



Short Communication

Ti-phenyl nanoparticles encapsulated in mesoporous silica as active and selective catalyst for the oxidation of alkenes

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ABSTRACT

Ti-phenyl nanoparticles encapsulated in mesoporous silica (Ti-phenyl@SiO₂) were synthesized and used as catalysts in the oxidation of styrene by aqueous H₂O₂. The Ti-phenyl@SiO₂(2) with Si/Ti mol ratio of two exhibited the best catalytic performance for the oxidation of styrene with 92% conversion and 99% selectivity towards benzaldehyde. This superior catalytic activity shown Ti-phenyl@SiO₂ catalyst was attributed to the presence of phenyl-group and SiO₂ on Ti and the ease in accessibility to the active sites by the porous SiO₂.

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1. Introduction

Metal nanoparticles have grown to be increasingly popular in catalysis. The main advantage of metal nanoparticles in catalysis is their large surface area and high efficiency under mild condition, when compared with micro or macro catalysts [1,2]. It has been shown that the catalytic activity and selectivity of metal nanoparticles are strongly dependent upon their size, substrate and active metals sites [3,4].

For catalytic applications, hydrophobic substrates can only be strongly adsorbed on hydrophobic surfaces of the catalysts. The hydrophobic moiety on the metal can be improved by modification with organic moieties through covalent bonding to the active sites on metals (M-C). These organic groups are also useful to prevent agglomeration of the metal nanoparticles [5]. However, metals nanoparticles are less stable in solutions [6]. To overcome this problem, encapsulation of metal nanoparticles in oxides such as, silica (SiO₂), alumina (Al₂O₃) and zirconium oxide (ZrO₂) has been carried out [7]. Silica is a good adsorbent and catalyst support due to its hydrophilicity and the ease of accessibility by organic substrates through the pores of SiO₂ [8]. Therefore, the synthesis of Ti-phenyl encapsulated by mesoporous SiO₂ shell could be an ideal catalyst to oxidize alkenes [9]. Here, the activity of Ti-phenyl nanoparticles encapsulated in mesoporous silica was evaluated in the

oxidation of different alkenes, namely 1-octene, 1-dodecene and styrene by aqueous H₂O₂ in order to prove the selectivity of the SiO₂'s pores. The catalytic activity and selectivity of Ti-phenyl@SiO₂ catalysts in the oxidation alkenes were compared to those of commercial TiO₂.

2. Experimental

2.1. Preparation of Ti-phenyl and Ti-phenyl@SiO₂

Ti-phenyl nanoparticles encapsulated in mesoporous SiO₂ were synthesized in three steps by following the original procedure reported [10,13], with some minor modifications. Typically, aniline (50 mmol) was dissolved in ice cold 50% fluoroboric acid (20 ml) and then the solution was placed in an ice bath with stirring for 30 min. Then, a cold solution of sodium nitride (50 mmol) was added to deionized water (10 ml). The solution was then allowed to stir for 1 h. The prepared phenyldiazonium fluoroborate was washed with cold ethanol. For the second step, phenyldiazonium fluoroborate (5 mmol) was dispersed in tetrahydrofuran (20 ml). After 1 h of vigorous stirring, 2.5 mmol of TiCl₄ was added directly into phenyldiazonium suspension. Typically, the reduction of TiCl₄ (5 mmol) and phenyldiazonium fluoroborate (10 mmol) with sodiumborohydride (12 mmol) was done to produce titanium-phenyl nanoparticles (Ti-phenyl), followed by coating of the Ti-phenyl using 5 to 20 mmol of tetraethyl orthosilicate (TEOS Fluka). The Ti-phenyl@SiO₂ formed has Si/Ti mol ratio of 1 to 4, and labeled as Ti-phenyl@SiO₂(x), where x corresponds to the Si/Ti mol ratio. The amount of Ti was constant for all of the samples.

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2.2. Characterization of catalysts

The structure of Ti–phenyl was confirmed by means of ^{13}C and ^1H nuclear magnetic resonance (NMR) measurements. Liquid ^{13}C and ^1H NMR experiments were carried using Bruker Avance 300 MHz spectrometer. The ^{13}C of Ti–phenyl and ^1H of Ti–phenyl spectra were analyzed with numbers of scan of 512 and 32, respectively. The lattice fringes, core particles size, and the existence of the SiO_2 shell of Ti–phenyl and Ti–phenyl@ SiO_2 were characterized using a Philips CM200/FEG high resolution transmission electron microscope (HRTEM), with acceleration voltage of 200 kV. The pore size distribution and the surface areas of Ti–phenyl@ SiO_2 formed were determined by nitrogen (N_2) sorption analysis utilizing the BET method with a Quantachrome instrument.

2.3. Catalytic testing

The catalytic activity of the Ti–phenyl@ SiO_2 being made was carried out in the oxidation of styrene with 30% H_2O_2 as an oxidant. The reactions were carried out with mixtures containing styrene (5 mmol), H_2O_2 (8 mmol), 50 mg of catalysts and acetonitrile (3.61 ml) in a spherical flask attached to a condenser at 80 °C with stirring for 24 h. The products from the reactions were separated by centrifugation and analyzed by gas chromatography (GC) Shimadzu GC-2014 equipped with BPX-5 column, with length of 30 m, inner diameter of 0.25 mm, film thicknesses of 0.25 μm and a flame ionization detector (FID).

3. Results and discussion

3.1. Characteristics of Ti–phenyl and Ti–phenyl@ SiO_2

The formation of phenyldiazonium and Ti–phenyl bonding were characterized by ^{13}C and ^1H nuclear magnetic resonance (NMR). Fig. 1

shows the ^{13}C NMR spectra of aniline, phenyldiazonium and Ti–phenyl. From Fig. 1a, it can be seen that five phenyl carbons of aniline can be clearly identified at 146.42, 129.13, 118.60 and 114.74 ppm. The four phenyl carbon peaks of phenyldiazonium also appeared at 155.44, 130.03, 120.70 and 115.44 ppm (Fig. 1b). Peak broadening and chemical shifting of carbon most adjacent to nitrogen can be seen at chemical shift of 146.42 to 155.44 ppm in the ^{13}C NMR of aniline (Fig. 1a) and phenyldiazonium (Fig. 1b). This might be due to the effect of substituent $\text{N}=\text{N}$ bonding to phenyl. For the ^{13}C NMR spectrum of Ti–phenyl nanoparticles shown in Fig. 1c, three types of phenyl carbon can be identified at chemical shift of 162.33, 161.17 and 103.74 ppm. Chemical shifts and broadening occurred for all the carbon of Ti–phenyl, which is caused by heteronuclear interaction of the bonding between Ti and phenyl. This is the results of fast spin–spin relaxation of carbon close to a metal core [11].

Fig. 2 shows the ^1H NMR spectra of aniline, phenyldiazonium tetrafluoroborate, and Ti–phenyl. In the Fig. 2a, the existence of five phenyl protons can be proven by the peaks at 6.8 (3H) and 7.2 (2H) ppm, and one of amine proton is at 6.8 ppm huddle with the phenyl proton peaks. As shown in Fig. 2b, for phenyldiazonium tetrafluoroborate, the five phenyl protons peaks have been broadening and shifting due to the $\text{N}=\text{N}$ functional group lying closer to titanium nanoparticles. Five of these peaks can be identified at 6.9, 7.3, 7.9, 8.3 and 8.6 ppm; the same case for ^1H NMR spectra of Ti–phenyl. The fact that there are no sharp peaks identified in the range 6.8–8.6 for ^1H NMR spectra indicates that there is a bond between phenyl with titanium nanoparticles, and the absence of any excessive free phenyl. The additional peak at 3.7 and 1.7 ppm was identified for existence of THF solvent residuals. Based on the ^{13}C NMR, and ^1H NMR spectra results, it can be concluded that Ti–phenyl were successfully synthesized, with no excessive diazonium [12].

The existence of titanium metal nanoparticles on the resulting Ti–phenyl and Ti–phenyl@ SiO_2 is clearly shown in the TEM image in

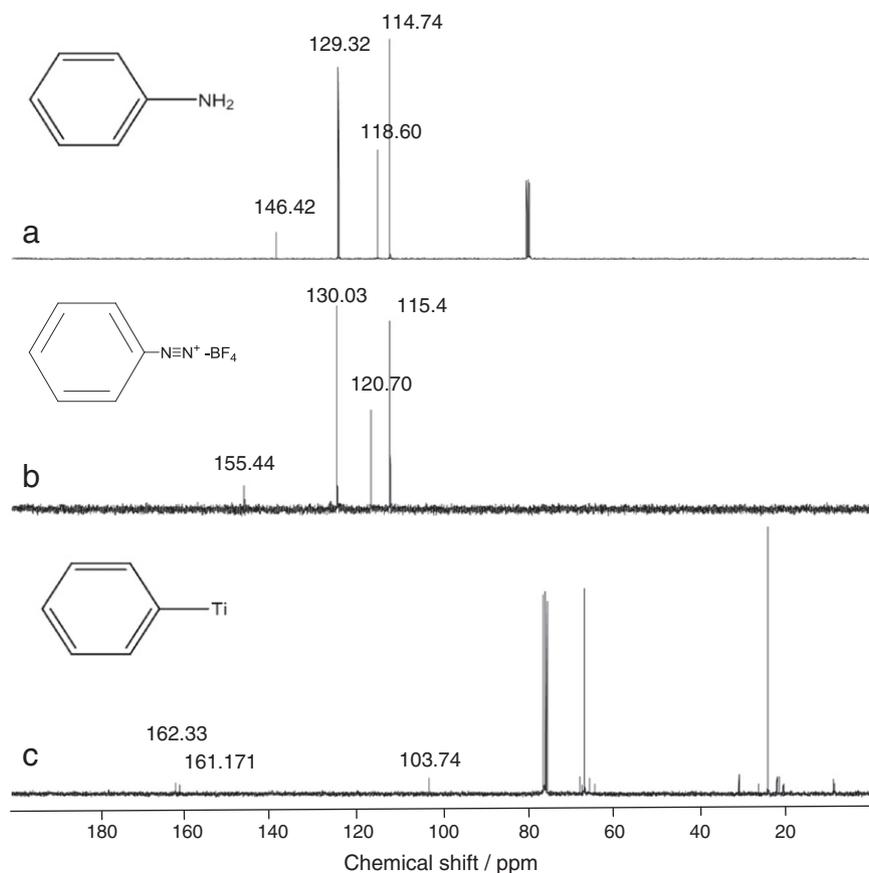


Fig. 1. ^{13}C NMR spectra of (a) aniline, (b) phenyl diazonium and (c) Ti–phenyl.

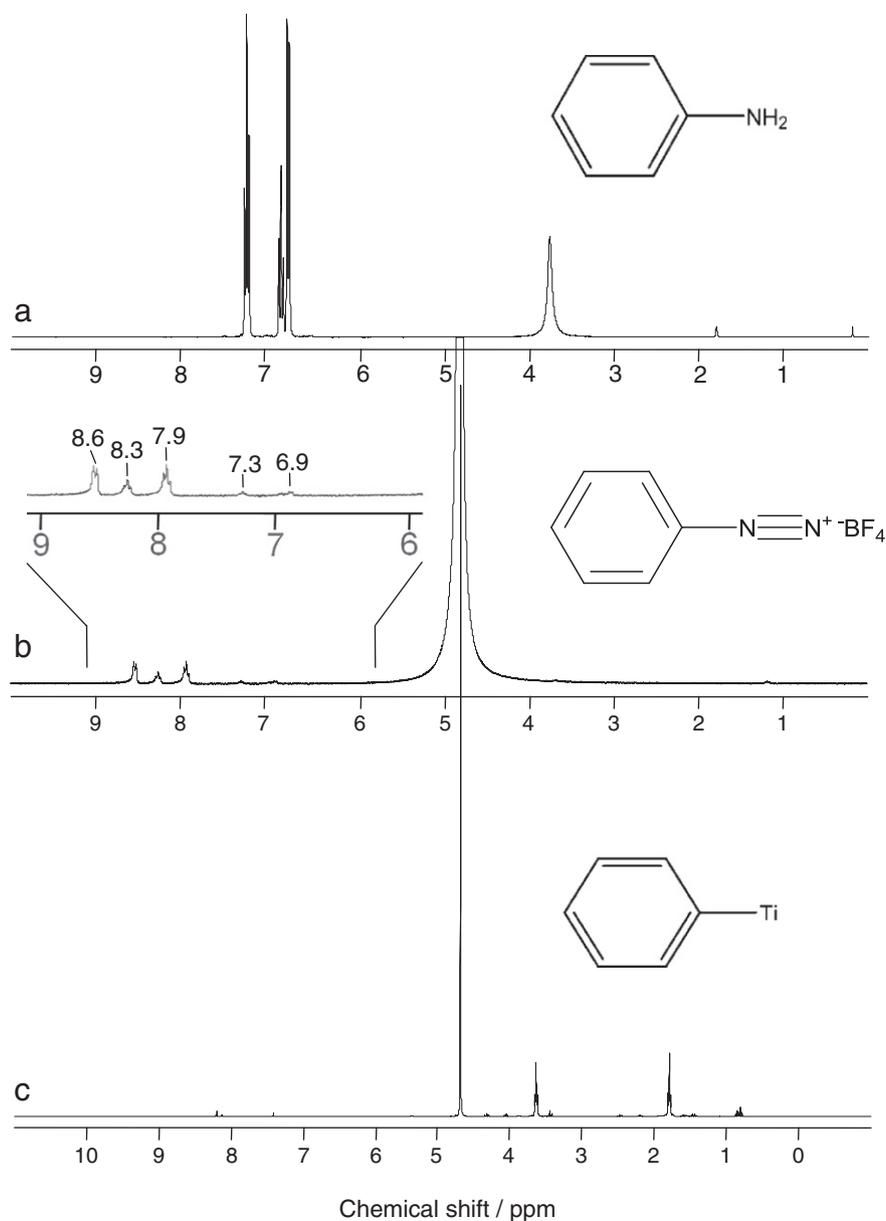


Fig. 2. ^1H NMR spectra of (a) aniline, (b) phenyldiazonium tetrafluoroborate and (c) Ti-phenyl.

Fig. 3. According to the TEM image and enlarged image of the square area on the right, all of the Ti in Ti-phenyl and in Ti-phenyl@SiO₂ is in metal form with lattice spacing of 2.2 Å for Ti (011) and lattice spacing of 1.8 Å for Ti (012) [13]. From these images it is also observed that the size and thickness of the SiO₂ shell is directly proportionate to the amount of TEOS used. The SiO₂ shell for Ti-phenyl@SiO₂(4) seemed denser than that of Ti-phenyl@SiO₂(1). The amount of Ti in Ti-phenyl@SiO₂ calculated by XRF were ca. 15–21% (w/w%) (see Table 1).

In order to examine the pores of the SiO₂ shell in the samples, the Ti-phenyl@SiO₂ samples, nitrogen (N₂) sorption analysis was utilized. As shown in Fig. 4, N₂ isotherm Ti-phenyl@SiO₂ sample gave a type IV isotherm, characteristics for mesoporous particles [14]. The BET surface area are 99, 103, 229 and 250 m² g⁻¹ for Ti-phenyl@SiO₂(1), Ti-phenyl@SiO₂(2), Ti-phenyl@SiO₂(3), and Ti-phenyl@SiO₂(4), respectively, while the average pore width calculated from the desorption branch (inset) are 69, 61, 100 and 102 Å, respectively. The porosity and surface area of the Ti-phenyl@SiO₂ increased with increasing mol ratio of Si/Ti. This shows that the SiO₂ shell of the Ti-phenyl@SiO₂ is porous and contributes significantly to the surface area of the catalysts.

3.2. Catalytic oxidation of alkenes

The catalytic results of the oxidation of styrene using (a) TiO₂, (b) Ti-phenyl, (c) Ti-phenylSiO₂(1), (d) Ti-phenyl@SiO₂(2), (e) Ti-phenyl@SiO₂(3) and (f) Ti-phenyl@SiO₂(4) as catalysts are summarized in Table 1. As can be seen from the table, Ti-phenyl and Ti-phenyl@SiO₂ catalysts were found to show the highest conversion and selectivity as compared to TiO₂.

Table 1 and Fig. 5 show the conversion and product selectivity of styrene oxidation with 30% H₂O₂ during the first run and also the second run using different catalysts. As shown in Table 1 and Fig. 5, the lowest conversion was shown by TiO₂ while Ti-phenyl@SiO₂ has the highest conversion for styrene oxidation. The Ti-phenyl@SiO₂ showed high reusability of only ca. 10% decrease in conversion. The highest conversion of styrene (92%) were shown by Ti-phenyl@SiO₂(2), while the lowest conversion of styrene (44%) for Ti-phenyl@SiO₂ samples were obtained when Ti-phenyl@SiO₂(4) was used, albeit still much higher than those shown by TiO₂ (1%). GC analysis indicated that benzaldehyde is the majority product in the oxidation of styrene by all of the catalysts.

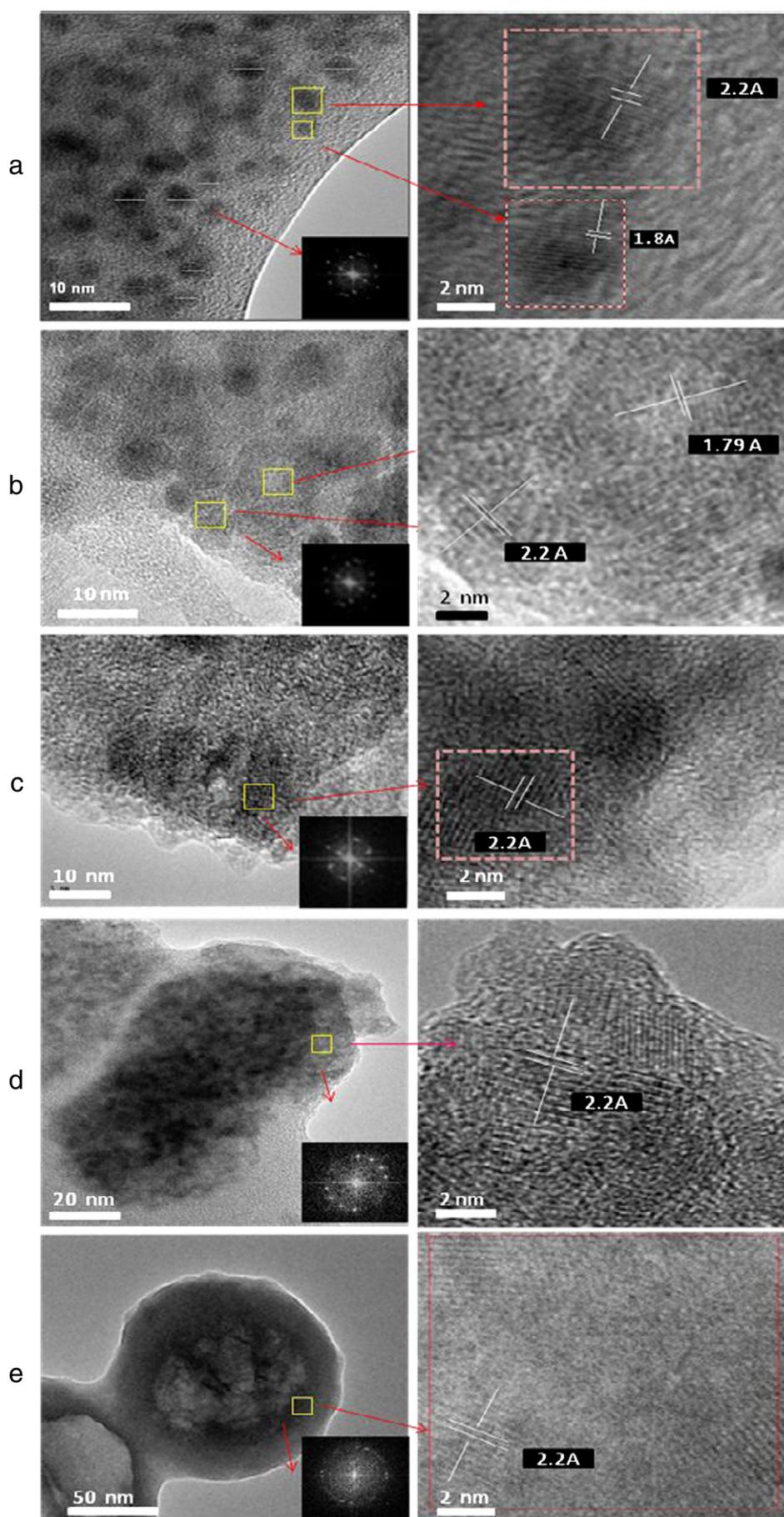


Fig. 3. TEM images of (a) Ti-phenyl, (b) Ti-phenyl@SiO₂(1), (c) Ti-phenyl@SiO₂(2), (d) Ti-phenyl@SiO₂(3) and (e) Ti-phenyl@SiO₂(4).

Table 1
Catalytic performances of TiO₂ and Ti-phenyl@SiO₂ catalysts in the oxidation of styrene by aqueous hydrogen peroxide.

Catalyst	Ti w/w% ^a	First run			Second run (reusability testing)		
		Conversion/%	Selectivity of benzaldehyde/%	TON ^b	Conversion/%	Selectivity of benzaldehyde/%	TON ^b
TiO ₂	–	2.3	1.0	0.1	–	–	–
Ti-phenyl	61.4	62.6	96.8	2.9	–	–	–
Ti-phenyl@SiO ₂ (1)	31.8	46.1	94.7	6.6	41.9	99.2	5.9
Ti-phenyl@SiO ₂ (2)	22.2	92.2	98.8	18.9	79.7	99.5	16.3
Ti-phenyl@SiO ₂ (3)	19.5	50.4	97.5	11.8	48.2	99.0	11.2
Ti-phenyl@SiO ₂ (4)	15.3	44.3	42.8	13.2	39.5	98.8	11.7

^a Weight/wt.% of Ti in the sample calculated by XRF.

^b TON = the amount of total product (mmol)/the amount of active site (mmol), where the amount of active site in Ti (mmol) was obtained from XRF data calculation.

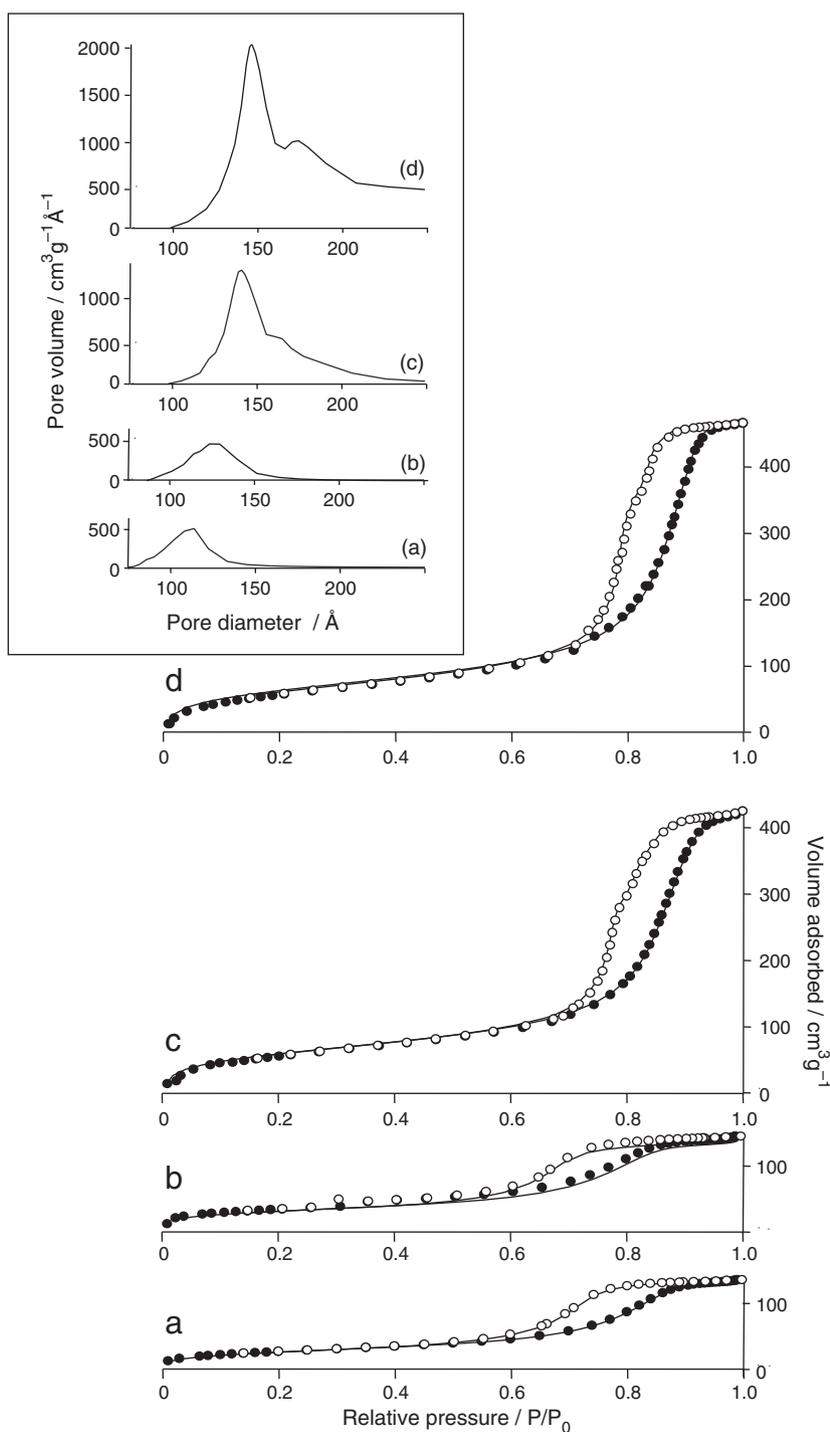


Fig. 4. Nitrogen adsorption–desorption isotherm, and pore size distribution calculated by BJH method (inset) of (a) Ti-phenyl@SiO₂(1), (b) Ti-phenyl@SiO₂(2), (c) Ti-phenyl@SiO₂(3) and (d) Ti-phenyl@SiO₂(4).

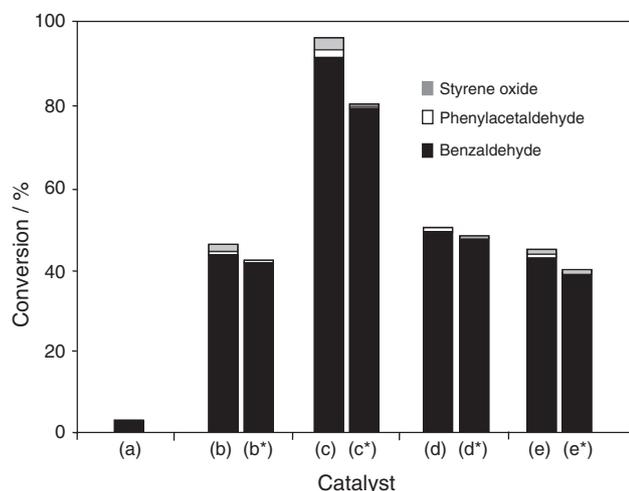


Fig. 5. The conversion and product selectivity of styrene oxidation with 30% H₂O₂ at 80 °C, by using (a) TiO₂, (b) Ti-phenyl@SiO₂(1), (c) Ti-phenyl@SiO₂(2), (d) Ti-phenyl@SiO₂(3), and (e) Ti-phenyl@SiO₂(4) as catalysts. The bars labeled as (b*), (c*), (d*) and (e*) were the conversion and product selectivity of the same catalysts during the second run.

The highest selectivity (99%) towards benzaldehyde was shown by Ti-phenyl@SiO₂(2), with a relatively high turnover number (TON) (19), while the lowest selectivity of benzaldehyde (95%) by Ti-phenyl@SiO₂(1), which was still very high. Other minor products detected were styrene oxide and phenylacetaldehyde. Another noteworthy point is that, as mentioned earlier and shown in Fig. 4, the surface area of the catalysts increased with increasing amount of SiO₂ in the sample. However, the catalytic activity results suggest that the catalytic activity was independent of the surface area of the catalysts.

The high catalytic activity shown by Ti-phenyl@SiO₂ catalysts in the oxidation of styrene can be explained on the basis of the similarity in structure of the phenyl group present at Ti-phenyl@SiO₂ catalysts with the structure of styrene. The phenyl groups in the Ti-phenyl@SiO₂ catalysts might have enhanced the adsorption of styrene onto the catalysts and thus enhancing the catalytic activity. The relationships between catalytic activity and Si/Ti mol ratio in the oxidation of styrene are shown in Fig. 5. In order for the catalyst to be really efficient in this reaction, the appropriate thickness of SiO₂ synthesized with different Si/Ti mol ratio is needed. If the SiO₂ is too thick, it will hinder the diffusion of the products from the catalyst. However, if the SiO₂ layer is too

thin or none existence, the adsorption of the reactants may be reduced. The optimum Si/Ti mol ratio of this catalyst in the oxidation of styrene with H₂O₂ determined was two.

4. Conclusions

Ti-phenyl nanoparticles encapsulated in mesoporous SiO₂ shell (Ti-phenyl@SiO₂) catalysts with different amounts of SiO₂ were prepared and used as catalysts in the oxidation of styrene with H₂O₂ as the oxidant. The porosity and surface area of SiO₂ shell increased with increasing Si/Ti mol ratio in Ti-phenyl@SiO₂. The Ti-phenyl showed high catalytic activity for styrene oxidation, but without reusability. On the other hand, the Ti-phenyl@SiO₂ catalysts are highly reusable and displayed very high catalytic activity for styrene oxidation, as the phenyl group in Ti-phenyl@SiO₂ allows strong interaction between the catalysts and styrene, which also possesses a benzene ring in its structure. The optimum Si/Ti mol ratio determined was two, showing highest turnover number, highest conversion of styrene and selectivity towards benzaldehyde.

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