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# Monodispersed poly(4-vinylpyridine) spheres supported Fe(III) material: An efficient and reusable catalyst for benzylic oxidation

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ABSTRACT

A novel ferric chloride immobilized poly(4-vinylpyridine) (P4VP) catalyst was developed via a coordination chemistry-based approach. The pyridine moiety of poly(4-vinylpyridine) spheres functioned as the nitrogen donor to bind iron ions, as well as to decrease the amount of pyridine used in the catalytic reaction system. The monodispersed catalyst was well dispersed in the organic solvent during the catalytic procedure, taking advantage of its nanomorphology and uniform size. The catalytic activity of various monodispersed catalysts based different mass fractions of the divinylbenzene (DVB) was investigated, meanwhile the capacities of supported Fe(III) in the various catalysts were also discussed. The P4VPDVB$_{10\%}$-Fe(III) catalyst exhibited high catalytic activity in the benzylic oxidation of benzylic methylenes and secondary benzylic alcohols. It was easily separated from the reaction system and reused several times without obvious degradation of catalytic activity. Moreover, leaching tests suggested that the as-synthesized P4VPDVB$_{10\%}$-Fe(III) catalyst was a true heterogeneous catalyst without significant metal leaching.

## 1. Introduction

Benzylic oxidation is one of most vital and highly useful transformations in organic chemistry, using inexpensive starting materials for the production of aldehydes or ketones [1]. These in turn are widely used as important building blocks in the fine chemical industry, as well as serving as medical intermediates [2]. The use of traditional oxidation methods that require highly polluting or toxic reagents such as chromium reagents, manganese reagents or sodium chlorite has been discouraged due to environmental concerns [3–4]. Therefore oxidation promoted by catalyst is highly preferred, since oxidative catalysis is green, efficient and sustainable when environmentally friendly oxidants are used [5–12]. In the past decade, tremendous efforts have been devoted to homogeneous catalysts for benzylic oxidation [13–14]. For example, transition metal salts and complexes containing $Cr(CO)_6$ [15], $CoCl_2$ [16], $Co(OAc)_2{\cdot}4H_2O$ [17], Mn(salen) [18–19], $RuCl_3$ [20–21], $RuCl_2(PPh_3)_3$ [22], $Rh_2(cap)_4$ [23] or $Cp_2VCl_2$ [24] have been shown to be good homogeneous catalysts for benzylic oxidation. However, the development of catalysts that are clean, inexpensive, efficient and selective and which reach the standards of green chemistry remains a challenging goal. Iron derived catalysts have been extensively studied in this oxidation process because of their easy synthesis and low toxicity [25]. For example, Bauer and co-workers described the catalytic application of iron(II) trifluomethanesulfonate, iron phosphinooxazoline complexes and iron(II) phosphoramidite complexes in the oxidation of benzylic methylenes to ketones, respectively [26–28]. Nakanishi and Bolm reported the catalytic activity of ferric trichloride in the oxidation of benzylic methylenes and secondary alcohols to the corresponding ketones [29]. It is worth mentioning that pyridine solvent, which is often employed in homogeneous iron catalysis for benzylic oxidation, was also crucial in these catalytic systems. As a result, the common difficulties of homogeneous catalytic systems for benzylic oxidations are the separation and reuse of the catalyst as well as the usage of large amounts of toxic pyridine [30].

Recently, there has been a concerted effort to develop iron complexes anchored on solid support, such as polymer [31–34], mesoporous silica [35–37] and metal-organic frameworks [38]. Among these, polymeric materials, complexed with chelating ligands or monomer containing coordination sites, are often used for this purpose [39–43]. In particular, poly(vinylpyridine) complexes which possesses the advantages of low toxicity, fine thermal stability, great recyclability and N-ligand chelation can be effectively utilized as supporting material for iron ions. Monodispersed catalysts at the nanoscale, which showed high surface-to-volume

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ratio characteristic, are available for catalysis [44]. Therefore, poly(vinylpyridine) spheres with monodispersed nanomorphology have been introduced to improve the catalytic activity in the reaction system.

Here, we report a novel poly(4-vinylpyridine) supported Fe(III)/TBHP (*tert*-butylhydroperoxide) catalytic system for benzylic oxidation. A series of monodispersed poly(4-vinylpyridine) spheres as solid supports to load heterogeneous Fe(III) catalysis was evaluated. The synthetic monodispersed poly(4-vinylpyridine) supported Fe(III) catalyst possessed high dispersion in the reaction system taking full advantage of its uniform sizes and nanomorphologies. The novel poly(4-vinylpyridine) supported Fe(III) catalyst showed excellent catalytic performance toward benzylic oxidation. Furthermore, the pyridine moiety of the synthesized catalyst was able to function as an organic base, which significantly reduced the amount of pyridine in the system. Therefore the design of monodispersed poly(4-vinylpyridine) supported Fe(III) catalyst provides a novel approach to advanced catalysts for organic systhesis.

## 2. Experimental

### 2.1. Materials

All substrates and solvents were purchased from Sigma–Aldrich, Alfa Aesar or Aladdin. 4-Vinylpyridine monomer (96%, 4VP; Aldrich) were stabilized with 100 ppm hydroquinone and used under further purification. Divinylbenzene (80 mol% DVB; Aldrich), Aliquat 336 (Mn = 404.17; Aldrich), poly(ethyleneglycol)methacrylate (PEGMA) macromonomer solution (Mn = 2080; 50 wt% in $H_2O$) and 2,2′-Azobis(2-methylpropionamidine)dihydrochioride (97%, AIBA; Aldrich) were used as received. $FeCl_3{\cdot}6H_2O$ were purchased from Alfa Aesar and TBHP (*tert*-butylhydroperoxide) (5.0–6.0 M; Aldrich) was preserved in decane.

### 2.2. Preparation of $P4VPDVB_{5–40\%}$ spheres

The monodispersed poly(4-vinylpyridine) (P4VP) spheres were achieved according to the literature synthesis of monodispersed poly(2-vinylpyridine) (P2VP) spheres [45]. In a typical emulsion polymerization procedure, the Aliquat 336 surfactant (0.5 g) and the PEGMA stabilizer (1.0 g) were dissolved in deionized water (80.0 g). Then the transparent solution turned into milk white emulsion under supersonic conditions. The emulsion was stirred at 300 rpm in a three-necked round-bottomed flask. The flask fitted with a reflux condenser was sealed and the solution was degassed with nitrogen cycles at ambient temperature. A mixture of 4VP (5.0 g) and 2.5–40 wt% DVB (based on 4VP monomer) cross-linker was then added. Meanwhile the solution was stirred continuously and heated at 60 °C. After 20 min, the initiator solution (0.05 g in 9 mL distilled water) was added dropwise into the above-mentioned solution. The solution was then stirred for 24 h. The $P4VPDVB_{2.5–40\%}$ spheres were synthesized and purified with centrifugation at 9000 rpm for 30 min, then washed with ethanol and distilled water several times so that the residual monomer was removed. Furthermore, the $P4VPDVB_{2.5–40\%}$ microgels were dried under vacuum for 12 h.

### 2.3. $P4VPDVB_{5–40\%}$-Fe(III) catalyst preparation

Powdered $P4VPDVB_{2.5–40\%}$ spheres 5.0 g were dispersed insaturated solution of $FeCl_3{\cdot}6H_2O$ in absolute ethanol with 1.0 mL of 1N HCl aqueous solution (pH 2) under supersonic conditions for high dispersion. The above solution was stirred at 300 rpm for 12 h and heated at 70 °C in an oil bath. The resulting product was collected with centrifugation and washed with absolute ethanol several times in order to remove HCl and free iron ions. Finally, the yellow powder catalyst was dried under vacuum at 40 °C for 12 h.

### 2.4. General procedure for the oxidation of benzylic methylenes

In a typical procedure, a mixture of 4,4′-difluorodiphenylmethane (178.4 μL, 1.0 mmol) and $P4VPDVB_{2.5–40\%}$-Fe(III) catalyst (2.0 mol%), pyridine (8.0 μL, 0.1 mmol), TBHP (5.0–6.0 M in decane, 545.0 μL, 3.0 mmol) and 1.0 mL acetonitrile was dissolved in a 25 mL single-necked flask fitted with a reflux condenser. The mixture was heated at 80 °C for 24 h under air atmosphere in an oil bath. Then the mixture was cooled to 25 °C and centrifuged to get a catalyst and supernatant solution. Then the solution was analyzed by Agilent 7890/5975C-GC/MSD using nitrobenzene as an internal standard. A calibration curve for each reactant and product has been built, which is included in the ESI†. The in situ $^1H$ NMR monitoring of the reaction conversion and yield was performed in the DMSO-$d_6$ solvent, the crude sample of entry 11 in Table 3 was filtered for direct $^1H$ NMR analysis (see ESI†). Furthermore, the products of entries 1 and 7 in Table 2 were isolated through column chromatography and the isolated yields were provided.

### 2.5. Reusability of the catalyst

On completion of each reaction cycle, the catalyst was centrifuged from solution mixture and then washed with ethanol (5.0–10.0 mL) several times. After being dried in an oven at 40 °C under vacuum for 6 h, the catalyst was reused.

### 2.6. Characterization

Field-emission scanning electron microscopy (FESEM) photographs were observed by a SUPRA 55 (Zeiss, Germany) instrument operated at acceleration voltage 10 kV. The iron content of the $P4VPDVB_{10\%}$-Fe(III) complex was measured by atomic absorption spectroscopy (Varian 240FS). An FEI Tecnai F20 electron microscope with EDX operating at an acceleration voltage of 200 kV and a ZEISS SUPRA55 instrument operating at an acceleration voltage of 10 kV were applied to characterize the morphology of the product. The spectra of Fourier transform infrared spectroscopy (FTIR) were obtained on a NICOLET 6700 infrared spectrophotometer using potassium bromide (KBr) disk samples. Thermal gravity analysis (TGA) curves were investigated using a Netzsch STA449F3 instrument with the heating rate of 10 °C/min. The X-ray photoelectron spectroscopy (XPS) spectra were measured on a Kratos AXIS Ultra DLD photoelectron spectroscope. The binding energies were adjusted by placing the C1s binding energy at 284.8 eV from adventitious carbon. The gas chromatographic (GC) data was obtained by Agilent 7890/5975C-GC/MSD, fitted with a capillary column (column: HP-5MS;injection temperature: 50 °C).

## 3. Results and discussion

### 3.1. Synthesis of the monodispersed spheres supported Fe(III)

In an initial study, $P4VPDVB_{2.5–40\%}$ complexes with different weight percentages of the DVB cross-linker were synthesized and used as the polymer supports for $FeCl_3{\cdot}6H_2O$. The porous structures were provided by DVB in a poly(4-vinylpyridine) network [46]. The iron content of $P4VPDVB_{2.5–40\%}$-Fe(III) was determined by AAS (atomic absorption spectroscopy) analysis. The P4VPDVB spheres with 2.5 wt%, 5 wt%, 10 wt%, 20 wt% and 40 wt% DVB offered the key advantage of high Fe(III) loading on $P4VPDVB_{2.5–40\%}$-Fe(III) catalyst which was 2.01, 1.91, 1.84, 1.80 and 1.55 mmol/g, respectively. The

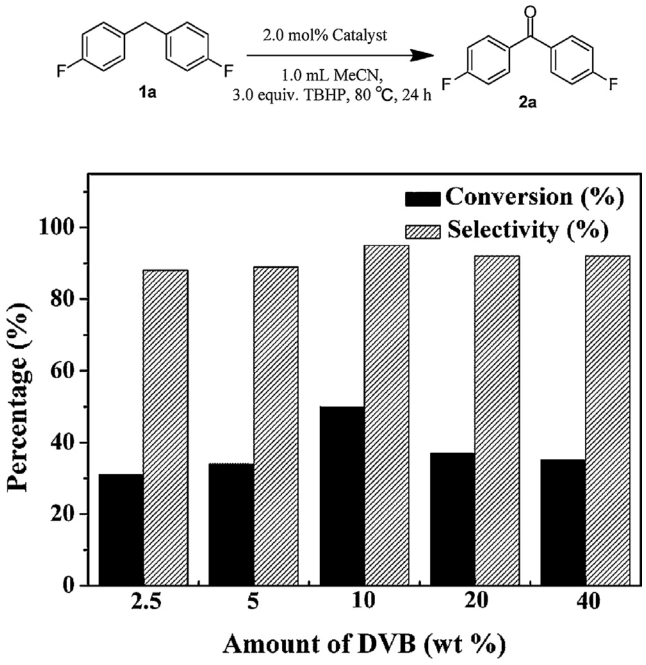


**Fig. 1.** The benzylic oxidation of 4,4′-difluorophenylmethane **1a** catalyzed by P4VPDVB$_{2.5-40\%}$-Fe(III) complexes, 1.0 mmol **1a** in 1.0 mL acetonitrile was heated at 80 °C for 24 h with 2.0 mol% different P4VPDVB$_{2.5-40\%}$-Fe(III) complexes catalyst and 3.0 mmol TBHP were detected by GC–MS using nitrobenzene as internal standard (conversion of **1a** and selectivity for **2a**, based on **1a**).

catalytic activities of the P4VPDVB$_{2.5-40\%}$-Fe(III) complexes were evaluated in a benzylic oxidation reaction using TBHP as oxidant. The oxidation of 4,4′-difluorodiphenylmethane **1a** for the formation of 4,4′-difluorodibenzophenone **2a** was chosen as the model reaction (Fig. 1). The conversion and selectivity of the oxidation of 4,4′-difluorophenylmethane **1a** are illustrated in Fig. 1. It was shown that the catalytic activities of the P4VPDVB$_{2.5-40\%}$-Fe(III) complexes were proportional to the DVB usage from 2.5 wt% to 10 wt% and decreased as the DVB usage was increased from 10 wt% to 40 wt%. The conversions of 4,4′-difluorophenylmethane **1a** were in the range of 31–50%. It is postulated that the P4VPDVB$_{2.5\%}$-Fe(III) and P4VPDVB$_{5\%}$-Fe(III) catalysts were highly saturated due to highly flexible fold structures and the high pyridyl/Fe(III) ratio. Thus the chemical interaction between P4VPDVB$_{2.5-5\%}$-Fe(III) catalysts and TBHP were prevented, resulting in low conversion of 4,4′-difluorodiphenylmethane **1a**. On the other hand, the low conversion of 4,4′-difluorophenylmethane **1a** using P4VPDVB$_{20\%}$-Fe(III) or P4VPDVB$_{40\%}$-Fe(III) as catalyst was observed due to the low degree of the poly(4-vinylpyridine) spheres swelling [46]. The best yield and selectivity were obtained using P4VPDVB-Fe(III) catalyst when 10 wt% DVB was employed. Hence, the P4VPDVB$_{10\%}$-Fe(III) complex was chosen as the most efficient catalyst for further investigation.

The microstructure of P4VPDVB$_{10\%}$-Fe(III) catalyst was investigated by SEM, as shown in Fig. 2a. The SEM photographs showed that the P4VPDVB$_{10\%}$ spheres were monodispersed. It was demonstrated that the surface morphology of the P4VPDVB$_{10\%}$ spheres was uniform and smooth, with a diameter of ca. 250 nm. Spheres of cross-linked P4VPDVB$_{10\%}$ supporting $FeCl_3{\cdot}6H_2O$ was prepared by stirring a mixture of P4VPDVB$_{10\%}$ spheres and $FeCl_3{\cdot}6H_2O$ in absolute alcohol for 12 h at 70 °C. The morphology of the P4VPDVB$_{10\%}$-Fe(III) spheres was slightly different from the P4VPDVB$_{10\%}$ spheres, which are shown in Fig. 2b. As shown in HRTEM images (Fig. 2c), the surface of the P4VPDVB$_{10\%}$-Fe(III) catalyst had a slightly rough surface after the immobilization reaction, and the size of the catalyst was ca. 280 nm, which was larger than the P4VPDVB$_{10\%}$ spheres. The elemental maps (Fig. 2d–f) further verified that $FeCl_3{\cdot}6H_2O$ was well dispersed in the shell of the P4VPDVB$_{10\%}$ spheres. The iron elemental maps of the P4VPDVB$_{10\%}$-Fe(III) spheres showed an excellent distribution of $FeCl_3$ over all the spheres (Fig. 2e).

Evidence of the formation of the complexes in the P4VPDVB$_{10\%}$ spheres and P4VPDVB$_{10\%}$-Fe(III) catalyst was further provided by the FTIR, as shown in Fig. 3. All the characteristic bands of P4VPDVB$_{10\%}$ spheres including the characteristic absorption of the pyridine rings at 1598 cm$^{-1}$, 1558 cm$^{-1}$ and 1413 cm$^{-1}$ were ascribed to $\upsilon$(C=N), $\upsilon$(C=C) and $\upsilon$(C—N), respectively. The $\upsilon$(=CH) groups of the out of plane vibrations appeared at 993–819 cm$^{-1}$,

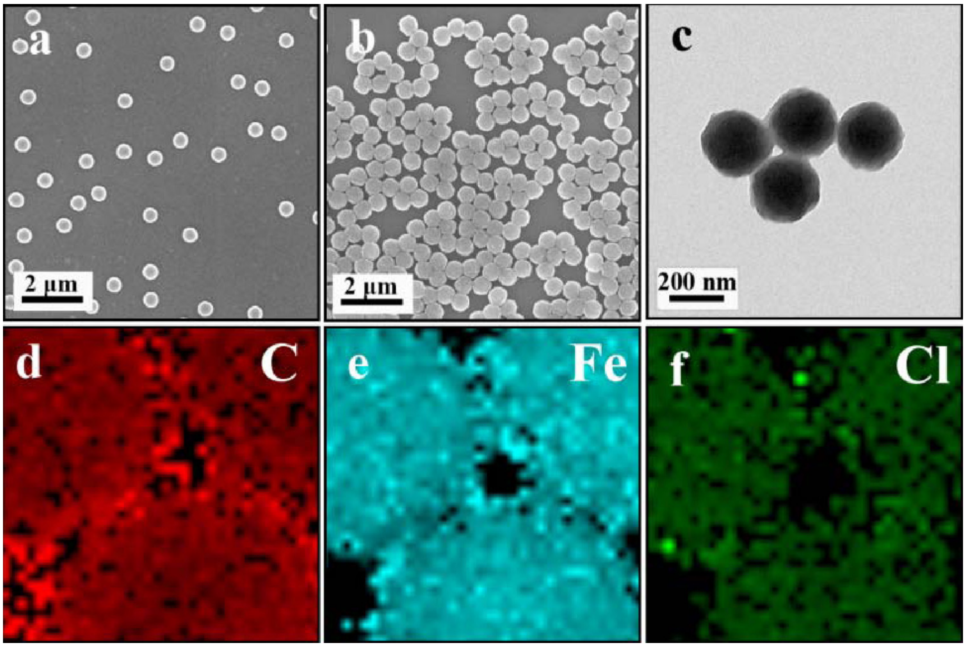


**Fig. 2.** The SEM images of (a) P4VPDVB$_{10\%}$ spheres; (b) the monodispersed P4VPDVB$_{10\%}$-Fe(III) microspheres. (c) The TEM images of the monodispersed P4VPDVB$_{10\%}$-Fe(III) microspheres; (d–f) EDX elemental maps of C, Fe and Cl, respectively.

while the characteristic vibration of the δ (C—C═C) band was also observed at 564 cm$^{-1}$. For the P4VPDVB$_{10\%}$-Fe(III) complexes, the red shift observed in the υ (C═N), υ (C═C), υ (C—N) bands and the υ (═CH) groups of the out of plane vibrations indicated the interaction of N atom of pyridine ring with iron ions. Furthermore, a new peak was observed at 1627 cm$^{-1}$, which indicated the interaction between the iron and the polymer [47].

Fig. 4 shows the XPS spectra of the P4VPDVB$_{10\%}$ spheres and the P4VPDVB$_{10\%}$-Fe(III) catalyst. The strong signals in the P4VPDVB$_{10\%}$ spheres are due to N1s and C1s binding energy, respectively. Compared to the P4VPDVB$_{10\%}$ spheres, four new peaks were discovered in the spectrum of the P4VPDVB$_{10\%}$-Fe(III) catalyst at 55 eV, 198 eV, 268 eV and 711 eV. The binding energy at 55 eV and 711 eV corresponded to the Fe3p and Fe2p2/3, respectively. The peaks at 198 eV and 268 eV were due to the existence of Cl2p and Cl2s binding energy, respectively. The results demonstrated the presence of the iron salts in the P4VPDVB$_{10\%}$-Fe(III) catalyst.

The thermal stability of the P4VPDVB$_{10\%}$ spheres and P4VPDVB$_{10\%}$-Fe(III) catalyst were examined by the TGA in the temperature range of 50–600 °C. The copolymer complex degradation mainly went through two procedures. The first weight loss between 80 °C and 100 °C was due to the moisture present in the complex. The decomposition of the P4VPDVB$_{10\%}$ spheres started at 350 °C and went to its completion at 430 °C. For the P4VPDVB$_{10\%}$-Fe(III) catalyst, the main decomposition stage started at 250 °C and finished at 480 °C. The results demonstrated that the P4VPDVB$_{10\%}$-Fe(III) catalyst is thermally stable under the conditions of benzylic oxidation [46].

### 3.2. Benzylic oxidation catalyzed by P4VPDVB$_{10\%}$-Fe(III) catalyst

The oxidation of 4,4′-difluorodiphenylmethane **1a** for the generation of 4,4′-difluorodiphenylketone **2a** was carried out in 1-mL acetonitrile at 80 °C for 24 h. Initially, only 12% conversion was obtained in the absence of the catalyst employing TBHP as the oxidant source (Table 1, entry 1). A conversion of 50% was obtained when P4VPDVB$_{10\%}$-Fe(III) catalyst was employed (Table 1, entry 2), which suggested that the heterogeneous Fe(III) catalyst was necessary for the conversion of 4,4′-difluorodiphenylmethane **1a**. Pyridine was also employed as an additive in the oxidation reaction system, and up to 82% conversion was achieved (Table 1, entry 3). In addition, other basic additives were examined. However, no further improvement was observed when triethylamine (Et$_3$N) or methanolamine (MEA) was employed (Table 1, entries 4 and 5). In the presence of 1-methylimidazole (1-MI), 69% conversion was obtained (Table 1, entry 6). When hexamethylenetetramine (HMTA) was used as the basic additive, 49% conversion of

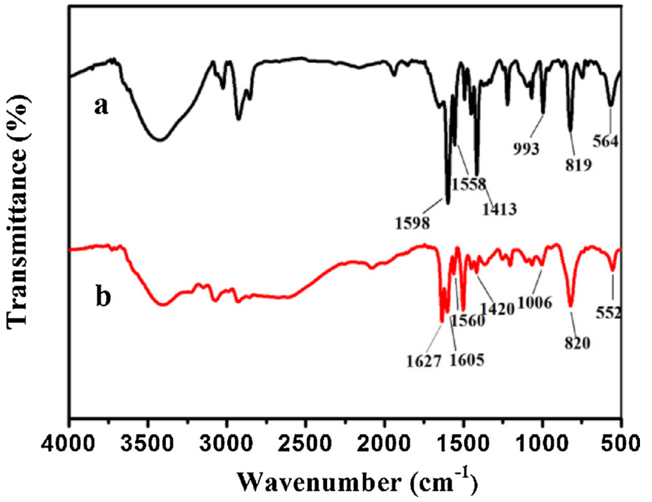


**Fig. 3.** FTIR spectra of (a) the monodispersed P4VPDVB$_{10\%}$ spheres and (b) the monodispersed P4VPDVB$_{10\%}$-Fe(III) catalyst.

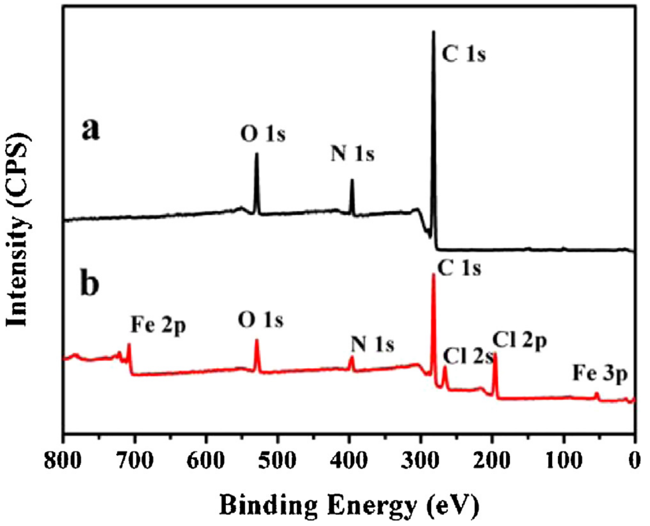
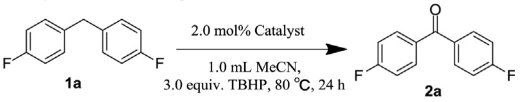


**Fig. 4.** XPS spectra of (a) the monodispersed P4VPDVB$_{10\%}$ spheres and (b) the monodispersed P4VPDVB$_{10\%}$-Fe(III) catalyst.

**Table 1**
Benzylic oxidation in presence of different additives.[a]

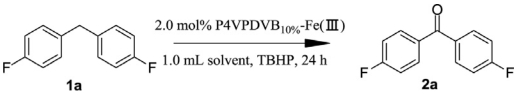


| Entry | Catalyst | Additive | Amount of additive (equiv.) | Conv. (%)[b] | Selec. (%)[b] |
|---|---|---|---|---|---|
| 1 | None | None | None | 12 | 96 |
| 2 | P4VPDVB$_{10\%}$-Fe(III) | None | None | 50 | 95 |
| 3 | P4VPDVB$_{10\%}$-Fe(III) | Pyridine | 1.0 | 82 | >99 |
| 4 | P4VPDVB$_{10\%}$-Fe(III) | Et$_3$N | 1.0 | 4 | >99 |
| 5 | P4VPDVB$_{10\%}$-Fe(III) | MEA | 1.0 | 36 | 96 |
| 6 | P4VPDVB$_{10\%}$-Fe(III) | 1-MI | 1.0 | 69 | 98 |
| 7 | P4VPDVB$_{10\%}$-Fe(III) | HMTA | 1.0 | 49 | 94 |
| 8 | P4VPDVB$_{10\%}$-Fe(III) | Pyridine | 0.5 | 88 | >99 |
| 9 | P4VPDVB$_{10\%}$-Fe(III) | Pyridine | 0.1 | >99 | >99 |
| 10 | FeCl$_3$·6H$_2$O | Pyridine | 0.1 | 76 | 79 |

[a] Reaction conditions: 1.0 mmol **1a**, 2.0 mol% P4VPDVB$_{10\%}$-Fe(III) catalyst, additive, 3.0 mmol TBHP, 1.0 mL acetonitrile, 80 °C, 24 h.

[b] Conversion of **1a**; Selectivity for **2a**, based on **1a**. Conversion and selectivity were detected by GC–MS using nitrobenzene as the internal standard.

**Table 2**
Reaction condition screen of the benzylic oxidation.[a]



| Entry | Solvent | Amount of TBHP (equiv.) | Temperature (°C) | Conv. (%)[b] | Selec. (%)[b] |
|---|---|---|---|---|---|
| 1[c] | None | 3.0 | 80 | 75 | 92 |
| 2 | EtOH | 3.0 | 80 | 19 | 96 |
| 3 | IPA | 3.0 | 80 | 28 | 98 |
| 4 | DMF | 3.0 | 80 | 29 | >99 |
| 5[d] | $H_2O$ | 3.0 | 80 | n.d. | n.d. |
| 6 | PhMe | 3.0 | 80 | 43 | 93 |
| 7[e] | MeCN | 3.0 | 80 | >99 | >99 |
| 8 | MeCN | 1.0 | 80 | 39 | 85 |
| 9 | MeCN | 2.0 | 80 | 79 | 94 |
| 10 | MeCN | 3.0 | 70 | 55 | 97 |
| 11 | MeCN | 3.0 | 90 | >99 | >99 |

[a] Reaction conditions: 1.0 mmol **1a** in 1.0 mL solvent was heated for 24 h with 2.0 mol% $P4VPDVB_{10\%}$-Fe(III) catalyst and TBHP as oxidant.
[b] Conversion of **1a**; Selectivity for **2a**, based on **1a**. Conversion and selectivity were detected by GC–MS with using nitrobenzene as internal standard.
[c] Isolated by column chromatography and the isolated yield was 64%.
[d] n.d. = Not detected.
[e] Isolated by column chromatography and the isolated yield was 93%.

4,4′-difluorodiphenylmethane **1a** was obtained (Table 1, entry 7). These results indicated that pyridine was the best base additive among several organic bases we screened. Based on this result, different amounts of pyridine additive were evaluated for the catalytic system. Over 99% yield was achieved, when 0.1 equivalent of pyridine was used, which significantly reduced the amount of pyridine in comparison to that achieved in the literature report (Table 1, entries 8 and 9) [29]. Furthermore, 76% conversion and 79% selectivity were observed, when iron(III) chloride was used instead of $P4VPDVB_{10\%}$-Fe(III) catalyst (Table 1, entry 10). The good catalytic resulted from $P4VPDVB_{10\%}$-Fe(III) catalyst showed the advantage for catalytic activity enhancement and heterogeneous immobilization in comparison to homogeneous iron(III) chloride.

To further optimize the reaction condition, different solvents were screened (Table 2). In the absence of organic solvent, 75% conversion and 64% isolated yield were obtained (Table 2, entry 1). Ethanol (EtOH), isopropanol (IPA) and dimethyl formamide (DMF) gave conversions of 19%, 28% and 29%, respectively (Table 2, entries 2–4). This may be ascribed to EtOH, IPA or DMF being oxygen or nitrogen-containing solvents with a strong Lewis basic donor, which leads to the deactivation of $P4VPDVB_{10\%}$-Fe(III) catalyst. $H_2O$ showed almost no reactivity due to the low solubility of the catalyst, as well as catalyst deactivation (Table 2, entry 5). When a non-coordinating solvent such as toluene was used, a conversion of only 43% was observed (Table 2, entry 6). Acetonitrile demonstrated good compatibility in the catalytic system and low coordination capacity with the catalyst, which resulted in significantly improved conversion, together with 93% isolated yield (Table 2, entry 7). Moreover, the amount of TBHP used in the reaction system was also examined. A yield of 39% or 79% was observed when the amount of TBHP was decreased to 1.0 or 2.0 equivalent, respectively (Table 2, entries 8–9). In addition, the reaction temperature was also optimized. Only 55% conversion was achieved, when 70 °C was employed as reaction temperature (Table 2, entry 10). When the reaction temperature was increased to 90 °C, no further improvement was observed (Table 2, entry 11). Therefore the optimal catalytic system was set at 2.0 mol% $P4VPDVB_{10\%}$-Fe(III) as catalyst, 0.1 equivalent of pyridine as additive, and 3.0 equivalents of TBHP as an oxidant with 1.0 mL acetonitrile at 80 °C.

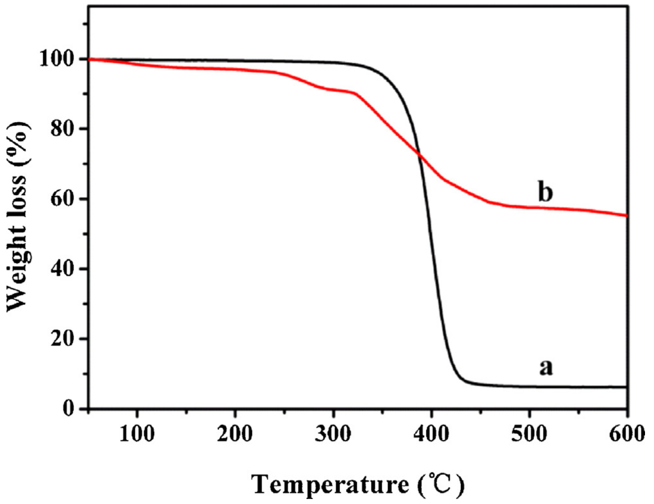


**Fig. 5.** TGA spectra of (a) monodispersed $P4VPDVB_{10\%}$ spheres and (b) monodispersed $P4VPDVB_{10\%}$-Fe(III) catalyst.

The optimized reaction condition was employed for the oxidation of other substrates (Table 3). Ethylbenzene **1b** was oxidized to 1-phenylethanone **2b** in 92% conversion and 97% selectivity (Table 3, entry 1). Moreover, the ethylbenzene bearing methoxy group at *para* position, 1-ethyl-4-methoxybenzene **1c**, was evaluated, the corresponding yield was slightly reduced (Table 3, entry 2). Ethylbenzene with the *para*-fluoro group, 1-ethyl-4-fluorobenzene **1d**, was employed in the reaction; the corresponding product was obtained with excellent conversion and selectivity (Table 3, entry 3). This difference in terms of the yield was attributed to the electron– withdrawing group at *para*-position of ethylbenzene favoring the oxidation. 2-Ethylthiphene **1e** containing a heterocyclic was also employed as the substrate and over 99% conversion and up to 97% selectivity were achieved (Table 3, entry 4). Isochroman **1f** underwent oxidation to give 4-isochromanone **2f** in high yield (Table 3, entry 5). By oxidation of 9H-fluorene **1g**, the reaction proceeded smoothly to form the corresponding ketones with excellent results (Table 3, entry 6). The oxidation of benzylic compounds with the β-methoxy group or β-ester group attached were also investigated (Table 3, entries 7–8); a satisfying result (>99% conversion; 90% selectivity) was observed on account of the β-methoxy group (electron-donating group) favoring this oxidation. In addition, secondary benzylic alcohols were tested, such as (±)-1-phenylethanol **1j**, diphenylmethanol **1k** and 1,4-dihydroxynaphthalene **1l**. (±)-1-Phenylethanol **1j** was completely converted into the corresponding product 1-phenylethanone **2j** when the reaction time reached 6 h (Table 3, entry 9). Then the

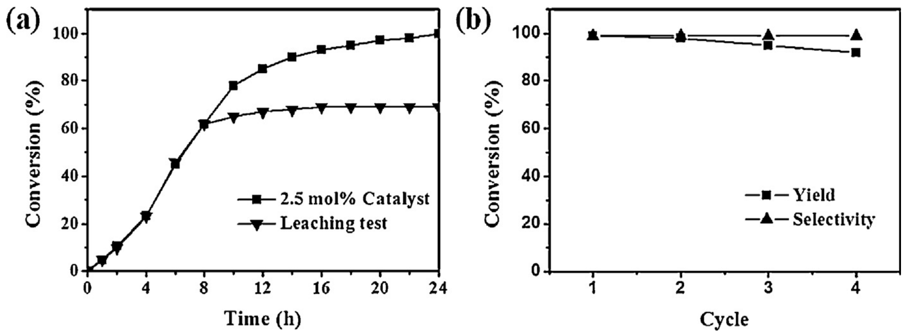
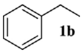
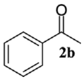
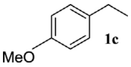
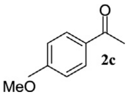
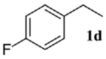
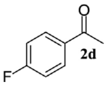
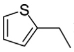
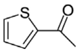
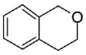
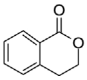
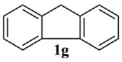
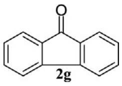
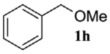
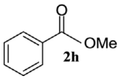
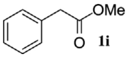
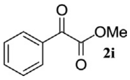
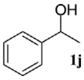
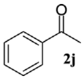
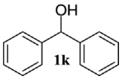
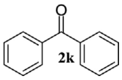
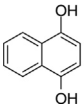
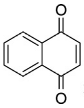


**Fig. 6.** Leaching test (a) and catalytic recycling studies (b).

**Table 3**
Benzylic oxidation of hydrocarbon derivatives.[a]

| Entry | Substrate | Product | Conv. (%)[b] | Selec. (%)[b] |
|---|---|---|---|---|
| 1 |  **1b** |  **2b** | 92 | 97 |
| 2 |  **1c** |  **2c** | 88 | 98 |
| 3 |  **1d** |  **2d** | 98 | 97 |
| 4 |  **1e** |  **2e** | >99 | 97 |
| 5[c] |  **1f** |  **2f** | >99 | 95 |
| 6 |  **1g** |  **2g** | >99 | >99 |
| 7[d] |  **1h** |  **2h** | >99 | 90 |
| 8 |  **1i** |  **2i** | 73 | 93 |
| 9[e] |  **1j** |  **2j** | >99 | >99 |
| 10 |  **1k** |  **2k** | >99 | >99 |
| 11[f] |  **1l** |  **2l** | >99 | >99 |

[a] Reaction conditions: 1.0 mmol **1a**, 2.0 mol% P4VPDVB$_{10\%}$-Fe(III) catalyst, 0.1 equivalent pyridine, 3.0 mmol TBHP, 1.0 mL acetonitrile, 80 °C, 24 h.
[b] Conversion of **1b–1l**; Selectivity for **2b–2l**, based on **1b–1l**. Conversion and selectivity were detected by GC-MS using nitrobenzene as internal standard.
[c] The reaction was performed at 60 °C.
[d] The reaction was performed for 65 °C.
[e] The reaction was performed for 6 h.
[f] The reaction was performed for 1 h, Conversion and selectivity were detected by $^1$H NMR in the DMSO-d6 solvent (see ESI†).

oxidation of diphenylmethanol **1k** to the corresponding product went smoothly in high yield (Table 3, entry 10). More interestingly, a binaphthoquinone **1l** product was rapidly obtained employing 1,4-dihydroxynaphthalene **2l** under mild oxidation condition in extremely short reaction time (Table 3, entry 11). In summary, the P4VPDVB$_{10\%}$-Fe(III) complex was a versatile catalyst for benzylic methylenes and secondary benzylic alcohols (Fig. 5).

A hot filtration test was introduced to prove the heterogeneous nature of the benzylic oxidation catalysis with P4VPDVB$_{10\%}$-Fe(III) catalyst (Fig. 6a). Firstly, the effect of the reaction time on reaction efficiency was investigated.

The conversion increased gradually with the increase of the reaction time and reached 85% at 12 h. The conversion of 4,4′-difluorophenylmethane **1a** went up slightly after an additional 12 h. It was observed that 4,4′-difluorophenylmethane **1a** was completely consumed after the reaction. Then the selectivity was held at 99% during the reaction process. When the conversion reached 60% at 8 h, the organic phase was separated from the 2.0 mol% P4VPDVB$_{10\%}$-Fe(III) catalyst by simple centrifugation. The reaction solution was transferred to a new reaction vessel and further stirred for another 16 h. There was no significant improvement observed after the catalyst was centrifuged from the reaction mixture.

The recyclability and reusability of P4VPDVB$_{10\%}$-Fe(III) catalyst was also tested with 4,4′-difluorophenylmethane **1a** converted into 4,4′-difluorodibenzophenone **2a**. The solid catalyst was reused after centrifugation, washed with ethanol three times and vacuum dried at 40 °C. The recovered catalyst retained excellent efficiency after four runs (Fig. 6b). The high conversion after four cycles indicated the high stability of P4VPDVB$_{10\%}$-Fe(III) catalyst and the low leakage of iron ion. And the SEM photograph and FTIR spectrum showed no significant difference between fresh P4VPDVB$_{10\%}$-Fe(III) catalyst and the one after four uses (Figs. S1 and S2).

## 4. Conclusions

In conclusion, P4VPDVB$_{2.5-40\%}$-Fe(III) complexes were synthesized and utilized as catalyst to promote the oxidation of 4,4′-difluorophenylmethane. The pyridine moiety of these P4VPDVB$_{2.5-40\%}$-Fe(III) complexes acted as an organic base, so the amount of pyridine for this catalytic system was significantly decreased. The relationship between the catalytic activity and the amount of DVB was studied and the P4VPDVB-Fe(III) spheres with 10 wt% DVB exhibited higher activity with good conversion of 4,4′-difluorophenylmethane. Furthermore, a variety of benzylic substrates were also tested and converted to their corresponding ketones in good yields. The initial catalytic activity of the catalyst was maintained after four runs. The catalytic reaction could only proceed in the presence of the P4VPDVB$_{10\%}$-Fe(III) catalyst, and filtrate of the reaction solution made no contribution to the catalytic activity. The further extension of our pyridine amount reducing strategy is currently under investigation.

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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.2015.04.011.

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