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Synthesis and Characterization of Titanium Catalyst Containing Polystyrene Composites for Epoxidation Of 1-Octene

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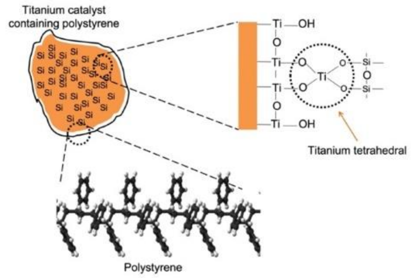
GRAPHICAL ABSTRACT



ABSTRACT

The titanium catalyst containing polystyrene composites have been prepared by reacting titanium (iv) isopropoxide (TTIP) with octadecyllthrichlorosilane (OTS) under ambient atmosphere with absence and presence of water. The resulting catalysts were characterized by diffuse reflectance ultraviolet-visible (DR UV-Vis) spectroscopy, X-ray diffraction (XRD) spectroscopy, field emission scanning electron microscopy (FESEM) attached with energy dispersive X-ray (EDX) spectroscopy, Fourier transform infrared spectroscopy (FTIR) and ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonances (^{29}Si MAS NMR). XRD patterns demonstrated that the as-synthesized titanium containing catalysts were in amorphous phase. DR UV-Vis analysis showed that the shifting of absorption spectra to shorter wavelength indicated that more titanium tetrahedral species were formed when the amount of water was increased. This result suggests that the presence of water during the reaction between TTIP and OTS has facilitated the formation of Ti – O – Si bond. The formation of Ti – O – Si bonds were also supported by NMR studies which demonstrated a peak shifting from lower to higher intensity in -40 ppm, which corresponds to the formation of Q^2. The as-prepared catalyst with the high content of titanium tetrahedral (0.5-TS) was selected as catalyst in polymerization of styrene in the presence of aqueous hydrogen peroxide (H_2O_2). The polymerization of styrene using the 0.5-TS produced the polystyrene-TiO_2 composite. The catalytic performance of polystyrene TiO_2 composites have been evaluated in the epoxidation of 1-octene in the presence of aqueous H_2O_2. However, it was demonstrated that the catalytic activity of polystyrene TiO_2 composites did not improve much as 17.3 mmol of 1,2-Epoxyoctane was obtained, a slight increase of 0.5% when compared to that of unmodified TiO_2.

Keywords: Epoxidation; Titanium containing polystyrene catalyst; Titanium(iv) isopropoxide; Octadecylthrichlorosilane; Octene Polymerization of styrene.

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1. INTRODUCTION

Catalyst is as a substance that can be added to a particular reaction to increase the rate of reaction without getting consumed in the process [1]. Generally, the catalysis can be divided into two categories; a homogeneous catalyst where the catalyst is in the same phase as the reaction mixture and heterogeneous catalysis where the catalyst and the reactants are in different phases. [1,2]. Homogenous catalyst is used over heterogeneous catalyst owing to it has more catalytical sites which give improved selectivity to a certain product. However, the difficulty in filtering the catalysts from the reaction media has limited the application of homogeneous catalysts in the industry. In addition, separation approaches such as distillation require an extra expenditure of energy and high-cost production [3, 4].

Like a homogenous catalyst, the heterogeneous catalyst also has its own drawbacks. For example, availability of surface area for reaction sites, limited activity and selectivity, and high cost in the production of catalyst. Therefore, a newly designed catalyst is expected to be commercially and economically viable. These include fabrication of low-cost catalysts, fulfil the objectives for ease of construction and dependability of operation [3-5]. The principle of this research is to design and fabricate a new catalyst that will increase the surface-active site and the interests of the research remains in the field of preparation, characterization and evaluation of the catalytic performance.

For over the last decades, titanium silicate (TS-1) has been widely used as a catalyst in epoxidation with hydrogen peroxide owing to its high activity and selectivity [6]. The synthesis of organic compounds to produce industrial materials based on epoxidation reaction which used TS-1 as a catalyst has shown an excellent result. Epoxides can be considered as useful intermediates that are widely applied in organic synthesis. Thus, the epoxidation of hydrocarbon compounds such as alkenes is important in research and development as well as in industrial applications [6,7]. Despite the excellent properties of TS-1 as a catalyst in the chemical industry, the large pore size has limited their application in the fabrication of large organic compounds. Therefore, TS-1 is only highly selective for catalysis of the small molecules [7-9].

Previous research that has been carried out showed that titania-silica mixture has successfully polymerized the styrene to form titanium catalyst containing polymer composites [10]. The titania composite was demonstrated to comprise high content of tetrahedral titanium which improve its catalytic activity. In addition, the presence of polymer in the catalyst can be utilised as fillers to enhance the strength, processability, and thermal stability [11, 12]. The concept is based on the idea that titanium catalysts containing polymer composites formed in the solid phase will be utilised as catalyst in the epoxidation of alkene. With these properties, polystyrene would be able to activate the active site by creating the active site with more electrophilic properties. Thus, it would be easier for the composites to be attacked by nucleophile such as alkenes [13]. Therefore, this study proposed to synthesize the titanium catalyst containing polystyrene with using titanium (IV) isopropoxide and octadecylthriclorosilane (OTS) as source of titania and silica. The prepared TiO_2-SiO_2 catalysts would then introduce with polystyrene to produce the titanium catalyst containing polystyrene for the application in epoxidation of 1-octene with the presence of hydrogen peroxide.

2. EXPERIMENTS

2.1 Preparation of titania-silica catalyst

The titania-silica catalysts were prepared by addition of 1.267 ml of titanium(iv) isopropoxide, TTIP (97%, Sigma-Aldrich) and 3.967 ml of octadecyltrichlorosilane, (>90%, Sigma-Aldrich) under ambient atmosphere with absence and presence of water (H_2O). The amount of water added into the reaction was varied to 0.25 ml, 0.50 ml, 1.00 ml, 2.5 ml and 5.0 ml. The toluene (95%, Merck) was used as a solvent in the synthesis step. The experiment was performed in a fume hood to avoid evaporation of compounds and was placed in an ultrasonic bath for 2 hours to complete the hydrolysis process. The mixture was then washed with methanol, CH_3OH, (99.8%, HmBG Chemical) up to three times to remove chloride ions. The prepared titania-silica samples were denoted as following; TS, 0.25-TS, 0.5-TS, 1.0-TS, 2.5-TS and 5.0-TS, respectively.

2.2 Preparation of titanium catalyst containing polystyrene composite

For the preparation of titanium catalysts containing polystyrene composite. A 100 mg of TS catalyst was added to 10.42 g of styrene in a 100 ml round bottom flask. An amount of 0.68 ml (10 mmol) of hydrogen peroxide, H_2O_2, (99%, Sigma-Aldrich) was added to the reaction. The mixture was then stirred at the temperature of 80 °C for eight (8) hours to undergo a reflux process. The mouth of condenser was covered with aluminium foil to prevent the mixture from evaporating. The experimental was repeated using 0.25-TS, 0.5-TS, 1.0-TS, 2.5-TS and 5.0-TS catalysts, respectively. The final composites (titanium catalyst containing polystyrene) were denoted as TS-PS, 0.25-TS-PS, 0.5-TS-PS, 1.0-TS-PS, 2.5-TS-PS and 5.0-TS-PS, respectively.

2.3 Characterization

The structural studies of prepared titania-silicate catalysts were characterized by X-ray diffraction (XRD) spectrometer using Bruker D8 Advance with CuK_a irradiation and wavelength of 1.5406Å. Optical studies were performed using Perkin Elmer Lambda 900 diffuse reflectance ultraviolet-visible (DR UV-Vis) spectrophotometer with wavelength recorded from 200 – 800 nm to study the phase of titania. In addition, the ^{29}Si magic angle spinning nuclear magnetic resonance, (^{29}Si MAS NMR) was used to study the Ti-O-Si linkages using Bruker Avance 400 MHz solid-state NMR. Investigation on the formation of Ti and Si bonds were also carried out using the Perkin Elmer Fourier transform infrared (FTIR) spectrometer. The KBr pellets technique was used in this analysis. The morphological properties of prepared catalysts were studied by field emission scanning electron microscope, FESEM (JSM-6330F).

2.4 Catalytic Activity

In this study, the catalytic performance of TiO_2, 5.0-TS and 5.0-TS-PS were evaluated in the epoxidation of 1-octene (99%, Sigma-Aldrich). The catalytic testing was carried out by mixing the 100 mg of the catalyst with 4 ml of 1-octene and 1 ml of hydrogen peroxide. The catalytic reactions were conducted at the temperature of 80 °C for eight (8) hours. The final product was analysed using gas chromatography with a flame ionization detector, GC (Agilent Ultra-1). For comparison, the epoxidation of 1-octene was also carried out without the presence of any catalysts.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the prepared titania-silica catalysts. Two major peaks were observed which were in low angle (2 - 10°) and high angle (21 - 24°).

At a lower angle, the appearance of three peaks with low intensity were corresponded to be (100), (111) and (220) planes. The appearance of the respective planes was corresponded to the formation of mesostructured materials or 2D-hexagonal mesophase [14]. The decreased intensity of the peaks associated with the planes as the amount of water increased might be due to the formation of individual titania and silica small particles that embedded in the mesostructured frameworks. Thus, affecting the mesostructured frameworks. The formation of titania and silica particles were due to the self-hydrolysis and condensation of individual TTIP and OTS [15, 17]. Meanwhile, the broad peak at *ca.* 2*q* of 22.1° was attributed to the presence of silica in the amorphous phase [15-17]. The absence of TiO_2 diffractograms possibly due to the low amount of titania presence in the samples. It was reported that titania-silica materials consist of two phases which are amorphous and mesostructured [16, 17]. Since all the diffractograms showed a similar pattern, it can be concluded that the addition of water did not affect the degree of crystallization of TS.

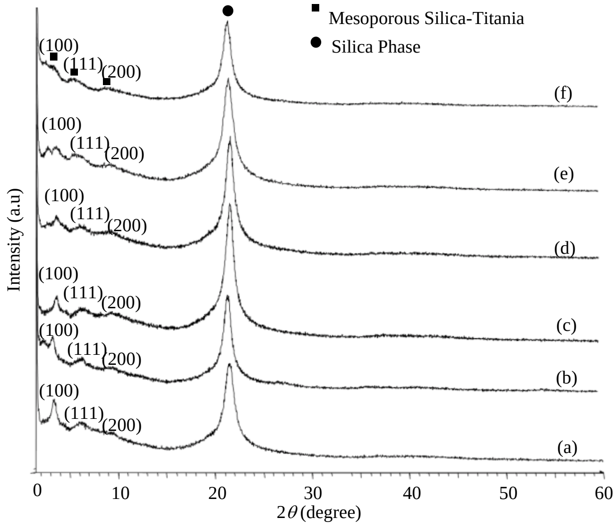


Fig. 1. XRD patterns of (a) TS, (b) 0.25-TS, (c) 0.5-TS, (d) 1.0-TS, (e) 2.5-TS and (f) 5.0-TS

The optical studies of the prepared catalysts were investigated using DR UV-Vis spectroscopy. The peak in the range of *ca.* 200 – 260 nm was attributed to a charge transfer of titanium tetrahedral while octahedral species showed an appearance peak at *ca.* 280 – 330 nm [17]. As shown in the Fig. 2, increasing the amount of water (Fig. 2(b)-(f)) caused the absorption spectra to shift to the shorter wavelength. The preparation of titania-silica catalysts with lesser amount of water (Fig. 2(b)-(c)), resulted in lower formation of titanium tetrahedral. Hence, the peak at *ca.* 280 – 330 nm, which corresponded to the titanium octahedral species was more prominent. These results suggest that the presence of water play a key role in the formation of titanium tetrahedral. However, the preparation of titania-silica catalyst without any addition of water (Fig. 2(a)) showed a prominent absorption peak at *ca.* 200 – 260 nm, which corresponded to the formation of titanium tetrahedral species. Without any addition of water, the titanium octahedral species are supposed to dominate the sample instead of tetrahedral species. Although the reason is still unclear, the formation of tetrahedral species might be due to a long hydrolysis process of TTIP and OTS that it was possible for the reaction to absorb moisture from the environment. Thus, leading to the formation of titanium tetrahedral species. In addition, it has been reported in the literature [17] that preparation of titania-silica catalyst without addition of water produces a TiO_2 cluster containing OH groups that makes the catalyst more hydrophilic.

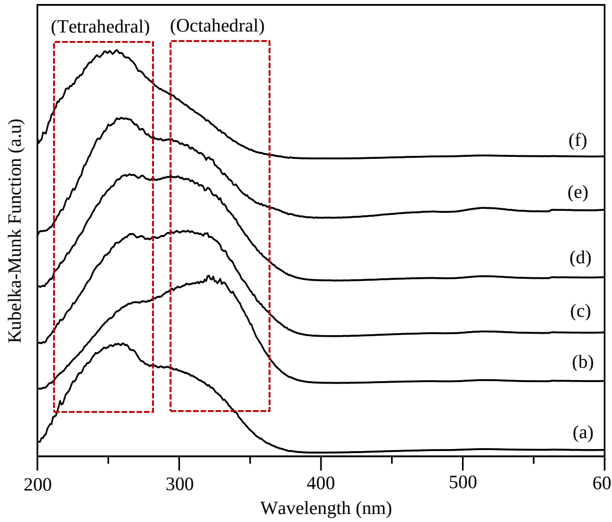


Fig. 2. DR UV-Vis spectra of (a) TS, (b) 0.25-TS, (c) 0.5-TS, (d) 1.0-TS, (e) 2.5-TS and (f) 5.0-TS

The morphological properties of the prepared TS and 5.0-TS catalysts were shown in Fig. 3 and Fig. 4. The FESEM images of both samples show that the catalysts were in irregular shape with the agglomeration of individual particles on the surface of catalyst. With addition of water (Fig. 4(b)), less agglomeration of particles was observed on the surface, suggesting the formation of more Ti – O – Si bonds in the catalyst. The Ti and Si mapping by EDX show that both samples were composed of TiO_2 cluster and SiO_2 small particles. The formation of TiO_2 clusters and SiO_2 particles were resulted from self-hydrolysis and condensation of individual TTIP and OTS [17]. Thus, these findings were in agreement with the decreased intensity of XRD peaks related to the mesostructured frameworks (**Fig. 1**). In addition, it can be observed that the SiO_2 particles were distributed homogeneously on the surface of both samples. As shown in Fig. 4(b), the intensity of TiO_2 cluster in sample 5.0-TS was slightly reduced when compared to that of sample TS. These results suggest that the addition of water facilitate the formation of Ti and Si bonds. The EDX analysis as shown in Fig. 5 demonstrated that the composition of Si was much higher that Ti, thus supporting the reason why the titania peaks were not detected in XRD diffractograms. It was also observed that the composition of chloride ions (Cl^-) in both catalysts were below 1%, suggesting the methanol can be an effective treatment in removing Cl^- ions.

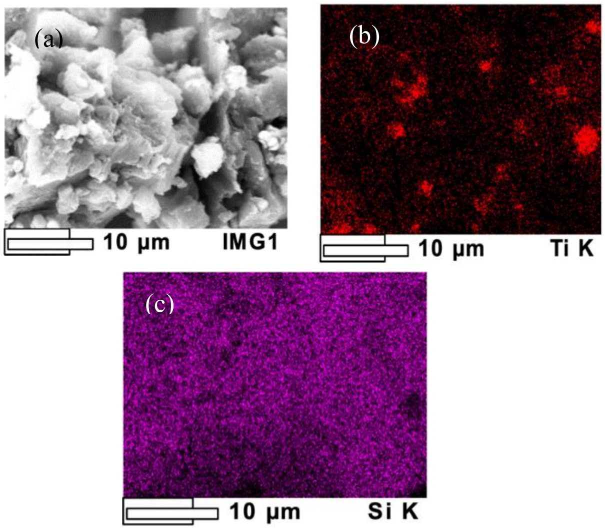


Fig. 3. The (a) FESEM micrograph and EDX mapping of (b)Ti and (c) Si for sample TS

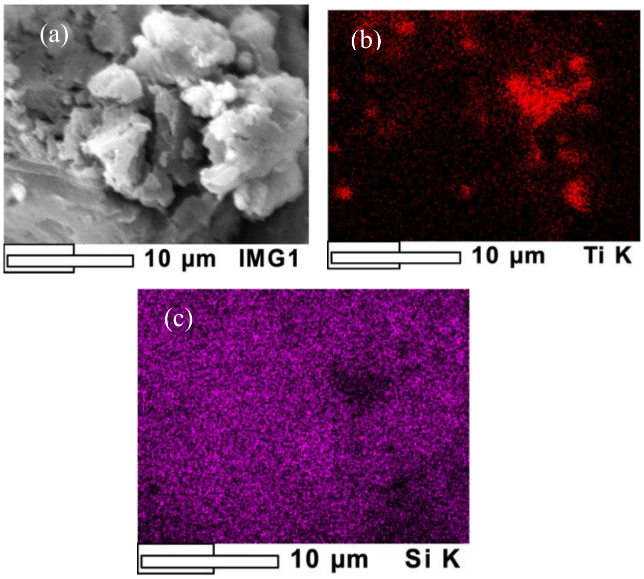


Fig. 4. The (a) FESEM micrograph and EDX mapping of (b)Ti and (c) Si for sample 5.0-TS.

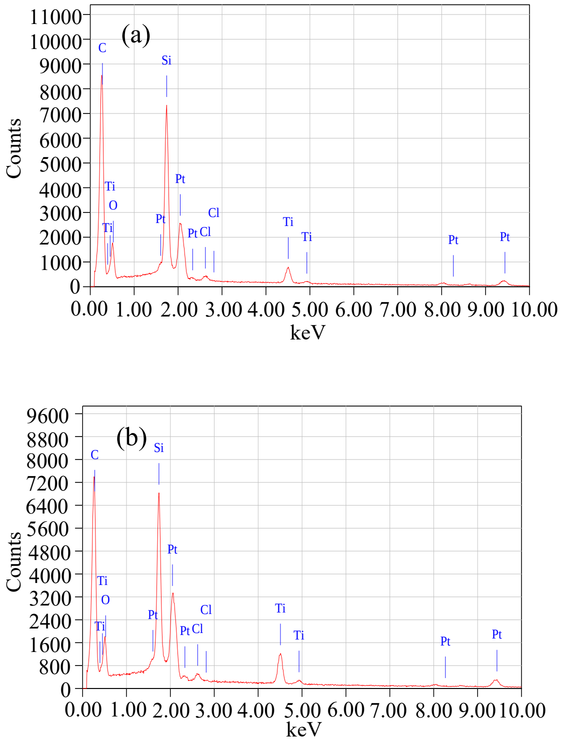


Fig. 5. Elemental analysis of: (a) TS and (b) 5.0-TS.

Fig. 6 shows the spectra of ^{29}Si Magic Angle Spinning Solid Nuclear Magnetic Resonance (MAS Solid NMR). As shown in the figure, T denominates the presence of corresponding Si sites in spectra. T^3 peak was corresponded to the formation of $C_{18}H_{37}Si(OSi)_3$ while T^2 indicated to formation of $C_{18}H_{37}Si(OTi)(OSi)_2$ [18]. It was demonstrated that increasing the amount of water led to an increase in the intensity of T^2, suggesting the increase in the formation of titanium tetrahedral in the catalyst.

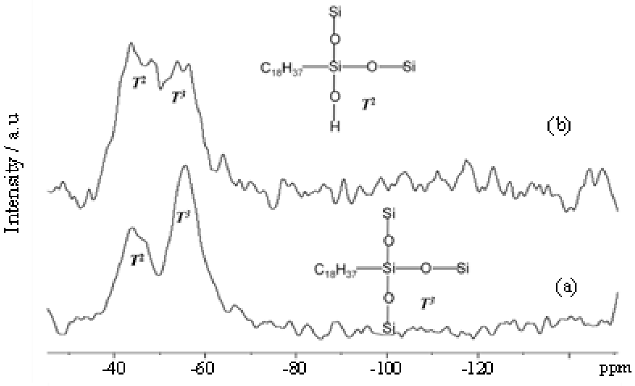
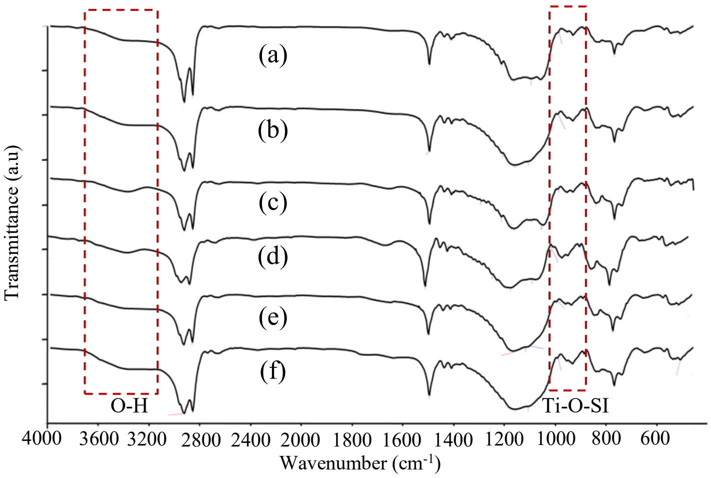


Fig.6. ^{29}Si MAS NMR spectra for (a) 0.25-TS and (b) 5.0-TS.

FTIR studies were carried out in order to determine the chemical bonds and functional groups of the prepared TS catalysts. Based on Fig. 7, the broad peak in the region of 3000 – 4000 cm^{-1} was corresponded to the bending and stretching mode of O-H of silanol group, respectively [19]. It was observed that increasing the amount of water led to a decrease in the peak intensity of OH. The decrease in the peak intensity was due to the conversion of O-H group to Ti – O – Si bond. The successful formation of Ti – O – Si can be observed from the peak that appeared at region of *ca*. 950 cm^{-1} [20]. The presence of Ti – O – Si bond in TS catalyst was possible due to the absorption of water from the environment during the hydrolyzation process. Thus, explain the formation of Ti – O – Si in the catalyst.



The catalytic activity of the prepared catalysts was evaluated in the epoxidation of 1-Octene. For comparison, the epoxidation of 1-Octene with the presence of hydrogen peroxide without addition of catalyst was also conducted (Fig.8(a)). The product of 1-Octene epoxidation which was 1,2-Epoxyoctane was also analysed as a reference by gas chromatography. Based on the GC analysis, the retention times of the sample appeared after the sixth minute. The observed peak was corresponded to 1,2-Epoxyoctane as according to the retention time of reference. As shown in Fig. 8(a), there was no amount of 1,2-Epoxyoctane detected, suggesting the epoxidation of 1-Octene could not be performed without a catalyst. When TiO_2 was used as catalyst, about 17.2 mmol of 1,2-Epoxyoctane was obtained. However, the catalytic activity was dropped to 12.4 mmol when titania-silica (5-TS) was used a catalyst. A slight increase in catalytic activity was demonstrated by sample 5-PS-TS composite as 17.3 mmol of 1,2-Epoxyoctane was obtained. These findings suggest that the titanium containing polystyrene composite has slightly improved the catalytic performance of TiO_2. Although the reason for the decrease in the catalytic activity of 5-TS is not entirely clear, it is suggested that the small particles of SiO_2 which were distributed homogeneously on the surface of the sample have reduced the catalytic active sites for the material. The formation of small particles of SiO_2 as demonstrated by EDX mapping (Fig. 3 and 4) were resulted from the self-hydrolysis and condensation of individual OTS and TTIP during hydrolysis process. It can be suggested that the introduction of polystyrene in the titania-silica has slightly improved back the composite performance in catalytic testing. Therefore, more findings and analyses are required in order to fully conclude the effectiveness of polymer in improving the catalytic properties of TiO_2.

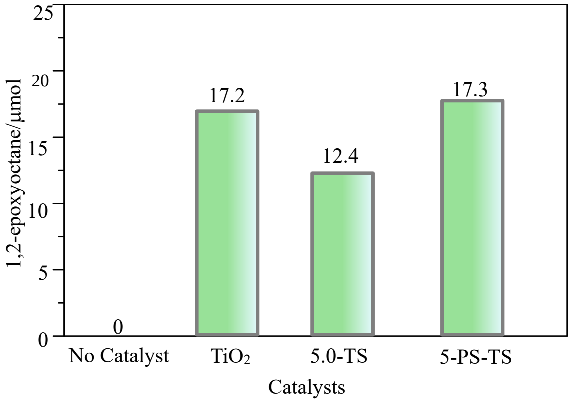


Fig. 8. Catalytic activity of (a) without catalyst (b) TiO_2, (c) 5.0-TS and (d) PS-TS

4. CONCLUSION

Titanium catalyst containing polystyrene composites have been successfully prepared by polymerization of styrene using titania-silica catalyst. The catalysts were prepared first by mixing the titanium(iv) isopropoxide (TTIP) and octadecyltrichlorosilane (OTS) in toluene as solvent. The role of water in formation of Ti and Si bond was investigated by the different amounts of water added to the mixture of TTIP and OTS. The DR UV-Vis and NMR studies showed that the formation of Ti – O – Si bonds were facilitated by the addition of water. Hence, more tetrahedral titanium active sites were produced. The presence of titanium tetrahedral in the titania-silica catalyst and electrophilic properties of polystyrene were expected to improve the catalytic performance of the composite in epoxidation of 1-Octene. The catalytic testing demonstrated the prepared composite slightly improved the catalytic activity of unmodified TiO_2. However, the formation of individual SiO_2 particles on the surface of catalyst during self-hydrolysis of OTS and TTIP may result to the decrease in its catalytic activity as it would reduce the catalytic active sites. For future studies, it is recommended to improve the technique in the preparation of titania-silica catalysts to obtain catalyst with high content of titanium tetrahedral species.

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