#### Tetrahedron 68 (2012) 9423-9428

Contents lists available at SciVerse ScienceDirect

# Tetrahedron

journal homepage: www.elsevier.com/locate/tet

# Poly(4-vinylpyridine-co-divinylbenzene) supported iron(III) catalyst for selective oxidation of toluene to benzoic acid with $H_2O_2$

Weeranuch Karuehanon<sup>a,b</sup>, Chinnapat Sirathanyarote<sup>a,b</sup>, Mookda Pattarawarapan<sup>a,b,\*</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand <sup>b</sup> Center of Excellence for Innovation in Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

#### ARTICLE INFO

Article history: Received 12 June 2012 Received in revised form 15 August 2012 Accepted 3 September 2012 Available online 10 September 2012

Keywords: Toluene oxidation Heterogeneous catalyst 4-Vinylpyridine Hydrogen peroxide Iron(III)

## ABSTRACT

Poly(4-vinylpyridine-*co*-divinylbenzene) supported iron(III) catalysts were developed for the selective oxidation of toluene to benzoic acid in the presence of  $H_2O_2$ . The influence of the DVB content on the capacity of immobilized Fe(III) and on the catalytic activities of the polymeric complexes was investigated. The extent of Fe(III) uptake by the copolymers varied slightly with the concentration of DVB. The catalytic activities generally increase with increasing degree of crosslinker from 2 to 10% and decrease further with increasing the DVB content. Under the optimal conditions (80 °C, 6 h), the catalyst containing 10% DVB was found to be highly efficient in conversion of toluene to benzoic acid with 90% conversion and 96% selectivity.

© 2012 Elsevier Ltd. All rights reserved.

# 1. Introduction

The catalytic oxidation of hydrocarbons has been a topic of interest in synthetic, industrial, and biological chemistry. Oxidation of toluene to benzoic acid, for example, represents a highly significant reaction since benzoic acid is widely used in medicine, in dye, plasticizer, and as a food preservative.<sup>1,2</sup> It is also a key intermediate in the preparation of fine chemicals. Industrially, benzoic acid is produced from catalytic oxidation of toluene with molecular oxygen using a cobalt(II) acetate or bromide promoter in acetic acid under extreme reaction conditions (~200 °C, 10 atm).<sup>3</sup> However, there are several drawbacks of this process such as low energy efficiencies, low selectivity, and the generation of environmentally hazardous waste.

Recently, there has been a considerable effort focusing on the development of new catalysts for the selective oxidation of toluene. Both homogeneous and heterogeneous catalysts based on transition metal complexes have so far been reported. For example, the combination of  $MnO_2$  and *N*-hydroxyphthalimide was used as a catalyst in aerobic oxidation of toluene to yield benzoic acid with 94% conversion and 98% selectivity at 110 °C, 0.3 MPa.<sup>4</sup>

The copper(II) chloride with 6-hydroxy-pyrrolo[3,4-*b*]pyrazine-5,7-dione system could convert toluene to benzoic acid with 70.9% conversion and 93.5% selectivity at 90 °C.<sup>5</sup> Pt/ZrO<sub>2</sub> oxidation of toluene by molecular oxygen in liquid phase-solvent free conditions (90 °C, 101 kPa) produced benzoic acid with up to 60% selectivity at 40% conversion within 3 h.<sup>6</sup>

In order to develop sustainable, inexpensive, and environmentally friendly oxidation reactions, several bioinspired catalytic systems have also been investigated. Among those in particular are biomimetic homogeneous catalytic systems based on iron salts, often complexed with nitrogen-containing ligands such as porphyrins, phthalocyanines, and pyridine derivatives.<sup>7–13</sup> These catalysts have been applied in the oxidation of aliphatic and/or aromatic hydrocarbons using either oxygen or hydrogen peroxide as an oxidant. Nevertheless, many of these systems give low conversion and low product selectivity. Difficulty in the catalyst preparation, recovery, and reuse also further limit such systems from practical use.

To circumvent the problems related with homogeneous catalytic systems, the catalysts can be anchored on the insoluble solid supports to make it heterogeneous.<sup>14–16</sup> Polymeric materials are often used for this purpose since they are typically non-toxic, non-volatile, insoluble, and recyclable. Often metal ions are supported on the surface of polymer using chelating ligands or using monomer containing coordination sites in order to prevent leaching of the metals from the polymer catalysts.<sup>17</sup> Catalytic activity and catalyst stability could be enhanced as a consequence of active site isolation.<sup>18</sup>





<sup>\*</sup> Corresponding author. Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand. Tel.: +66 5394 3341; fax: +66 5389 2277; e-mail address: mookdap55@gmail.com (M. Pattarawarapan).

<sup>0040-4020/\$ —</sup> see front matter @ 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tet.2012.09.004

So far, only precedent exists on hydrocarbon oxidations with polymer supported iron catalysts.<sup>9,19,20</sup> For example, poly(4-vinylpyridine-*co*-divinylbenzene), 6% crosslinked iron salts complexes have been used as co-catalysts with palladium in cyclohexane oxidation in the presence of molecular oxygen and hydrogen.<sup>19</sup> Cyclohexanol and cyclohexanone were obtained in 2.5 mol% with the polymer supported FeCl<sub>2</sub>. In another work, metal–copolymer complexes of poly-4-vinylpyridine grafted on polymer films were used as catalysts in the oxidation of cyclohexene with *tert*-butylhydroperoxide.<sup>20</sup> With an Fe(III)-containing complex, cyclohexene oxide and the side-product, 2-cyclohexene-1-one, were produced in 41.6% and 54.2% yields, respectively.

In search for a simple and environmental friendly catalytic system capable of catalyzing toluene oxidation efficiently, herein, poly(4-vinylpyridine-*co*-divinylbenzene) copolymers containing various amount of divinylbenzene (DVB) were synthesized and used as supports to form polymer complexes with iron(III). The catalytic activities of these complexes in the oxidation of toluene with hydrogen peroxide ( $H_2O_2$ ) were investigated. The best candidate complex was selected for further characterization and applied in the reaction optimization to improve conversion of toluene and enhance the product selectivity. The catalyst reusability was also investigated.

# 2. Results and discussion

In a preliminary study, various poly(4-vinylpyridine-*co*-divinylbenzene) copolymers containing different amounts of DVB crosslinker, PVPDVB<sub>2–50%</sub>, were synthesized to be used as the polymer supports for complexation with iron(III). The pyridine moiety in 4-vinylpyridine can act as nitrogen-donor ligand to bind iron species, while DVB provides a porous structure in the polymeric network. Iron(III) chloride was used as an iron(III) source to form complex with the pyridine moiety in the synthesized copolymers. Since iron(III) has the ability to coordinate from 3 to 8 ligands, depending on the folded structure of the copolymers, complex formation involving more than one pyridine unit per iron ion is likely to occur.

The synthesis parameters and physicochemical properties of the synthesized copolymers were summarized in Table 1. The nitrogen contents of the copolymers determined by elemental analysis were in agreement with the theoretical values calculated from the feed monomer contents. Swelling in both methanol and acetonitrile decreased along with increasing the DVB content. A high concentration of DVB is commonly known to create a more rigid polymeric network having a lesser degree of swelling. The surface area of the

#### Table 1

Copolymers characteristics and iron content of the Fe(III)-copolymer complexes

copolymers determined by BET analysis was also varied according to the DVB content. The highest surface area was obtained with PVPDVB<sub>10%</sub> containing 10% DVB. Lower surface area observed at 2% DVB content is presumably attributed to the absence of porosity at dry state in gel-type copolymer while that at 50% DVB is undoubtedly due to the highly rigid cross-linking polymeric network.

The degree of iron ions introduced into the polymer matrices should be directly dependent on the relative content of the functional groups in the polymers. It is thus expected that copolymer with lower DVB content should exhibit higher loading of Fe(III) due to their high ligand capacity. Surprisingly, according to Table 1, the percentage of Fe(III) anchored on the polymeric complexes varied slightly with the copolymer type and correlation with the DVB content cannot be observed. The degree of swelling and fold structure of the polymeric network may lead to various coordination modes in complex formation, which in turn affect on the degree of iron uptake.

The catalytic activities of the synthesized polymer metal complexes were screened in the oxidation of toluene using  $H_2O_2$  as an oxidant in acetonitrile. Excess amount of  $H_2O_2$  was used in this study (1:9.4 mole ratio of toluene/ $H_2O_2$ ) due to the possibility of its decomposition in the presence of Fe(II/III) salts. Acetonitrile was used as the solvent since it has been shown to provide high catalytic activity in other iron catalytic systems due to a comparatively good solubility power for both the organic substrate and the aqueous  $H_2O_2$ .<sup>16,22,23</sup> All oxidation reactions were carried out at 80 °C for 1 and 6 h. It was found that the catalytic oxidation reaction involved both the benzylic oxidation and the benzene ring hydroxylation, which yielded benzoic acid (PhCOOH), benzaldehyde (PhCHO), benzyl alcohol (PhCH<sub>2</sub>OH), *o*-cresol, *m*-cresol, and *p*cresol as the oxidative products (Scheme 1). Nevertheless, in all cases, benzoic acid was obtained as the predominant product.

The conversion of toluene and selectivity toward benzoic acid formation are summarized in Table 2. Generally, the catalytic activities of the Fe(III)–copolymer complexes increase with increasing the degree of DVB cross-linking from 2 to 10% and decrease further with increasing the DVB content. When the oxidation reaction was performed at 80 °C for 1 h, the toluene conversions were in the range between 13.3 and 32.6% while the selectivity to benzoic acid was relatively high in all cases (72.8–88.1%). Increasing the reaction time from 1 to 6 h resulted in enhancement in both conversion (73.0–89.7%) and selectivity toward benzoic acid (88.3–91.2%).

Since the loading of Fe(III) on the polymer complexes was almost invariable according to the polymer type, the low conversion



Fe(III)-copolymer complex	Polymer characterization					Fe content (mmol/g)
	Yield (%)	N <sup>a</sup> (%)	Swelling (%)		Surface area <sup>c</sup> (m <sup>2</sup> /g)	
			MeOH	CH₃CN		
Fe(III)–PVPDVB <sub>2%</sub>	75	12.4 [13.0] <sup>b</sup>	150	150	8.1	0.55
Fe(III)-PVPDVB <sub>6%</sub>	75	11.5 [12.4] <sup>b</sup>	110	110	13.2	0.54
Fe(III)-PVPDVB <sub>10%</sub>	96	10.7 [11.8] <sup>b</sup>	90	100	14.4	0.41
Fe(III)-PVPDVB <sub>25%</sub>	73	10.2 [10.1] <sup>b</sup>	60	60	13.4	0.52
Fe(III)-PVPDVB <sub>50%</sub>	97	8.4 [8.2] <sup>b</sup>	50	50	4.4	0.46

<sup>a</sup> From elemental analysis (CHN).

<sup>b</sup> [Theoretical value].

<sup>c</sup> Determined by BET method.



Scheme 1. Catalytic oxidation of toluene with hydrogen peroxide.

Table 2	
Toluene oxidation with	the Fe(III)-copolymer complexes

Entry	Fe(III)-copolymer complex	Reaction time				
		1 h		6 h		
		Conversion (mol%)	Selectivity to PhCOOH (mol %)	Conversion (mol%)	Selectivity to PhCOOH (mol %)	
1	Fe(III)—PVPDVB <sub>2%</sub>	20.1	81.4	73.0	91.0	
2	Fe(III)-PVPDVB <sub>6%</sub>	24.1	86.9	78.8	90.2	
3	Fe(III)-PVPDVB10%	32.6	88.1	89.7	91.2	
4	Fe(III)-PVPDVB <sub>25%</sub>	30.4	87.0	77.0	89.3	
5	Fe(III)-PVPDVB50%	13.3	72.8	77.9	88.3	

<sup>a</sup> All reactions were carried out with toluene (1.46 mmol), 35% H<sub>2</sub>O<sub>2</sub> (13.7 mmol) using 10 mg of the Fe(III)-copolymer complex in CH<sub>3</sub>CN at 80 °C.

observed when using the copolymer complexes with low DVB content (entries 1 and 2) could be attributed to the saturation in the Fe(III) coordination sphere, due to the high pyridyl/Fe(III) ratio and highly flexible fold structures of the polymer complex, thus preventing the coordination of hydrogen peroxide.<sup>20,24,25</sup> On the other hand, the low conversion of toluene when using the complexes with higher DVB content (entries 4 and 5) could be associated with the low surface area and low degree of swelling of the polymer supports, which hinder mass transfer process in the heterogeneous catalytic system.

The best conversion and selectivity were observed using the Fe(III)–PVPDVB<sub>10%</sub> catalyst (entry 3). Though it should be noted that the amount of Fe(III) incorporated in this catalyst was significantly less than the estimated loading presuming that iron(III) forms eight maximum coordinate bonds with pyridines (0.41 mmol/g vs 0.95 mmol/g). This data indicated that some pyridyl units may have limit accessibility, while the fold structures of the polymeric chains can also affect on the degree of iron uptake.

Complex formation in the Fe(III)–PVPDVB<sub>10%</sub> catalyst was further investigated by FTIR. The IR spectrum of PVPDVB<sub>10%</sub> (Fig. 1) showed the characteristic absorption bands of pyridine ring at 1595, 1555, and 1413 cm<sup>-1</sup> attributed to  $\nu$ (C=N),  $\nu$ (C=C), and  $\nu$ (C–N), respectively.<sup>26</sup> A band at 993–819 cm<sup>-1</sup> is the out-of-plane

а 562 C-C=C 1555 =CH C=N/ 819 C=C 1414 1595 b 548 813 1635 1602 2000 500 1500 1000 Wavenumber (cm<sup>-1</sup>)

Fig. 1. FTIR spectra of (a) PVPDVB<sub>10%</sub> and (b) Fe(III)–PVPDVB<sub>10%</sub>.

vibrations of the v(=CH) groups, while the  $\delta(C-C=C)$  vibration at 562 cm<sup>-1</sup> was also observed. For the iron(III)–polymer complex, the corresponding v(C=N), v(C=C), and v(C-N) bands as well as a band at 993 cm<sup>-1</sup> were shifted toward longer wavelength. These shifts indicated the interaction of the nitrogen atom in the pyridyl moiety with iron(III) ion.<sup>18</sup>

Since the Fe(III) is a very acidic cation with hydrolytic properties above pH 2, the production of iron(III) hydroxide, Fe(OH)<sub>3</sub>, during the complexation is therefore possible and can lead to the precipitation of Fe(OH)<sub>3</sub> on polymer supports. To further confirm that iron(III) was complexed with the nitrogen of the pyridyl moiety of the support, the Fe(III)–PVPDVB<sub>10%</sub> catalyst was further investigated by FT-Raman spectroscopy. As shown in Fig. 2, no peaks at 303, 387, and 698 cm<sup>-1</sup> (characteristic of Fe(OH)<sub>3</sub>) were observed in the spectrum of the prepared catalyst, indicating that the precipitation of Fe(OH)<sub>3</sub> on polymer support was not occurred.<sup>29</sup> The assignment of Raman spectrum was listed in Table 3.<sup>27,28</sup>

Unfortunately, at this point, it was unable to characterize the exact structure of the catalyst due to its heterogeneity, though it was believed that various coordination modes of Fe(III)–ligand complex may take place. From the FT-Raman result, since Fe(OH)<sub>3</sub> was not observed in the iron–polymer complex, it was assumed that Fe(OH)<sub>3</sub> was not present as the active catalyst species. However, the presence of Fe(Py)Cl stretching at 330 cm<sup>-1</sup> further indicated coordination complex between Fe(III) and the nitrogen atom in the pyridyl moiety of the support.



Fig. 2. Raman spectrum of Fe(III)-PVPDVB<sub>10%</sub>.

#### Table 3

Raman si	pectrum	assignment	of the	Fe(III)	-PVPDVB109	comi	olex
					10/	o · · ·	C

Assignment of the pyridyl moiety and Fe(Py)Cl bond	Frequency (cm <sup>-1</sup> )		
Ring stretching	1631		
Ring stretching	1448		
In-plane CH bending	1201		
In-plane CH bending	1064		
Assym. ring breathing	1005		
In-plane ring deformation	648		
Fe(Py)Cl stretching	330		

The thermal stability of the Fe(III)–PVPDVB<sub>10%</sub> complex relative to the corresponding copolymer support was examined using the TGA technique, over the temperature range of 50–600 °C. From the TGA curves (Fig. 3), both the polymers degraded mainly in two stages. The initial weight loss was attributed to the loss of adsorbed



Fig. 3. TGA curves for PVPDVB $_{10\%}$  and Fe(III)–PVPDVB $_{10\%}$  complex.

moisture. The polymer decomposition started at ca. 350 °C and virtually completed at 450 °C for the support and at 500 °C for the Fe(III)–PVPDVB<sub>10%</sub> complex. The TGA results suggested that both materials should be thermally stable under the applied reaction conditions.

To optimize the reaction conditions, various parameters that influence the outcome of toluene oxidation including reaction temperature, the amount of the catalyst, and reaction time were further investigated using the Fe(III)–PVPDVB<sub>10%</sub> complex as the catalyst. The effect of temperature on the oxidation of toluene was studied over the reaction temperature range from 25 to 80 °C while keeping other parameters constant. According to Fig. 4, at a reaction temperature below 60 °C, a slight increase in the toluene conversion along with the selectivity toward benzoic acid was observed with a sharp enhancement from 60 to 80 °C. At elevated temperature, the diffusion rate of the H<sub>2</sub>O<sub>2</sub> and toluene molecules to the catalytic sites of the polymeric complex is accelerated thus causes the reaction to proceed at a faster rate.<sup>4</sup>

The influence of the amount of the catalyst on the oxidation reaction was then investigated at 80 °C after 6 h over the catalyst quantity range of 1–200 mg (0.03–5.62 mol %). No toluene oxidation was observed when using 1 mg of the catalyst (Fig. 5). When increasing the catalyst quantity from 1 to 10 mg, toluene oxidation, as well as selectivity toward benzoic acid formation, increased significantly and reached the highest values in this range. However, both the conversion and the selectivity reduced considerably with further addition of the catalyst. This observation could be due to low capability of mass transfer in the reaction and the non-availability of catalytic sites when using excessive amounts of the catalyst.<sup>16,30,31</sup>

Effect of the reaction time on the efficiency of the reaction was further studied using 10 mg of the Fe(III)–PVPDVB<sub>10%</sub> catalyst at 80 °C. As shown in Fig. 6, the degree of toluene oxidation increases slightly at the beginning then increases rapidly from 4 to 6 h. After 6 h, no significant change in the conversion as well as the selectivity toward benzoic acid was observed indicating the reaction was completed within 6 h.

It is notable that in control experiments where the reactions were carried out under the optimal conditions (80  $^{\circ}$ C at 6 h with



Fig. 4. Influence of reaction temperature on (a) the reaction conversion and (b) product selectivity after 6 h of reaction time using 10 mg (0.28 mol %) of Fe(III)-PVPDVB10% catalyst.



Fig. 5. Influence of the amount of the Fe(III)-PVPDVB10% catalyst on (a) the reaction conversion and (b) product selectivity after 6 h of reaction time at 80 °C.



Fig. 6. Influence of reaction time on (a) the reaction conversion and (b) product selectivity at reaction temperature of 80 °C using 10 mg of the Fe(III)-PVPDVB10% catalyst.

10 mg of the catalyst) but in the absence of the supported catalyst or in the presence of free PVPDVB, no toluene oxidation was observed. The oxygen released in the H<sub>2</sub>O<sub>2</sub> decomposition should also play no role in the toluene oxidation since no conversion was observed when performing the reaction under similar conditions but using atmospheric oxygen as oxidant. When FeCl<sub>3</sub>·6H<sub>2</sub>O was added as a catalyst, less than 58% toluene conversion with up to 92% selectivity toward benzoic acid was observed indicating higher catalytic activity of the Fe(III)–PVPDVB<sub>10%</sub> complex than a simple salt. The catalyst turnover number calculated from the mole ratio of total products/catalyst was 319.

According to the previous reports on the other iron–nonheme complexes catalyzed hydrocarbons oxidation,<sup>23,32,33</sup> the reaction between the catalyst and H<sub>2</sub>O<sub>2</sub> is likely to start with the formation of an Fe(III)–hydroperoxo species (LFe<sup>III</sup>OOH). Upon decomposition by O–O bond heterolysis gives rise to a high-valent iron-oxo species (LFe<sup>V</sup>=O), both of which could be involved in substrate oxidation in a highly selective manner. However, homolytic cleavage of LFe<sup>III</sup>OOH will generate LFe<sup>IV</sup>=O along with a highly reactive •OH radical, which are responsible for nonselective oxidation.

Interestingly, in all cases, selectivity toward the benzylic oxidation was always accompanied by high toluene conversion whereas ring hydroxylation products increased at low toluene conversion. This observation suggested that the selectivity outcome of Fe(III)–PVPDVB<sub>10%</sub> catalyzed oxidation of toluene could be governed by more than one of the oxidizing species described above depending on the reaction conditions. In addition, •OH radical generated from  $H_2O_2$  decomposition could also be able to oxidize toluene non-selectively, especially when performing the reaction under a short period of time at low temperature.

The recyclability of Fe(III)–PVPDVB<sub>10%</sub> in toluene oxidation was also investigated under the optimal reaction conditions. Preliminary study showed a decrease in toluene conversion by 11% after the first cycle, which could be due to leaching of iron ions from the polymer support. It is possible that the reaction products such as cresols and benzoic acid can act as a catalyst deactivator by competing coordination against the pyridyl moiety of the copolymer and cause leaching of the iron ions. After each cycle, the used catalyst was regenerated by treating the used material with a saturated methanolic solution of FeCl<sub>3</sub>·6H<sub>2</sub>O before the subsequent runs. With the pretreatment step, there was no significant change in the conversion and selectivity after five consecutive recycles. High substrate conversions (74–90%) and excellent benzoic acid selectivity (88–96%) can be obtained.

#### 3. Conclusions

Various Fe(III)–PVPDVB complexes were synthesized and applied as catalysts in the oxidation of toluene in the presence of H<sub>2</sub>O<sub>2</sub>. The degree of DVB in the polymer supports was found to have a direct influence on the catalytic activities of the polymeric complexes by controlling the catalyst surface area, degree of swelling, and plausibly the coordination mode in the iron(III)—copolymer complexes. Using the catalyst containing 10% DVB, toluene can be converted to benzoic acid with up to 96% selectivity and 90% conversion within 6 h at 80 °C. Since this heterogeneous catalyst can be simply removed by filtration then recovered and reused, it also enhances product purity, environmental friendly, and promises economic.

#### 4. Experimental

#### 4.1. Material and methods

All reagents were purchased from Fluka and Aldrich and were used without further purification. Acetonitrile was analytical grade and was purified prior use. The iron content of the polymer complex was determined using atomic absorption spectrophotometer (Shimadzu, AA-670). Elemental analysis was performed using CHNS/O ANALYSER, Perkin Elmer PE2400 Series II. Infrared (IR) spectra were recorded in the range of 4000–400 cm<sup>-1</sup>on a Shimadzu FT-IR 8900 spectrometer in KBr pellet. Raman spectra were recorded on FT-IR Raman Spectrometer, Spectrum GX, Perkin Elmer, USA. BET surface area measurement was performed by N2 adsorption on Autosorb-1-MP (Quantachrome Corporation, Boynton Beach, Florida, USA). Thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer Model TG-7 Instrument. TG sample was heated in air in the range of 50-600 °C at 20 °C/min. Gas chromatographic (GC) measurements were carried out on Agilent GC-6890A (G2163A), equipped with a capillary column (column: innowax; column length: 30 m; column temperature: 40–260/270 °C).

## 4.2. Preparation and characterization of the polymer support

Poly(4-vinylpyridine-*co*-divinylbenzene) crosslinked with various mol% of DVB, PVPDVB, was synthesized by suspension copolymerization according to the reported procedure.<sup>21</sup> The reaction was carried out in 250 mL three-necked round bottom flask fitted with reflux condenser. A solution of polyvinyl alcohol (PVA) (150 mg) in water (50 mL) was stirred at 50 °C under N<sub>2</sub> for 15 min. Whilst the mixture of 4-vinylpyridine (1.03 g, 10 mmol), divinylbenzene (as indicated in Table 1), and benzoyl peroxide (0.025 g, 0.1 mmol) in test tube was also bubbled by N<sub>2</sub> for 15 min before adding to the PVA solution under N<sub>2</sub> atmosphere. The reaction mixture was then purged by N<sub>2</sub> gas for 10 min and heated up to 85 °C. After stirring for 16 h, the obtained polymer was poured into 50 mL of water, filtered off, then washed sequentially with water, THF, and methanol and dried at 80 °C overnight. The polymer was characterized by elemental analysis, swelling degree, FTIR, and BET analysis.

# **4.3.** Preparation and characterization of the polymer support iron(III)

PVPDVB (0.50 g) was stirred with a saturated solution of FeCl<sub>3</sub>·6H<sub>2</sub>O in methanol (pH=2) at reflux temperature for 16  $h^{.20}$ 

After filtration, the polymer complex was washed repeatedly with methanol to remove free iron ions and dried at 60 °C to obtain yellow-brown beads of the Fe(III)-copolymer complex. AAS analysis was used to analyze the methanol filtrate in the final wash to ensure no trace of iron ion was left in the solution. The complexation between PVPDVB and iron(III) ion was investigated by FTIR and FT-Raman techniques. The iron content in the Fe(III) supported polymer was determined by atomic absorption spectroscopy (AAS) using the standard AOAC method.

#### 4.4. Oxidation of toluene: general procedure

Toluene oxidation reaction was carried out following the previous reported procedure with modification.<sup>16</sup> The amount of the catalyst, reaction temperature, and time were applied as indicated in each table and figure. Briefly, a mixture of toluene (1.46 mmol) and 35% aqueous H<sub>2</sub>O<sub>2</sub> (13.7 mmol) in acetonitrile (4 mL) was added with an appropriate amount of the polymer catalyst and continued stirring vigorously at the desired temperature. After required hours, the excess of H<sub>2</sub>O<sub>2</sub> was then quenched with saturated solution of sodium thiosulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) and the reaction mixture was filtered to remove the catalyst, followed by extraction with ethyl acetate. The organic layer was combined and evaporated. The crude mixture was reconstituted in 1 mL acetonitrile before analysis by GC using bromobenzene as an internal standard. The amount of toluene and its products was quantitatively analyzed using calibration curve based on the relative area of authentic sample relative to internal standard. The conversion of reaction was estimated as a mole ratio of total products/substrate × 100. Selectivity was calculated from a mole ratio of product/reacted substrate×100. The experiment was duplicated to ensure reproducibility of the data.

## 4.5. Fe leaching study

The leaching of Fe(III) from the used polymer supported catalyst was investigated by AAS technique. The toluene oxidation was carried out according to the general procedure. After completion of the reaction, followed by aqueous workup, the crude reaction mixture was reconstituted in 1 mL acetonitrile. The volume of the acetonitrile solution was then re-adjusted again to 25 mL with 1% HNO<sub>3</sub> then the Fe content was analyzed by AAS.

#### Acknowledgements

This research was supported by the grant under the program Strategic Scholarships for Frontier Research Network for the Ph.D. Program Thai Doctoral degree from the Commission on Higher Education (CHE), Thailand (to W.K.). The authors also gratefully

acknowledge the Center of Excellence for Innovation in Chemistry (PERCH-CIC), and the National Research University Project under Thailand's Office of the Higher Education Commission for additional financial support to this research. Valuable discussion and suggestions from and Associate Prof. Apinpus Rujiwatra and Dr. Praput Thavornyutikarn (Chiang Mai University) are greatly appreciated.

#### **References and notes**

- 1. Shijina, A. V.; Renuka, N. K. React. Kinet. Catal. Lett. 2008, 94, 261-270.
- Fraga-Dubreuil, J.; Garcia-Serna, J.; Garcia-Verdugo, E.; Dudd, L. M.; Aird, G. R.; Thomas, W. B.; Poliakoff, M. J. supercritical 2006, 39, 220-227.
- 3. Ilyas, M.; Sadiq, M. Catal. Lett. 2009, 128, 337-342.
- Jiang, J.; Jing, Y.; Zhang, Y.; Zhang, N.; Jiao, J.; Zhu, W.; Xue, H.; Zong, Y.; Yang, G. Catal. Lett. 2011, 141, 544-548.
- Zhang, Q.; Chen, C.; Xu, J.; Wang, F.; Gao, J.; Xia, C. Adv. Synth. Catal. 2011, 353, 226-230.
- 6. Ilyas, M.; Sadiq, M. Catal. Lett. 2008, 1-6.
- Louloudi, M.; Bilis, G. Bioinorg. Chem. Appl. 2010, no. 861892.
- Bilis, G.; Christoforidis, K. C.; Deligiannakis, Y.; Louloudi, M. Catal. Today 2010, 157, 101-106.
- 9. Gupta, K. C.; Kumar Sutar, A.; Lin, C. C. Coord. Chem. Rev. 2009, 253, 1926-1946. 10. Que, L., Jr.; Tolman, W. B. Nature 2008, 455, 333-340.
- 11. Lee, S. H.; Han, J. H.; Kwak, H.; Lee, S. J.; Lee, E. Y.; Kim, H. J.; Lee, J. H.; Bae, C.; Lee, S. N.; Kim, Y.; Kim, C. Chem.-Eur. J. 2007, 13, 9393-9398.
- 12. Balland, V.; Mathieu, D.; Pons-Y-Moll, N.; Bartoli, J. F.; Banse, F.; Battioni, P.; Girerd, J. J.; Mansuy, D. J. Mol. Catal. A: Chem. 2004, 215, 81-87.
- 13. Costas, M.; Chen, K.; Que, L., Jr. Coord. Chem. Rev. 2000, 200-202, 517-544.
- 14. Valkenberg, M. H.; Holderich, W. F. Catal. Rev.-Sci. Eng. 2002, 44, 321-374.
- Schlick, S.; Bortel, E.; Dyrek, K. Acta Polym. 1996, 47, 1-15. 15.
- 16. Monfared, H. H.; Amouei, Z. J. Mol. Catal. A: Chem. 2004, 217, 161-164.
- 17. Gauli, K.; Ram, R. N.; Soni, H. P. J. Mol. Catal. A: Chem. 2005, 242, 161-167.
- 18. Lu, J.; Toy, P. H. Chem. Rev. 2009, 109, 815-838.
- Jun, K.-W.; Shim, E.-K.; Kim, S.-B.; Lee, K.-W. Stud. Surf. Sci. Catal. 1994, 82, 19. 659–666.
- 20. Turmanova, S.; Vassilev, K.; Boneva, S. React. Funct. Polym. 2008, 68, 759-767. 21. Borhan, B.; Wilson, J. A.; Gasch, M. J.; Ko, Y.; Kurth, D. M.; Kurth, M. J. J. Org.
- Chem. 1995, 60, 7375-7378. 22. Tanase, S.; Reedijk, J.; Hage, R.; Rothenberg, G. Top. Catal. 2010, 53, 1039–1044.
- 23. Gozzo, F. J. Mol. Catal. A: Chem. 2001, 171, 1-22.
- 24. Kumar, G. S. V.; Mathew, B. J. Appl. Polym. Sci. 2004, 92, 1271-1278.
- 25. Gupta, K. C.; Abdulkadir, H. K.; Chand, S. J. Mol. Catal. A: Chem. 2003, 202, 253-268.
- 26. Jandrey, A. C.; de Aguiar, A. P.; de Aguiar, M. R. M. P.; de Santa Maria, L. C.; Mazzei, J. L.; Felzenszwalb, I. Eur. Polym. J. 2007, 43, 4712-4718.
- 27. Gu, R. A.; Cao, P. G.; Yao, J. L.; Ren, B.; Xie, Y.; Mao, B. W.; Tian, Z. Q. J. Electroanal. Chem. 2001. 505. 95-99.
- 28. De Silva, C.; Czarnecki, K.; Rvan, M. D. Inorg, Chim. Acta 1999, 287, 21-26.
- 29. Larroumet, D.; Greenfield, D.; Akid, R.; Yarwood, J. J. Raman Spectrosc. 2007, 38,
- 1577-1585. 30. Huang, G.; Luo, J.; Deng, C. C.; Guo, Y. A.; Zhao, S. K.; Zhou, H.; Wei, S. Appl. Catal. A 2008, 338, 83-86.
- 31. Guo, C.-C.; Huang, G.; Zhang, X.-B.; Guo, D.-C. Appl. Catal., A 2003, 247, 261–267.
- 32. Ramirez, J. H.; Costa, C. A.; Madeira, L. M.; Mata, G.; Vicente, M. A.; Rojas-Cervantes, M. L.; Lopez-Peinado, A. J.; Martin-Aranda, R. M. Appl. Catal., B 2007, 71 44-56
- 33. Lubben, M.; Meetsma, A.; Wilkinson, E. C.; Feringa, B.; Que, L., Jr. Angew. Chem., Int. Ed. Engl. 1995, 34, 1512-1514.