

## SYNTHESIS AND CHARACTERIZATION OF Ti-PHENYL@SiO<sub>2</sub> CORE-SHELL NANOPARTICLES CATALYST

(Penyediaan dan Pencirian Pemangkin Ti-Phenyl@SiO<sub>2</sub> Teras-Cangkerang Nanopartikel)

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### Abstract

This study highlights the potential use of Ti-Phenyl@SiO<sub>2</sub> core-shell nanoparticles as heterogeneous catalysis in oxidation reaction. The Ti-Phenyl@SiO<sub>2</sub> was synthesized by reduction of TiCl<sub>4</sub> and diazonium salt with sodiumborohydride to produce phenyl titanium nanoparticles (Ti-Phenyl), followed by the silica shell coating using tetraethyl orthosilicate (TEOS). The Ti-Phenyl@SiO<sub>2</sub> nanoparticles were characterized by Fourier transform infrared (FTIR) spectrometer, diffuse reflectance (DR) UV-visible spectrometer, thermogravimetric analyzer (TGA), X-ray diffraction (XRD) spectrometer, field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). The core-shell size of Ti-Phenyl@SiO<sub>2</sub> was in the range of 40 to 100 nm with its core composed with an agglomeration of Ti-Phenyl. The Ti-Phenyl@SiO<sub>2</sub> was active as a catalyst in the liquid phase epoxidation of 1-octene with aqueous hydrogen peroxide as an oxidant.

**Keywords:** Ti-Phenyl@SiO<sub>2</sub>, core-shell, nanoparticles, epoxidation, aqueous hydrogen peroxide

### Abstrak

Kajian ini menekankan potensi penggunaan Ti-Phenyl@SiO<sub>2</sub> nanopartikel teras-cangkerang sebagai pemangkinan heterogen dalam tindak balas pengoksidaan. Ti-Phenyl@SiO<sub>2</sub> telah disediakan dengan pengurangan TiCl<sub>4</sub> dan garam diazonium dengan natrium borohidrida untuk menghasilkan titanium-fenil nanopartikel (Ti-Phenyl), diikuti oleh salutan cangkerang silika menggunakan tetraetil ortosilikat (TEOS). Ti-Phenyl@SiO<sub>2</sub> nanopartikel telah dicirikan oleh spektrometer jelmaan Fourier inframerah (FTIR), spektrometer pantulan meresap (DR) UV-nampak, analyzer termogravimetri (TGA), spektrometer pembelauan sinar-X (XRD), bidang pelepasan mikroskop imbasan elektron (FESEM) dan mikroskop elektron penghantaran (TEM). Saiz teras-cangkerang Ti-Phenyl@SiO<sub>2</sub> adalah dalam lingkungan 40 hingga 100 nm dengan terasnya terdiri daripada penumpukkan Ti-Phenyl. Ti-Phenyl@SiO<sub>2</sub> adalah pemangkin aktif dalam pengepoksidaan fasa cecair 1-oktene dengan hidrogen peroksida berair sebagai oksidan.

**Kata kunci:** Ti-Phenyl@SiO<sub>2</sub>, teras-cangkerang, nanopartikel, pengepoksidaan, hidrogen peroksida berair.

### Introduction

The chemical properties of heterogeneous catalysts can vary depending on the dimensions of structure, the nature of environment of active site and depending on how the absorption of reactants takes place to the catalysts surface [1–4]. The ability to prepare catalysts in nanometer size for oxidation of hydrophobic reactant will open significant opportunities in chemistry and material science. Recently, metal-carbon nanoparticles with various organic moieties have been utilized for a number of applications, such as electronics, and catalysts [5–7].

The nanoparticles of metal-carbon covalent bonding with core-shell structures (M-C) are the compound with stronger metal-carbon bond, and with hydrophobic moiety at the surface. The addition of silica to the shell of M-C (M-C@SiO<sub>2</sub>) is an exciting challenge that improves the stability and selectivity of the resulting catalyst [8,9]. The unique method, structure and catalytic activity of Ti-Phenyl@SiO<sub>2</sub> had not been explored. In this compound, the

titanium has an empty d orbital, which can act as acidic Lewis and is a highly potential compound used as a catalyst [10]. The organic moiety (phenyl) at the surface of metal-carbon nanoparticles can act as absorbent of the organic substrate, and silica-shell (SiO<sub>2</sub>) to increase stability of the metal-carbon nanoparticles. This paper reports the synthesis, characterization and catalytic activity of Ti-Phenyl@SiO<sub>2</sub> nanoparticles in the core-shell structure for oxidation of 1-octene, with H<sub>2</sub>O<sub>2</sub> as an oxidant.

## Materials and Methods

### Preparation of Ti-Phenyl@SiO<sub>2</sub>

The Ti-Phenyl@SiO<sub>2</sub> was synthesized by reduction the TiCl<sub>4</sub> (5 mmol) and phenyl diazonium fluoroborate (10 mmol) with sodiumborohydride (12 mmol) to produce titanium-phenyl nanoparticles (Ti-Phenyl), followed by coating of the Ti-Phenyl using tetraethyl orthosilicate (TEOS Fluka) in the range of 5 to 20 mmol. The Ti-Phenyl@SiO<sub>2</sub> formed has a Si to Ti the mol ratio varied from 1 to 4, and labeled with Ti-Phenyl@SiO<sub>2</sub>(1), Ti-Phenyl@SiO<sub>2</sub>(2), Ti-Phenyl@SiO<sub>2</sub>(3), and Ti-Phenyl@SiO<sub>2</sub>(4).

### Characterizations

The Ti-Phenyl, Ti-Phenyl@SiO<sub>2</sub>(1), Ti-Phenyl@SiO<sub>2</sub>(2), Ti-Phenyl@SiO<sub>2</sub>(3), and Ti-Phenyl@SiO<sub>2</sub>(4) were characterized by Fourier transform infrared (FTIR) spectrometer, UV-Vis diffuse reflectance (UV-Vis DR) spectrometer, thermogravimetric analyzer (TGA), X-ray diffraction (XRD) spectrometer, field emission scanning electron microscope (FESEM), and transmission electron microscope (TEM). The FTIR spectra of all samples were collected on a Perkin Elmer Spectrum One (FTIR) spectrometer with 10 scans and resolution of 4 cm<sup>-1</sup>, in the range of 4000 – 400 cm<sup>-1</sup>. UV-Vis spectra of resulting catalysts were recorded using Perkin-Elmer Lambda 900 spectrometer. TGA and DTA graphs were obtained by using a Matter Toledo TGA/SDTA 851 instrument under N<sub>2</sub> atmosphere with a flow rate of 20 ml min<sup>-1</sup>, in the temperature range of 25 to 900 °C, at the heating rate of 10 °C min<sup>-1</sup>, with 12 mg of sample. XRD patterns were recorded on a Bruker D8 advance instrument using Cu K<sub>α</sub> radiation (λ = 1.5418 Å, kV = 40, mA = 40). Morphological structure and particle size were observed by field emission scanning electron microscopy (FESEM, JEOL JSM 6701F) with platinum coating (2 kV, 10 mA).

### Activity of Ti-Phenyl@SiO<sub>2</sub>

To study the catalytic activity of Ti-Phenyl@SiO<sub>2</sub>, the oxidation of 1-octene by using aqueous H<sub>2</sub>O<sub>2</sub> was used as a model reaction. In the oxidation, 1-octene (8 mmol, Merck), 30% aqueous H<sub>2</sub>O<sub>2</sub> (15 mmol), and Ti-Phenyl@SiO<sub>2</sub> (50 mg) were placed in round bottle glass with condenser. The reaction was performed with stirring at 80 °C for 8 h, and the resulting products were analyzed with the Gas Chromatograph (GC).

## Results and Discussion

### Physical properties

The Ti-Phenyl@SiO<sub>2</sub> nanoparticles have been synthesized in this research. Schematic representation of the reaction for synthesis of Ti-Phenyl@SiO<sub>2</sub> is shown in Fig. 1. The mol ratio of TEOS to TiCl<sub>4</sub> used to synthesize Ti-Phenyl@SiO<sub>2</sub> nanoparticles catalysts were summarized in Table 1.

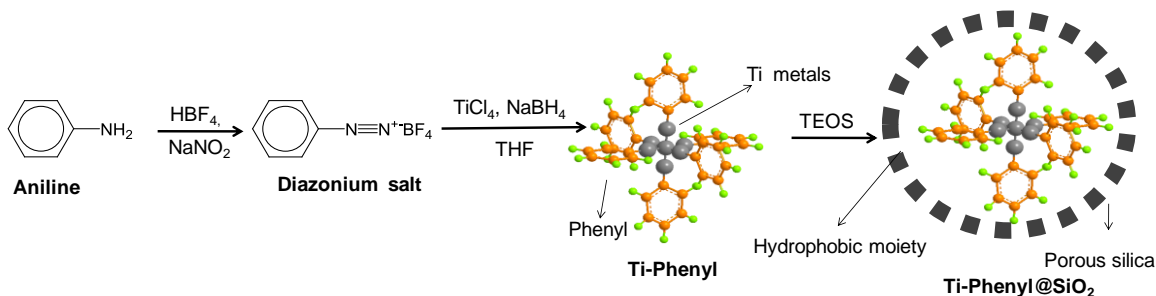


Figure 1. Schematic representation of the reaction for synthesis of Ti-Phenyl@SiO<sub>2</sub>.

Table 1. The mole ratios of TEOS to  $\text{TiCl}_4$  used to synthesize Ti-Phenyl@ $\text{SiO}_2$  nanoparticles catalyst.

No.	Mole ratios of TEOS to $\text{TiCl}_4$	Catalysts
1	1 : 1	Ti-Phenyl@ $\text{SiO}_2(1)$
2	2 : 1	Ti-Phenyl@ $\text{SiO}_2(2)$
3	3 : 1	Ti-Phenyl@ $\text{SiO}_2(3)$
4	4 : 1	Ti-Phenyl@ $\text{SiO}_2(4)$

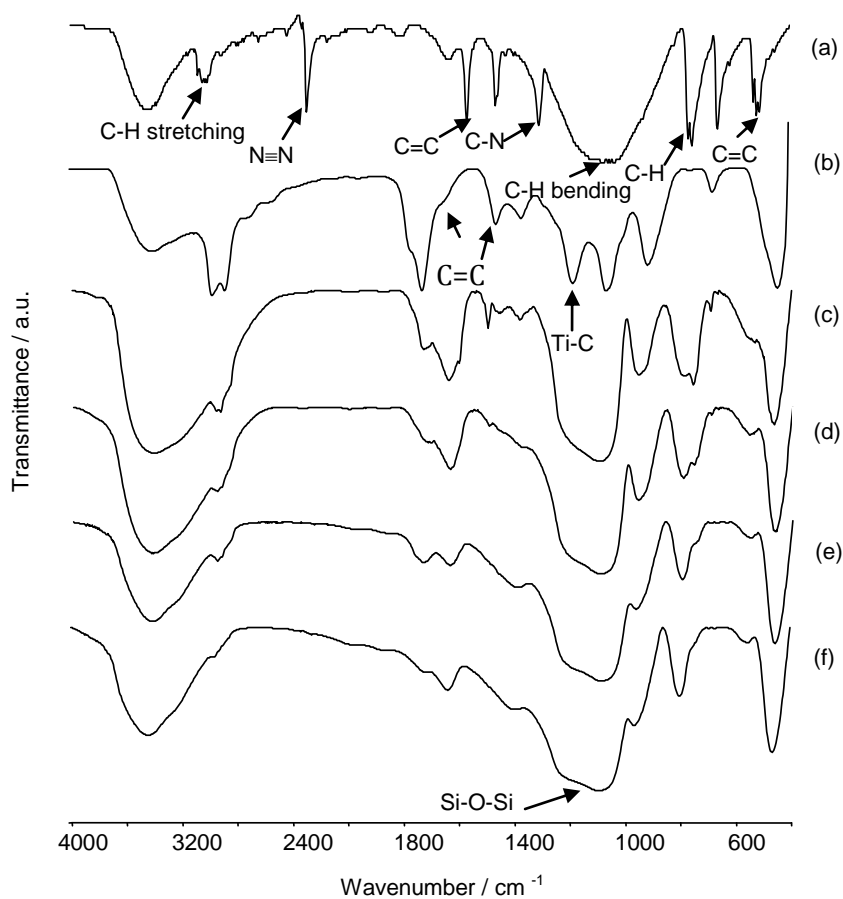


Figure 2. The FTIR spectra of (a) Phenyl diazonium, (b) Ti-Phenyl, (c) Ti-Phenyl@ $\text{SiO}_2(1)$ , (d) Ti-Phenyl@ $\text{SiO}_2(2)$ , (e) Ti-Phenyl@ $\text{SiO}_2(3)$ , and (f) Ti-phenyl@ $\text{SiO}_2(4)$ .

Fig. 2 shows the FTIR spectra of phenyl diazonium, Ti-Phenyl, and Ti-Phenyl@SiO<sub>2</sub> with Si to Ti mole ratio 1 – 4. The existence of aromatic ring on the phenyldiazonium can be seen from the =C–H stretch peak at 3075 cm<sup>-1</sup> and 3014 cm<sup>-1</sup>, the =C–H bend out of plane at 667 cm<sup>-1</sup> and 749 cm<sup>-1</sup>. The C=C stretch vibration at 1462 cm<sup>-1</sup> and 1566 cm<sup>-1</sup>. On other hand for the Ti-Phenyl and Ti-Phenyl@SiO<sub>2</sub> all of the =C–H and C=C peak shifted to the lower wavenumber. This is caused by the influence of Ti and SiO<sub>2</sub> substituent into the aromatic ring. The sharp peak at 2294 cm<sup>-1</sup> and at 1306 cm<sup>-1</sup> correspond to N≡N and C–N vibration of phenyl diazonium (C<sub>6</sub>H<sub>5</sub>N≡N<sup>+</sup>) respectively, for the Ti-Phenyl (C<sub>6</sub>H<sub>5</sub>-Ti) and Ti-Phenyl@SiO<sub>2</sub> (Ti-C<sub>6</sub>H<sub>5</sub>@SiO<sub>2</sub>) the peak at 2294 cm<sup>-1</sup> and 1306 cm<sup>-1</sup> disappeared. It means that led to the release of N≡N and the binding of the phenyl to the titanium core via Ti–C covalent linkages. The existence of SiO<sub>2</sub> shell on the Ti-Phenyl@SiO<sub>2</sub> spectra can be seen with Si–O–Si vibration at 1000 – 1200 cm<sup>-1</sup>. The same FTIR spectra have been reported previously [6] for preparation of the palladium nanoparticles using aryl diazonium salt. The existence of Ti-Phenyl and Ti-Phenyl@SiO<sub>2</sub> was further examined by UV-Vis measurements.

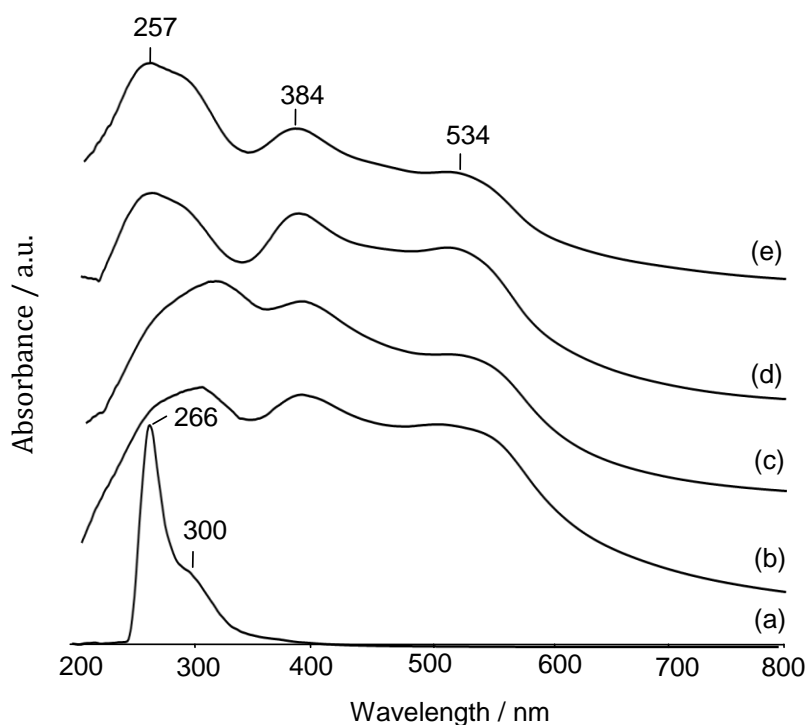


Figure 3. The UV-Vis spectra of (a) Ti-Phenyl, (b) Ti-Phenyl@SiO<sub>2</sub>(1), (c) Ti-Phenyl@ SiO<sub>2</sub>(2), (d) Ti-Phenyl@SiO<sub>2</sub>(3) and (e) Ti-Phenyl@SiO<sub>2</sub>(4).

The UV-Vis spectra of Ti-Phenyl and Ti-Phenyl@SiO<sub>2</sub> are depicted in Fig. 3. The UV-Vis absorption of Ti-Phenyl showed a band at 266 nm. Band at 266 nm is ascribed as the forbidden transition to a homo nuclear excited state ( $\pi-\pi^*$ ) of aromatic bond to Ti. The broad band at 300 nm indicated that there is Ti metal in nanometer size [11]. The UV-Vis absorption of Ti-Phenyl@SiO<sub>2</sub> shows bands at 257, 384 and 534 nm. Ti-Phenyl@SiO<sub>2</sub> showed a longer wavelength with more intense peaks compared to than that of Ti-Phenyl. This is due to substitution of Ti to aromatic and dipole-dipole interaction on the surface of Ti-Phenyl with SiO<sub>2</sub> (bathochromic and red shift) [6].

Chemical composition or thermal stability of the Ti-Phenyl and Ti-Phenyl@SiO<sub>2</sub> was examined by using the TGA and Differential TGA (DTA) analysis, as presented in Fig. 4. A distinct degradation step can be clearly observed for Ti-Phenyl observed at 185 °C and 433 °C (see Fig. 4a). The weight loss at *ca.* 185 and 433 °C is associated with decomposition of organic moiety of Ti-Phenyl. When the decomposition of the organic moiety of Ti-Phenyl was

compared to those of Ti-Phenyl@SiO<sub>2</sub>, only the weight loss at ca. 425 was observed in Ti-Phenyl@SiO<sub>2</sub> suggesting that the Ti-Phenyl was trapped in the core structure (see Fig. 4b).

Diffraction patterns of the Ti-Phenyl and Ti-Phenyl@SiO<sub>2</sub> prepared with Si/Ti ratio was 1 to 4 are presented in Fig. 5. It is observed that Ti-Phenyl sample had very broad peaks at  $2\theta = 35, 38, 40, 53,$  and  $62$  suggesting the titanium metal was in metallic form and nanometer size [12-14]. The very broad peaks were also observed in Ti-Phenyl@SiO<sub>2</sub>(1), Ti-Phenyl@SiO<sub>2</sub>(2), Ti-Phenyl@SiO<sub>2</sub>(3) and Ti-Phenyl@SiO<sub>2</sub>(4) samples. This suggests that the titanium metal particles were also in metallic form and nanometer size in the Ti-Phenyl@SiO<sub>2</sub> samples.

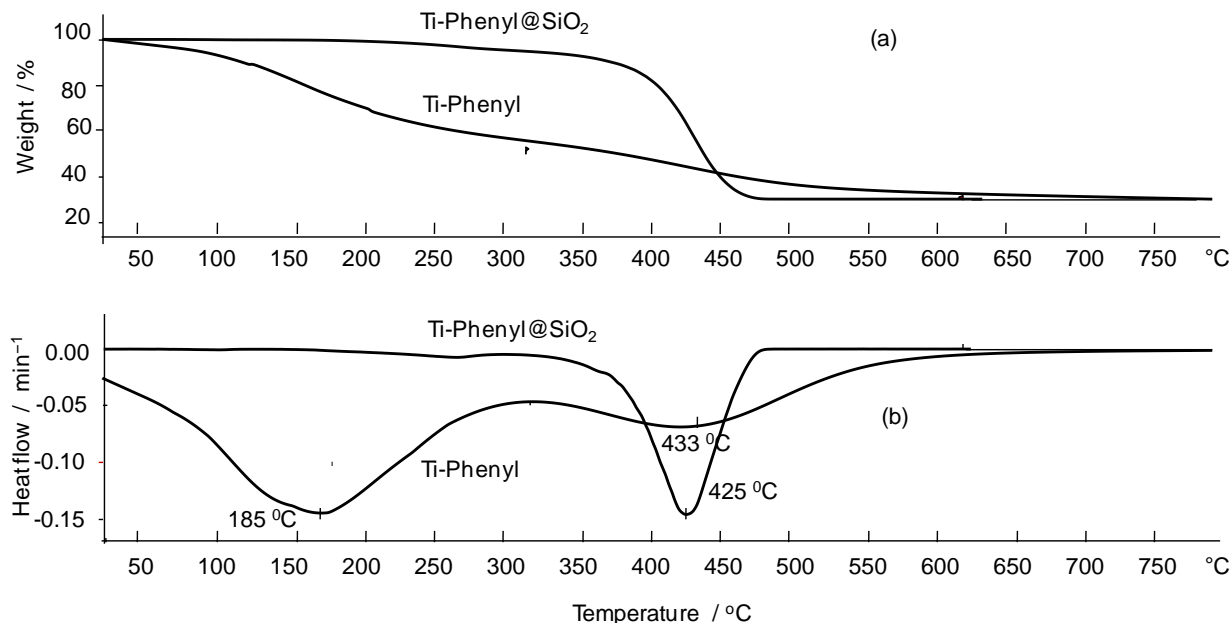


Figure 4. (a) TGA and (b) DTA curves for Ti-Phenyl and Ti-Phenyl@SiO<sub>2</sub>.

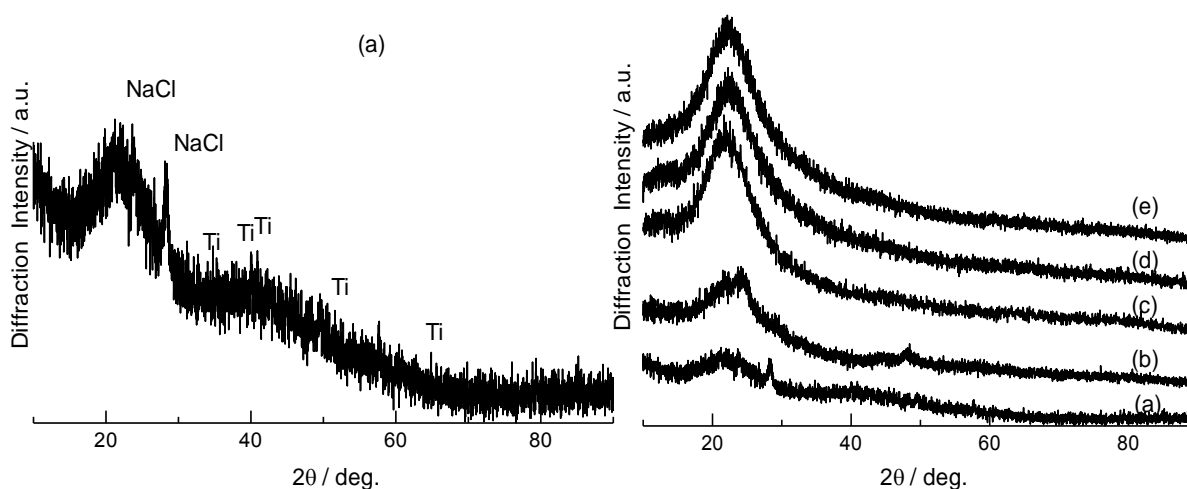


Figure 5. The XRD patterns of (a) Ti-Phenyl, (b) Ti-Phenyl@SiO<sub>2</sub>(1), (c) Ti-Phenyl@SiO<sub>2</sub>(2), (d) Ti-Phenyl@SiO<sub>2</sub>(3) and (e) Ti-Phenyl@SiO<sub>2</sub>(4).

The morphologies of Ti-Phenyl@SiO<sub>2</sub> were obtained by a field emission scanning electron microscope (FESEM). As shown in Fig. 6, the catalyst particles are nearly spherical shape. The particles size of Ti-Phenyl@SiO<sub>2</sub>(1), Ti-Phenyl@SiO<sub>2</sub>(2), Ti-Phenyl@SiO<sub>2</sub>(3) and Ti-Phenyl@SiO<sub>2</sub>(4) are in the range of 20 to 35 nm. The size and crystallinity of Ti-Phenyl nanoparticles and the shell of Ti-Phenyl@SiO<sub>2</sub> was verified with TEM image as below.

Fig. 7 shows the TEM image of Ti-Phenyl and Ti-Phenyl@SiO<sub>2</sub>. The Ti-Phenyl particles size was in the range of 3 to 5 nm. The Ti-Phenyl@SiO<sub>2</sub> has a core composed by agglomerate Ti-Phenyl with the core-shell sizes were in the range of 40 to 100 nm. The diffraction pattern obtained from the TEM image in Fig. 7 proved that the Ti was crystalline.

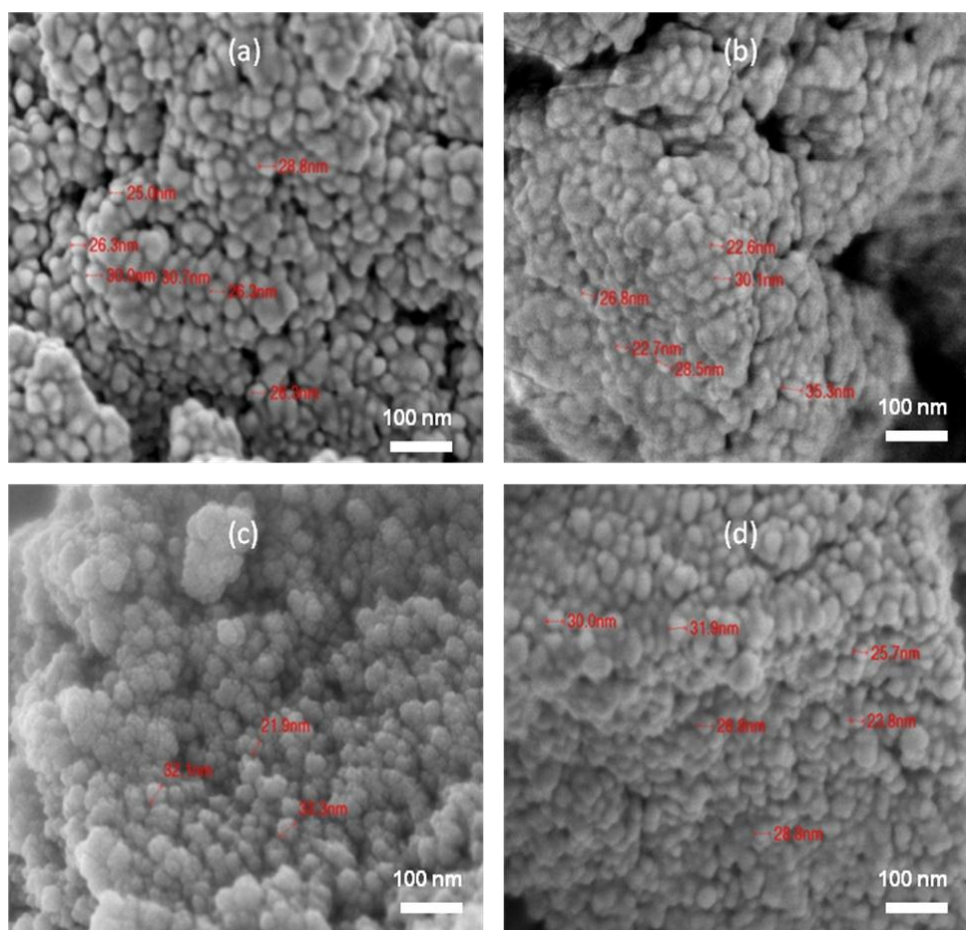


Figure 6. The FESEM photomicrograph of (a) Ti-Phenyl@SiO<sub>2</sub>(1), (b) Ti-Phenyl@SiO<sub>2</sub>(2), (c) Ti-Phenyl@SiO<sub>2</sub>(3) and (d) Ti-Phenyl@SiO<sub>2</sub>(4).

#### Activity of Ti-Phenyl@SiO<sub>2</sub>

Fig. 8 shows the turn over number (TON) of 1, 2-epoxyoctane and 1, 2-octanediol in the oxidation of 1-octene over Ti-Phenyl@SiO<sub>2</sub>(1), Ti-Phenyl@SiO<sub>2</sub>(2), Ti-Phenyl@SiO<sub>2</sub>(3), Ti-Phenyl@SiO<sub>2</sub>(4) catalysts with aqueous hydrogen peroxide. All the Ti-Phenyl@SiO<sub>2</sub> catalysts showed the higher TON than that of TiO<sub>2</sub> in the epoxidation of 1-octene to 1, 2-epoxyoctane. The reusability of the catalysts was carried in this study. Only *ca.* 15% decreases in the TON

was observed when the catalysts were recycled (see Fig. 8). The other possible products, i.e. 1,2-octanediol and 2-octanone were not observed in this catalytic reaction.

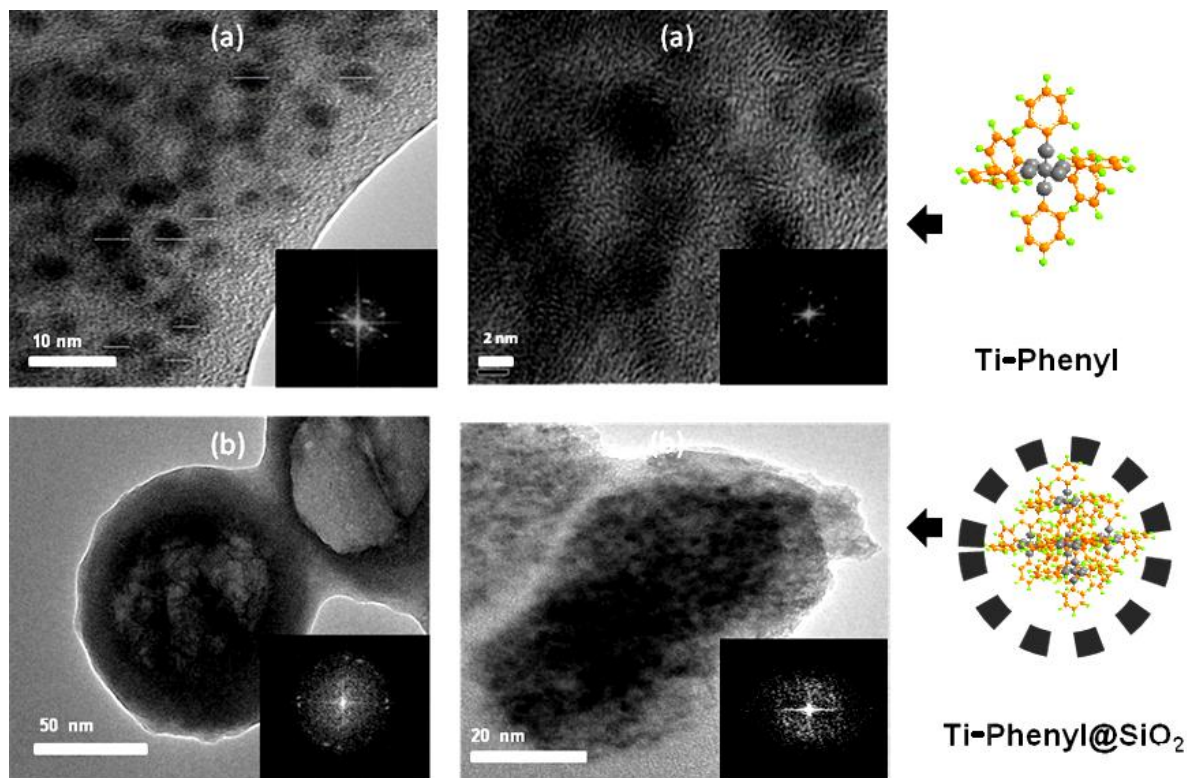


Figure 7. TEM image of (a) Ti-Phenyl and (b) Ti-Phenyl@SiO<sub>2</sub> core shell nanoparticles.

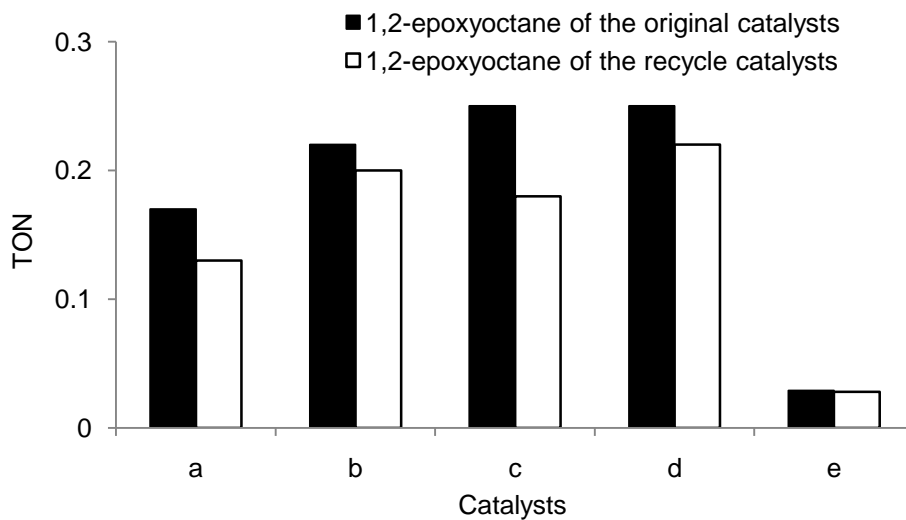


Figure 8. Epoxidation activity of (a) Ti-Phenyl@SiO<sub>2</sub> (1), (b) Ti-Phenyl@SiO<sub>2</sub> (2), (c) Ti-Phenyl@SiO<sub>2</sub> (3), (d) Ti-Phenyl@SiO<sub>2</sub> (4) and (e) TiO<sub>2</sub>.



### Conclusion

The Ti-Phenyl@SiO<sub>2</sub> with core-shell structure was successfully synthesized by the silica coating to Ti-Phenyl by using tetraethyl orthosilicate (TEOS). The Ti-Phenyl@SiO<sub>2</sub> has a core containing agglomerate Ti-Phenyl with the core-shell size was in the range of 40 to 100 nm. The Ti-Phenyl@SiO<sub>2</sub> was active and reusable in the liquid phase epoxidation of 1-octene with aqueous hydrogen peroxide.

### Acknowledgement

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