is very dependent upon the preparation conditions. Impregnation of PW on support surface was examined by using different solvents (Fig. 1). The quantity of adsorbed PW is solvent dependent and decreases in following order (after 72 h): MeOH > water > MeCN. The adsorption profile of MeCN shows regular trends in comparison with MeOH and water. It seems that 24 h were enough to attain equilibrium adsorption of Fe@Si NPs with PW solutions. The adsorption of PW on support surface is affected by various factors including solvent polarity, PW-solvent, solvent-support, and PW-support interactions. Methanol and water molecules are not only adsorbed on the external surface of the support but also interact with PW anions thus showing irregular trends.

The quantity of adsorbed PW depends on diffusion of PW molecules from the solvent to the support surface. This factor is not considerable effect in the case of conventional solid supports [13], but it is important in magnetic γ -Fe₂O₃ NPs because of their nanometer dimensions and subsequently large surface area to volume ratio. The highest quantity of adsorbed PW was observed in methanol due to its high polarity, hydrogen bond ability and low surface tension that can be accelerate the diffusion of PW molecules from the solvent to the support surface. However, in water and MeCN, the quantity of adsorbed PW was decreased. These results are probably ascribed to the high surface tension of water [35]. In the case of MeCN relatively low polarity of this solvent and no hydrogen bond ability compare to water and MeOH decrease the diffusion in this solvent.

Table 1

Effect of impregnation conditions on chemical composition of PW/Fe@Si catalyst.

Entry	Solvent	PW content (wt.%) ^a	
		Washed samples	Dried samples
1	MeOH	0	32
2	Water	0	27
3	MeCN	11	42

^a PW content in washed and dried samples was determined by ICP-AES analysis.

All catalysts were separated by centrifugation, washed with excess solvent and their PW content was analyzed by ICP-AES technique. The results are listed in Table 1. A complete removal of PW from support surface was observed in the samples that prepared in MeOH and water solutions. In water, PW might be aggregated on the exterior surface of support due to the high surface tension of water and the secondary structure formed by aggregation of Keggin units within PW multilayer. From the fact that only the first layer of PW at the interphase with silica is significantly modified by interaction with the support, the non-interacting aggregated Keggin units are washed away by solvent. In MeOH, the formation of secondary structure involving $CH_3OH_2^+$ or clusters $(CH_3OH)_nH^+$ [36] can lead to the aggregation of PW units as multilayer that are leached from the support surface. In MeCN, PW prefers to form a monolayer of isolated Keggin anions to the exterior surface of support. Therefore, PW was strongly adsorbed on the surface of Fe@Si NPs in the MeCN solution, leading to the relatively high PW content in washed and dried samples.

When the samples were dried using a rotary evaporator without washing, PW was retained in the surface of Fe@Si solid (Table 1). Thus, the impregnation-evaporation technique was selected for the preparation of HPA/Fe@Si catalyst. Among various solvent used, the highest PW content was observed in the samples prepared in MeCN (Table 1, entry 3).

The nature of HPA species in impregnating solutions and after drying was studied by UV–vis and FTIR spectroscopy. The UV–vis spectra of PW in impregnating solutions after 72 h are shown in Fig. 2. An intense peak centered at λ = 265 nm is the characteristic



Fig. 2. UV-vis absorbance spectra of PW in impregnating solutions after 72 h.



Fig. 3. FTIR spectra of PW/Fe@Si catalyst impregnated in (a) MeOH, (b) MeCN and (c) aqueous solutions.

charge transfer band of PW heteropoly anion [37]. It is observed for MeOH and MeCN solutions. While, in the spectrum of aqueous solution, a slight shifting of the adsorption maximum toward lower wavelengths (about 250 nm) was observed. It may be due to the hydrolysis reaction of PW.

The FTIR spectra of supported samples after drying are presented in Fig. 3. The typical bands for absorption of P–O (1080 cm^{-1}), W=O (983 cm^{-1}), W–O–W ($895 \text{ and } 809 \text{ cm}^{-1}$) are clearly displayed in the impregnation with MeOH. On the other hand, from water and MeCN solutions the band placed at 1080 cm^{-1} is masked by the Si–O–Si absorption band in the Fe@Si NPs.

Any leaching of the catalyst from the support would make the catalyst unattractive for reusing. Therefore, it is necessary to investigate the stability of PW on Fe@Si NPs. Leaching experiments were performed using dried and calcined catalyst samples. Methanol was employed as the solvent since it further used in catalytic tests. The results are shown in Fig. 4. Without calcination, significant leaching of PW from Fe@Si surface in methanol was observed in all cases. The resistance to leaching improved significantly with increasing calcination temperature to $250 \,^\circ$ C.

Based on above results, the best preparation achieved was to immobilize HPA on Fe@Si NPs in MeCN solution followed by drying and calcination at 250 °C. Further investigations were carried out using PW, SiW and PMo as the main, convenient, popular and commercially available HPAs.

Adsorption of pyridine on Fe@Si NPs and PW, SiW and PMo supported on Fe@Si NPs (designed as PW/Fe@Si, SiW/Fe@Si and PMo/Fe@Si) from hexane was studied (Fig. 5 and Table 2). The obtained L-curves with the plateau for supported catalysts and Fe@Si NPs are shown in Fig. 5. The plateau level corresponds to surface concentration of acidic sites of samples that are listed in Table 2. Pyridine was adsorbed on Fe@Si NPs. Such adsorption is attributed to the presence of Si—OH groups on the outer surface of the support (Table 2, entry 5). The concentration of



Fig. 4. Effect of calcination temperature on the leaching stability of PW/Fe@Si catalyst impregnated in different solutions.

acid sites in supported HPAs decreases in the following order: PW/Fe@Si > SiW/Fe@Si > PMo/Fe@Si (Table 2, entries 6–8).

Leaching stability of supported HPA samples in methanol was studied. The relatively same values were obtained in different solvent (Table 2, entries 6–8).

The catalytic activities of samples were investigated in oxidative methylesterification of benzaldehyde using H_2O_2 as oxidant. Without any catalyst added, no ester was formed and only benzoic acid was detected (Table 2, entries 1). Bulk HPAs as catalyst showed lower activity in comparison with supported ones pointing out the importance of the concentration of surface acid sites (Table 2, entries 2–8). In most of the runs, methyl benzoate was a main product at the end of the reaction. However, using PMo and PMo/Fe@Si catalyst, the reaction gave benzoic acid and methylbenzoate with comparable yields.

The NH₃-TPD profiles for Fe@Si, PW/Fe@Si, SiW/Fe@Si and PMo/Fe@Si samples are shown in Fig. 6. All supported samples showed three desorption peaks occurred at different temperature ranges. It may be due to desorption of adsorbed ammonia on weak and strong acid sites. The first and second desorption peak at about 130–300 and 400–600 °C could be assigned to weak and strong acid sites respectively [38]. The remaining peaks in the 700–800 °C are probably due to dehydration rearrangements of the Keggin unit [39]. The desorption temperature of NH₃ on the strong acid site (400–600 °C) decreases as the following order:



Fig. 5. Adsorption of HPA/Fe@Si catalysts reacted with pyridine in hexane.

Та	ble 2	
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Surface acidity,	leaching and	catalytic acti	vity of HPA	and HPA/F	e@Si catalysts.
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Entry	Sample	H ⁺ /g of solid (mmol) ^a	Leaching (%)	Conversion (%)	Yield (%) ^{b,c}	
					Benzoic acid	Methyl benzoate
1	-	-	-	6	6	-
2	PW	_	-	36	9	27
3	SiW	_	-	17	4	13
4	PMo	-	-	32	25	7
5	Fe@Si	4.1	-	14	14	-
6	PW/Fe@Si	94.3	6.7	75	15	60
7	SiW/Fe@Si	46.9	8.3	67	12	55
8	PMo/Fe@Si	39.7	6.2	63	52	11

^a The number of acidic centers was determined by pyridine adsorption.

^b Conditions: catalyst (0.1 mol%), benzaldehyde (1 mmol); H₂O₂ (4 mmol); methanol (3 mL); Room temperature; 17 h.

^c The isolated yields were determined based on benzaldehyde.



Fig. 6. $\rm NH_3-TPD\ profiles\ of (a)\ Fe@Si, (b)\ PW/Fe@Si, (c)\ SiW/Fe@Si\ and (d)\ PMo/Fe@Si\ samples.$



Fig. 7. XRD patterns of (a) PW/Fe@Si and (b) PW/Fe@Si calcined at 250 °C.



Fig. 8. FTIR spectra of (a) PW/Fe@Si, (b) PW/Fe@Si calcined at $250 \degree C$ and (c) PW/Fe@Si calcined at $250 \degree C$ after reaction with 0.1 mol of pyridine per gram of catalyst [34].

PW/Fe@Si > SiW/Fe@Si > PMo/Fe@Si. It reveal that the PW/Fe@Si catalyst possess strongest acid sites in comparison with SiW/Fe@Si and PMo/Fe@Si catalysts. The desorbed amount of NH₃ from these acid sites was calculated and summarized in Table 3. It is evident that PW/Fe@Si catalyst has relatively higher number of acid sites compared to SiW/Fe@Si and PMo/Fe@Si catalysts.

The TPD results are not similar to the acidity data measured by pyridine chemisorption in liquid phase. This difference is mainly

The acid strength distribution of the catalysts calculated by the results of $\rm NH_3$ -TPD.

Catalyst	Total acidity (mmol/g)	Acidity distribution (mmol/g)	
		Weak ^a	Strong ^b
Fe@Si	1.33	0.25	1.08
PW/Fe@Si	3.31	0.74	2.57
SiW/Fe@Si	2.09	0.62	1.47
PMo/Fe@Si	1.95	0.62	1.33

^a Desorption temperature: 130–300 °C.

^b Desorption temperature: 400–600 °C.



Fig. 9. SEM images of (a) PW/Fe@Si and (b) PW/Fe@Si calcined at 250 °C, (c) TEM image of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si and W atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si atoms of PW/Fe@Si calcined at 250 °C, (d) elemental maps of Fe, Si atoms of PW/Fe

due to differences between measurements in gas- and liquid-phase. In addition, pyridine and ammonia have different size, basicity and adsorption capability, and comparison is not straight. However, it can be conclude, independent of the measurement method, PW/Fe@Si showed strongest acidity and highest number of acid sites among the others. As a result, PW/Fe@Si showed better results in terms of strength and number of acid sites, and leaching stability than any others and chosen as the suitable catalyst for more investigations.

3.2. Characterization of PW/Fe@Si catalyst

Stability of the PW anion upon calcination was investigated by XRD and FTIR spectroscopic analysis. The XRD pattern for the PW/Fe@Si catalyst is shown in Fig. 7. Silica shows a broad band centered at $2\theta = 25^{\circ}$. γ -Fe₂O₃ displays typical sharp peaks at $2\theta = 30.4^{\circ}$, 35.5° , 55.7° , and 62.5° and PW displays reflections at $2\theta = 9.7^{\circ}$ and 26.3° [40,41]. The presence of the intense peaks in calcined sample indicates that there is no significant change in the structure of the PW and its crystalline character after calcination.

The four fingerprint peaks at approximately 1080, 983, 895 and 809 cm^{-1} assigned to Keggin anions of PW are clearly observed when the sample was calcined at 250 °C (Fig. 8). It should be noted

that the decreasing of infrared absorption peak at 3450 cm⁻¹ (corresponding to bridging hydroxyl groups) in calcined sample, might result in the dehydroxylation between PW anions and the silanol groups on the surface of Fe@Si support.

Brönsted or Lewis acidity of the PW/Fe@Si catalyst was distinguished by studying the FTIR spectrum of the catalyst after reaction with pyridine (Fig. 8). Pyridine molecules were adsorbed on Lewis acid sites (1610 and $1450 \,\mathrm{cm^{-1}}$) and formed the pyridinium ion by interaction with Brönsted acid sites (1640 and $1540 \,\mathrm{cm^{-1}}$) [42]. Both types of adsorbed species contribute to the band at $1490 \,\mathrm{cm^{-1}}$ [42]. FTIR spectrum of the catalyst shows contribution of pyridine adducts in the region $1400-1700 \,\mathrm{cm^{-1}}$. The formation of pyridinium ion was observed by absorptions at 1488, 1542 and 1648 $\,\mathrm{cm^{-1}}$ (expanding region in Fig. 8). It should be mentioned that absorption band at $1648 \,\mathrm{cm^{-1}}$ is not totally conclusive although considered as pyridinium ion because of contributions of pyridinium ion and moisture, since the spectrum was taken at ambient conditions.

The morphological features of the PW/Fe@Si catalyst were investigated by SEM and TEM techniques. Fig. 9(a) shows the SEM micrograph of the catalyst with different magnifications. The particles were almost spherical, regular in shape and dispersed uniformly. However, some particle aggregations were clearly

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mization of the	e oxidative esterification of be	enzaldehyde with metha	H_2^{CHO}	PW/Fe@Si O ₂ , MeOH, r.t.	COOH + COOMe
try	Catalyst (mol%)	MeOH (mL)	H ₂ O ₂ (mmol)	Time (h)	Conversion (%)
	0.1	3	4	17	75

6

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^a The isolated yields were determined based on benzaldehyde.

^b Results in parentheses are second; third and fourth runs. The conversion remained constant during four successive runs.

observed. After calcination at $250 \,^{\circ}$ C, the relatively smooth surface could be easily noted and it was attributed partial collapse of the NPs as well as sintering of the particles (Fig. 9(b)).

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TEM observation indicated that PW/Fe@Si NPs have welldefined core-shell structure (Fig. 9(c)). Wavelength dispersive X-ray (WDX) image studied that are map of individual elements of iron, silica and tungsten elements in cross-section were shown in Fig. 9(d). It showed an excellent uniform distribution of PW on Fe@Si NPs. According to WDX analysis, the atomic Si/Fe and W/Fe ratios in PW/Fe@Si NPs were 0.795 and 5.86 respectively, which are close to the values obtained for PW/Fe@Si calcined at 250 °C (Si/Fe: 0.722 and W/Fe: 5.78).

The size distribution of the γ -Fe₂O₃, Fe@Si and PW/Fe@Si NPs derived from a laser particle size analyzer, illustrated in Fig. 10. γ -Fe₂O₃NPs had a mean diameter of 70.43 nm and a wide size distribution with a polydispersity of 0.719. In this case, the magnetostatic interactions between particles can cause agglomeration. Fe@Si NPs showed a mean diameter equal to 91.28 nm with polydispersity of 0.352. The relatively narrow size distribution implied that the Fe@Si NPs were highly stable in suspension, with the silica coating. PW functionalized Fe@Si NPs yielded a hydrodynamic diameters of 91.77 nm (polydispersity of 0.48), which corresponds to a size increase of about 21 nm in comparison with γ -Fe₂O₃ NPs.

3.3. Catalytic activity of PW/Fe@Si catalyst

In order to examine the effects of catalyst on the direct transformation of aldehydes to corresponding esters, benzaldehyde and

Table 5

PW/Fe@Si catalyzed oxidative esterification of aldehydes with methanol^a .



(%) ^b

 $^a\,$ Conditions: aldehyde (1 mmol); H_2O_2 (6 mmol); catalyst (0.25 mol%); methanol (4 mL); Room temperature; 8 h.

^b Conversion and selectivity were calculated from the yield of isolated products.

methanol were chosen as test substrates to react in the presence of hydrogen peroxide as oxidant. The conversion was improved by increasing the amount of oxidant from 4 to 6 mmol, but selectivity remained relatively constant. Further increasing of H_2O_2 amount to 8 mmol had no effect on the selectivity (Table 4, entries 1–3). The selectivity to ester product increased with increasing the amount of the catalyst and only ester product was observed using 25 mg of the catalyst in relatively short reaction time (Table 4, entries 2, 4–7). The yield of the ester was decreased to 70% by using 2 mL of methanol as the solvent (Table 3, entry 8). In contrast, 98% of methyl benzoate (with 100% selectivity) was achieved with 4 mL of

98

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98

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70

98

98

Ester selectivity (%)

100 (96, 91, 87)^b

80

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100

100

95

91



Fig. 10. Grain size distribution of (a) γ -Fe₂O₃, (b) Fe@Si and (c) PW/Fe@Si NPs.

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methanol as the solvent in shorter reaction time (Table 4, entry 9). Reusability of PW/Fe@Si catalyst was investigated under the optimized reaction conditions (Table 4, entry 9). The catalyst could be facilely recycled through magnetic separation and no significant loss of activity and selectivity was found even after four subsequent runs.

With the best reaction conditions in our hand (Table 4, entry 9), we decided to test the generality and efficiency of this methodology (Table 5). In general, the corresponding aromatic esters were obtained in good to excellent yields regardless of the electron-donating or electron-withdrawing group in the benzene ring.

4. Conclusions

The catalyst Fe@Si-PW was prepared using different solvents by the impregnation-evaporation technique. The results clearly indicated the dependence of acidity, activity and leaching stability of supported catalyst on different basic points, as which are the impregnating solutions, calcination temperatures and the type of HPA. The best preparation achieved was to impregnate PW on Fe@Si NPs in MeCN solution, followed by evaporation of solvent and calcination at 250 °C. The Fe@Si-PW NPs are mostly spherical in shape and have an average size of approximately 92 nm. Experiments assessing the stability of supported HPA catalysts indicated their resistance to leaching by methanol as polar solvent. The acidity of the samples was determined by NH3-TPD and chemisorption of pyridine. The strength and dispersion of the protons on PW/Fe@Si NPs was considerably high and active surface protons became more available for reactant. Catalytic activity of HPA/Fe@Si and pure HPA catalysts was examined in oxidative esterification of benzaldehvde with methanol. The Fe@Si-PW NPs was found as an effective magnetically recoverable heterogeneous catalyst for the liquid-phase oxidative esterification of a wide range of arylaldehydes with hydrogen peroxide as green oxidant.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata. 2013.02.024.

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