

Modification of titanium surface species of titania by attachment of silica nanoparticles

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Abstract

Silica nanoparticles-attached titania ($\text{TiO}_2@\text{SiO}_2$) was prepared by modification of the surface of titania (TiO_2) with octadecyltrichlorosilane (OTS) as a source of silica. The attachment of silica was achieved through repeated deposition–hydrolysis–calcination of OTS on the surface of titania particles. For comparison, the silica–titania composite ($\text{TiO}_2\text{–SiO}_2$) containing titania and silica agglomerated particles was also prepared. The physicochemical characteristics of $\text{TiO}_2@\text{SiO}_2$ and $\text{TiO}_2\text{–SiO}_2$ particles are experimentally studied by X-ray diffraction (XRD), UV–vis diffuse reflectance (UV–vis DR), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and ^{29}Si solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) techniques. The effect of silica attaching on activity of titanium surface species has been tested in the liquid phase epoxidation of 1-octene to 1,2-epoxyoctane with aqueous hydrogen peroxide. It is demonstrated that the surface attachment of titania with silica nanoparticles enhances the epoxidation activity of titania. UV–vis DR spectra of the solid particles showed the increase in intensity of the tetrahedral titanium in $\text{TiO}_2@\text{SiO}_2$. This indicates the occurrence of the transformation of some of the octahedral titanium to the tetrahedral structure during silica attaching of $\text{TiO}_2@\text{SiO}_2$ in which titanium tends to bond with $-\text{Si}(\text{OH})_2(\text{OSi})_2$ to make it stable in tetrahedral form. Considering that the tetrahedral titanium was considered the most active species in epoxidation of alkene, it can be concluded that a high epoxidation activity of $\text{TiO}_2@\text{SiO}_2$ particle was related to the modification of the local environment of titanium surface species by attachment of silica nanoparticles.

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1. Introduction

Titanium dioxide or titania is one of the most utilized particulate materials in the world. Although it was discovered more than 200 years ago and has been commercially processed for 85 years, it is still being actively researched. Titania is the most widely used as pigment in cosmetic and paint products, and photocatalyst. The photochemical activity of titania is modified by promoting or suppressing the recombination of electron and hole pairs which are formed by UV light excitation [1]. High photochemical activity is required when titania is used as photocatalyst, whereas low photochemical activity is preferred for paint or cosmetics application. One of methods to improve the photocatalytic activity of titania is by attachment of silica. It

has been reported that the photoactivity of silica-incorporated titania was three times higher than that of the Degussa P25 [2]. However, the reason why the photoactivity of silica-incorporated titania gave a higher activity compared to that of bare titania have not yet been clearly understood.

Recently room temperature sol–gel attachments of silica have been successfully adopted in order to coat titania with silica [3]. The attachment of titania with stable oxide layers has been also done by spraying of a metal oxide precursor solution on the surface of titania nanoparticles [4–6], acid hydrolysis of polysilicate [7] and hydrolysis of tetraethylorthosilicate (TEOS) using chloroform catalyst [8]. However, attachment of silica on the surface of titania by using octadecyltrichlorosilane (OTS) as a source of silica had not been investigated yet. OTS was selected because it is well-known compound used in surface-modification reactions with surface hydroxyl groups.

Recently, Park and Kang [9] also successfully prepared silica-coated titanium dioxide by using TEOS as a source of silica. In such system, silica is evenly coated on the surface of

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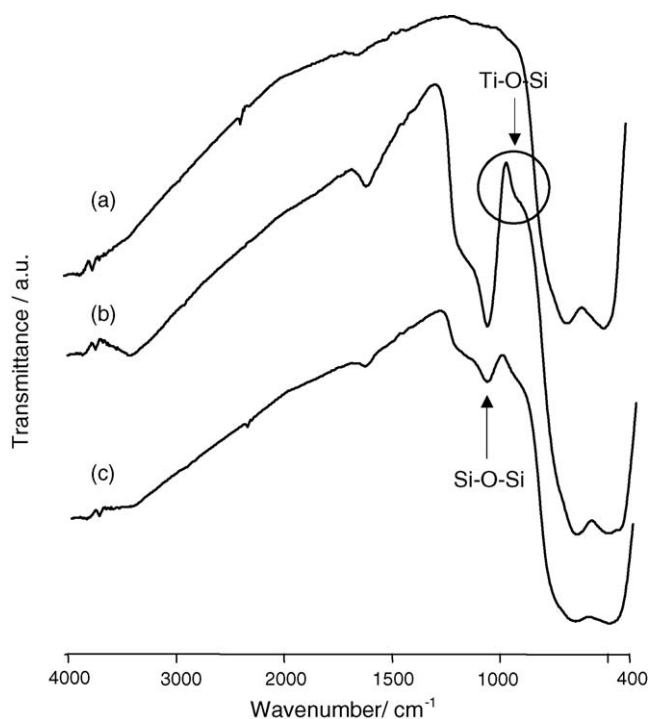


Fig. 1. IR spectra of (a) TiO_2 , (b) $\text{TiO}_2@SiO_2$, and (c) TiO_2-SiO_2 .

tania with thickness in the range of 10–15 nm. However, in this study, the strategy is different from those previously reported [2–9] because the aim is not to cover titania with silica but to attach silica nanoparticles on the surface of titania. One expects that the local environment of titanium surface species of titania are modified by attachment of silica. Evenly-coated silica on the surface of titania could not be achieved by using this method, since the presence of long chain alkyl groups (C_{18}) of OTS hinder the formation of silica layer during the surface modification. To examine the activity Ti surface species, the epoxidation of 1-octene by using aqueous H_2O_2 was used as the probe reaction.

In contrast to well-documented techniques to attach the silica on the surface of titania, to date, there is very limited understanding on the correlation between preparation and the nature of the titanium surface species after attachment of silica. It has been generally accepted that functional attachment of silica on the surface of titania must be controllable, reproducible and tailored surface structures. The tailoring of the surface properties is especially important for functional attachment. In this paper, attachment of titania particles with silica nanoparticles involves

Table 1
Atomic percentage of silicon and titanium of TiO_2 , $\text{TiO}_2@SiO_2$, and TiO_2-SiO_2 ^a

Element	Percentage of titanium and silicon (%)	
	Ti	Si
TiO_2	100	0.0
$\text{TiO}_2@SiO_2$	91.3	8.7
TiO_2-SiO_2	97.6	2.5

^a Chemical analysis using energy dispersive X-ray analysis (EDAX).

a simple deposition–hydrolysis–calcination of OTS on the surface of titania particles. It is demonstrated that the attachment of silica provides the modification of the local environment of titanium surface species of titania.

2. Experimental

2.1. Preparation of silica nanoparticles-attached titania

Silica nanoparticles-attached titania catalyst was prepared by modification of the surface of anatase TiO_2 (Riedel-de Haën) with octadecyltrichlorosilane (OTS) (Sigma–Aldrich) as a source of silica. The TiO_2 powder (6 g) was immersed in toluene (20 ml) containing OTS (3000 μmol) and the suspension was stirred for 20 min at room temperature. The suspension was centrifuged to remove unreacted OTS and wash with toluene (60 ml) and precipitated were dried at 383 K overnight. Then, the sample was ground to obtain a fine powder. In the next step, the sample was calcined at 550 °C for 4 h. Now, the silica-attached titania was achieved through deposition–hydrolysis–calcination processes. All the steps were repeated nine times, starting from the beginning until the accumulation of silica on the surface of titania was achieved. The silica-attached titania obtained was labeled as $\text{TiO}_2@SiO_2$. A similar procedure was also carried out to prepare the titania–silica composite (TiO_2-SiO_2) without

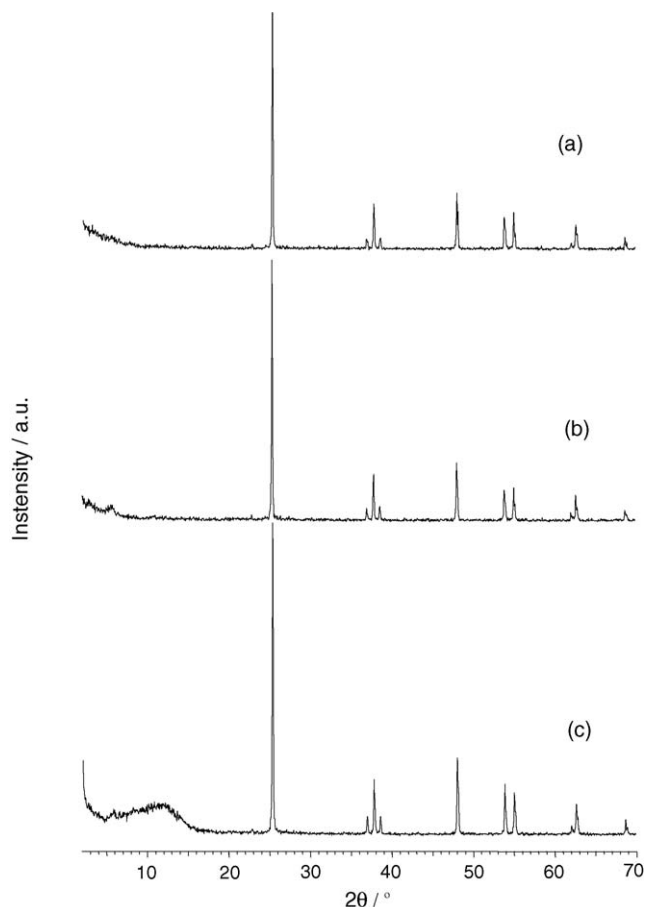


Fig. 2. X-Ray diffractograms pattern of (a) TiO_2 , (b) $\text{TiO}_2@SiO_2$, and (c) TiO_2-SiO_2 .

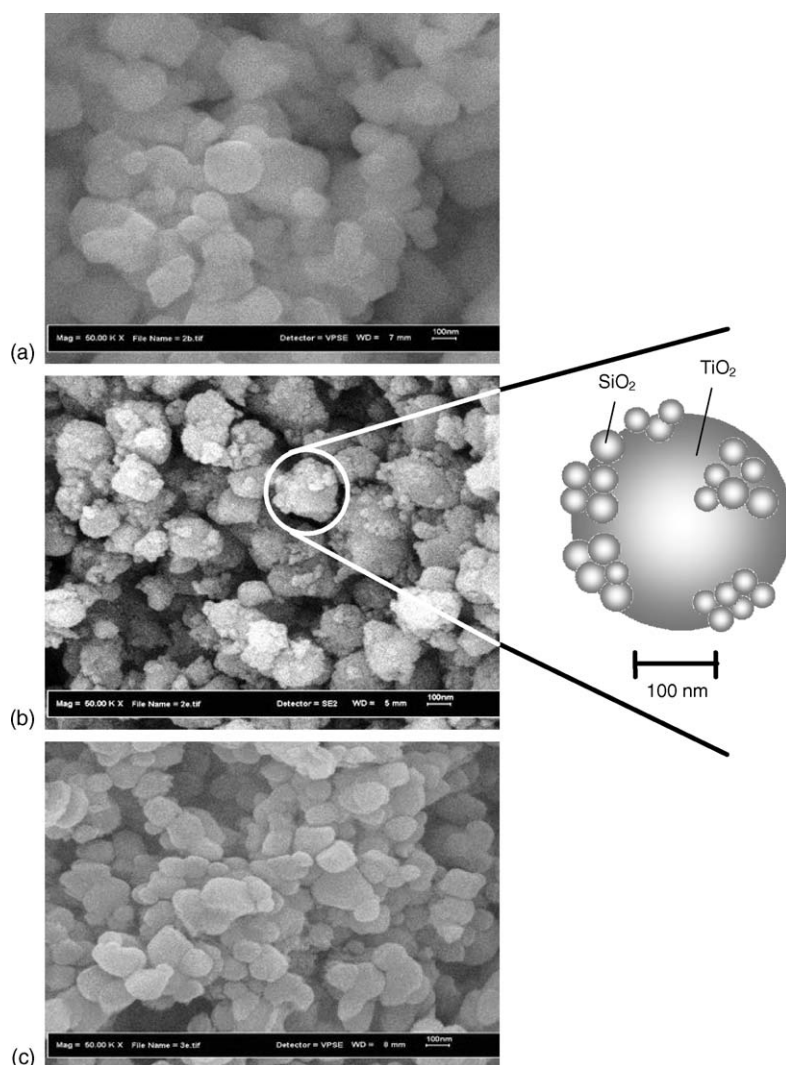


Fig. 3. SEM photographs of (a) TiO_2 , (b) $\text{TiO}_2@SiO_2$, and (c) TiO_2-SiO_2 .

washing with toluene in the above procedure for preparation of $\text{TiO}_2@SiO_2$. In a typical experiment, OTS (3000 μmol) was dissolved in toluene (20 ml). A dried titania powder (6 g) was added to the solution and the mixture was stirred in the fume cupboard until the solvent was completely dry. Then, the sample was ground to obtain a fine powder and calcined at 550 $^\circ\text{C}$ for 4 h.

2.2. Characterizations

The TiO_2 , $\text{TiO}_2@SiO_2$ and TiO_2-SiO_2 were characterized by UV–vis diffuse reflectance (UV–vis DR), X-ray diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and ^{29}Si solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) techniques. UV–vis spectra were recorded using Perkin-Elmer Lambda 900 spectrometer. XRD patterns were acquired on a Bruker D8 Advance instrument using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, $kV = 40$, $mA = 40$). SEM photographs and elemental analysis of silica and titanium elements in the

solid particles were obtained by using Philips XL 40 instrument. The ^{29}Si MAS NMR experiments were performed using Bruker Avance 400 MHz 9.4T spectrometer. The spectra were recorded at 79.44 MHz using 4 μs radio frequency pulses, a recycle delay of 60 s and spinning rate of 7.0 kHz using a 4 mm zirconia sample rotor. ^{29}Si MAS NMR chemical shifts were referred to external TMS at 0 ppm.

2.3. Activity of Ti surface species

To examine the activity Ti surface species, the epoxidation of 1-octene by using aqueous H_2O_2 was used as the probe reaction. It is generally known that silica is not active in this reaction [10–12]. In the epoxidation reaction, 1-octene (4 ml, Aldrich), 30% aqueous H_2O_2 (1 ml) and solid powder (50 mg) were placed in a glass tube, and the reaction was performed with stirring for 24 h at ambient temperature. The resulting product were withdrawn and analyzed with gas chromatograph (GC). Gas chromatograph–mass spectrometer (GC–MS) was also used to verify the resulting product.

3. Results and discussion

3.1. Physical properties

Fig. 1 shows the FTIR spectra of TiO_2 , $\text{TiO}_2@\text{SiO}_2$ and $\text{TiO}_2\text{-SiO}_2$ particles, respectively. The peaks at 678 and 505 cm^{-1} are attributed to Ti–O bond and the peak at 678 cm^{-1} refers to symmetric O–Ti–O stretch while 505 cm^{-1} is due to the vibration of Ti–O bond. A new distinct and strong peak at 1081 cm^{-1} can be observed in $\text{TiO}_2@\text{SiO}_2$ which assigned to the asymmetric Si–O–Si stretching vibration indicating the presence of silica in the $\text{TiO}_2@\text{SiO}_2$. The band of silica at 1075 cm^{-1} can be observed in $\text{TiO}_2\text{-SiO}_2$ but it is less intense compared to the peak of silica of $\text{TiO}_2@\text{SiO}_2$. An absorption peak of Ti–O–Si was observed at 950 cm^{-1} in $\text{TiO}_2@\text{SiO}_2$ particles indicating the Ti–O–Si bond formation [9]. The C–H peaks were not observed in the FTIR spectra of $\text{TiO}_2@\text{SiO}_2$ and $\text{TiO}_2\text{-SiO}_2$ due to alkyl groups of OTS have been removed after calcinations.

Table 1 shows the percentage of Ti and Si in TiO_2 , $\text{TiO}_2@\text{SiO}_2$ and $\text{TiO}_2\text{-SiO}_2$ samples. The atomic percentage of Si in TiO_2 , $\text{TiO}_2@\text{SiO}_2$ and $\text{TiO}_2\text{-SiO}_2$ are 0.0%, 8.7% and 2.5%, respectively. Fig. 2 shows the XRD pattern of TiO_2 , $\text{TiO}_2@\text{SiO}_2$ and $\text{TiO}_2\text{-SiO}_2$. The major peaks appear at 25.4° corresponds to the monoclinic phase of titania anatase. The X-ray diffractograms show that $\text{TiO}_2@\text{SiO}_2$ and $\text{TiO}_2\text{-SiO}_2$ possess a similar XRD pattern with bare titania indicating the anatase structure of titania remain unchanged after the attachment of silica. As shown in Fig. 2, a broad hump with maxima at about 12° which is attributed to amorphous silica is clearly observed in $\text{TiO}_2\text{-SiO}_2$ diffractogram. However, there is no a broad hump about 12° can be observed for $\text{TiO}_2@\text{SiO}_2$ although the amount of silica in $\text{TiO}_2@\text{SiO}_2$ is higher than that of $\text{TiO}_2\text{-SiO}_2$ (see Table 1). This phenomenon was also observed in the FTIR spectra of $\text{TiO}_2@\text{SiO}_2$ and $\text{TiO}_2\text{-SiO}_2$. The band of silica at 1075 cm^{-1} can be found in $\text{TiO}_2\text{-SiO}_2$ but it is less intense compared to the silica peak of $\text{TiO}_2@\text{SiO}_2$ (see Fig. 1). This suggests that the silica particles attached on the surface of TiO_2 in $\text{TiO}_2@\text{SiO}_2$ is very well dispersed with very small crystallite size which cannot be observed by XRD. This observation was supported by SEM photographs shown in Fig. 3.

Fig. 3 shows the SEM photographs of TiO_2 , $\text{TiO}_2@\text{SiO}_2$ and $\text{TiO}_2\text{-SiO}_2$. It reveals the difference in surface morphology among the samples. It is clearly observed the existence of silica nanoparticles, with the size in the range of 20–50 nm, attached on the surface of $\text{TiO}_2@\text{SiO}_2$. However, TiO_2 and SiO_2 particles are very difficult to distinguish in $\text{TiO}_2\text{-SiO}_2$ since their size and shape are almost similar.

UV–vis DR spectra of TiO_2 , $\text{TiO}_2@\text{SiO}_2$ and $\text{TiO}_2\text{-SiO}_2$ are shown in Fig. 4. As shown in spectra, the band in the range of 230–280 nm is attributed to a charge transfer of the tetrahedral titanium sites between O^{2-} and the central Ti (IV) atom, while octahedral Ti was reported appear at around 260–330 nm [13,14]. It shows that the increase in intensity in the range of 230–280 nm indicates the occurrence of the transformation of some of the octahedral titanium framework to the tetrahedral structure during the attachment of silica.

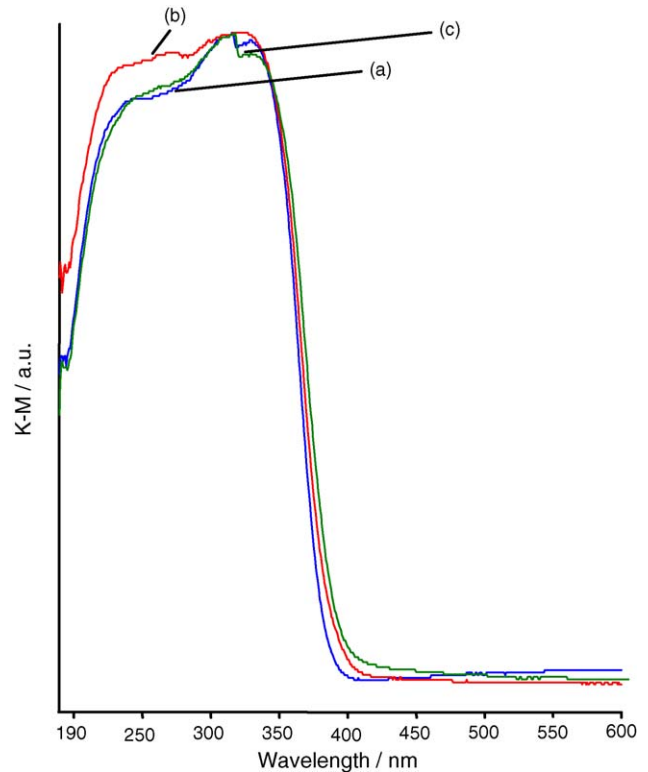


Fig. 4. UV–vis spectra of (a) TiO_2 , (b) $\text{TiO}_2@\text{SiO}_2$, and (c) $\text{TiO}_2\text{-SiO}_2$.

The short-range order structure of the $\text{TiO}_2@\text{SiO}_2$ and $\text{TiO}_2\text{-SiO}_2$ was characterized by ^{29}Si MAS NMR measurements (see Fig. 5). As a measure of cross-linkage, the ratio of Q^4 to Q^3 sites are attributed to the degree of cross-linking. It has been calculated that the ratio Q^4 to Q^3 sites of $\text{TiO}_2@\text{SiO}_2$

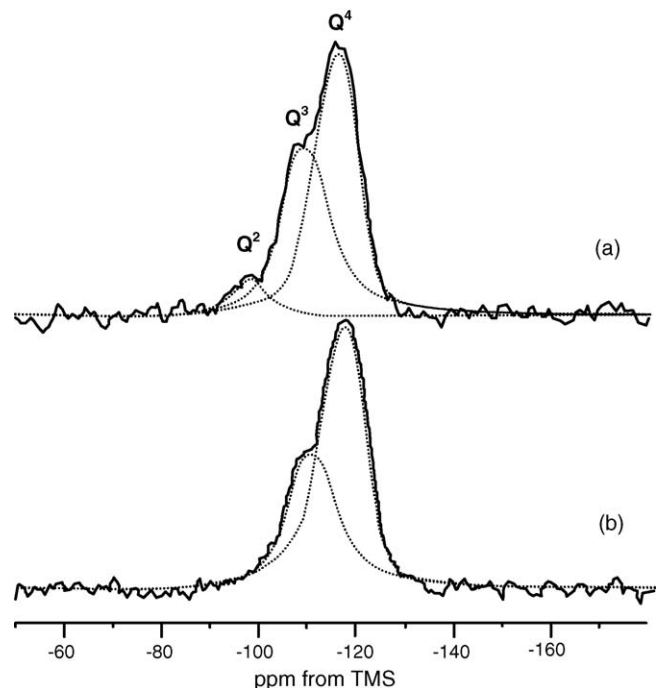


Fig. 5. ^{29}Si MAS NMR spectra of (a) $\text{TiO}_2@\text{SiO}_2$ and (b) $\text{TiO}_2\text{-SiO}_2$.

and $\text{TiO}_2\text{-SiO}_2$ is almost similar (ca. 1.7). Q denominates the presence of the corresponding Si sites in the spectra: $Q^4 = \text{Si}(\text{OSi})_4$, $Q^3 = \text{SiOH}(\text{OSi})_3$, and $Q^2 = \text{Si}(\text{OH})_2(\text{OSi})_2$ [15]. Interestingly, as shown in Fig. 5, attachment of silica on the surface of TiO_2 in $\text{TiO}_2@\text{SiO}_2$ led to the formation of Q^2 site. However, the amount of Q^2 type of bonding is only ca. 6% due to a partial condensation of Q^2 to Q^3 and Q^4 sites during repeated deposition–hydrolysis–calcination of octadecyltrichlorosilane (OTS) processes. Based on the above results, it is suggested that the deposition–hydrolysis–calcination of OTS to produce silica nanoparticles led to the formation of $\text{Si}(\text{OH})_2(\text{OSi})_2$ bonding in the sample, although this type bonding is considerably a little amount in $\text{TiO}_2@\text{SiO}_2$.

3.2. Activity of Ti surface species

As can be seen in Fig. 6, all of solid particles showed activity for epoxidation of 1-octene to give 1,2-epoxyoctane. In particular, attachment of silica nanoparticles ($\text{TiO}_2@\text{SiO}_2$) led to better activity than $\text{TiO}_2\text{-SiO}_2$ composite. This phenomenon could be explained in terms of the local environment of Ti active site. As described previously, the difference in the UV–vis DR spectra of TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and $\text{TiO}_2@\text{SiO}_2$ samples is due mainly to coordination of titanium on the surface of titania. It is generally accepted that isolated Ti (IV) in tetrahedral form are considered the most active species in epoxidation reaction [10–12]. Based on these facts, the effect of attachment of silica on increasing the epoxidation activity of $\text{TiO}_2@\text{SiO}_2$ can be explained by the presence of isolated Ti (IV) in tetrahedral form. However, the apparent rate of epoxidation over $\text{TiO}_2@\text{SiO}_2$ was much lower than those previously reported [16]. One of the reasons for the low epoxidation activity in $\text{TiO}_2@\text{SiO}_2$ particles is the presence of few four-coordinate Ti species which are considered to be the most active species in olefin epoxidation [17]. On the basis of these results, a model of the titanium surface species after

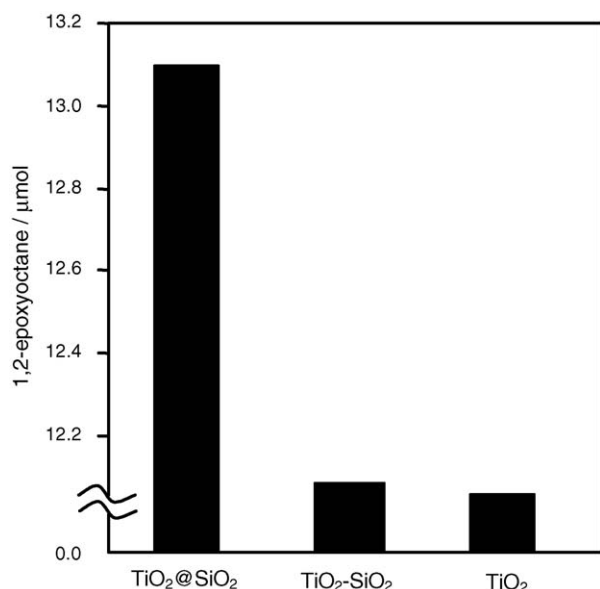


Fig. 6. Epoxidation activity of (a) TiO_2 , (b) $\text{TiO}_2@\text{SiO}_2$, and (b) $\text{TiO}_2\text{-SiO}_2$.

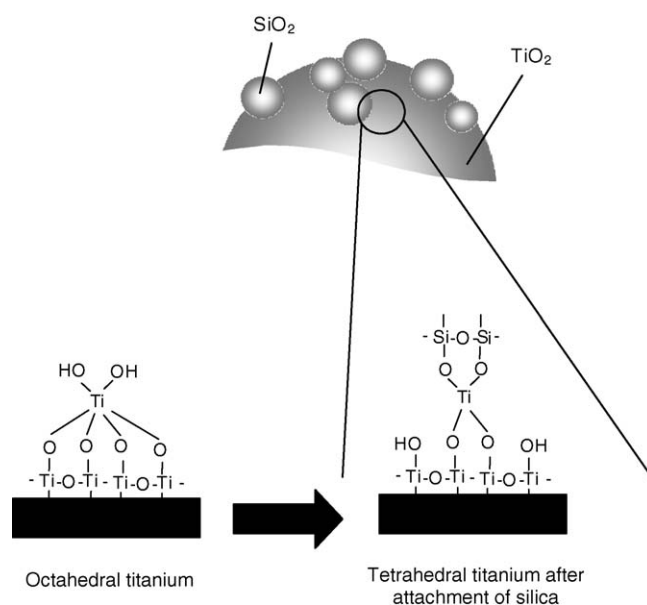


Fig. 7. The transformation of some of the octahedral titanium to the tetrahedral structure during the attachment of silica.

attachment of silica nanoparticles is proposed (see Fig. 7). One considers that titanium tends to bond with $\text{Si}(\text{OH})_2(\text{OSi})_2$ to make it stable in tetrahedral form.

4. Conclusions

The silica nanoparticles has been successfully attached on the surface of titania by deposition–hydrolysis–calcination of octadecyltrichlorosilane (OTS). It is demonstrated that the surface attachment of titania with silica nanoparticles enhances the epoxidation activity of titania. UV–vis DR spectra of the solid particles showed the increase in intensity of the tetrahedral titanium in $\text{TiO}_2@\text{SiO}_2$. This indicates the occurrence of the transformation of some of the octahedral titanium to the tetrahedral structure during silica attaching of $\text{TiO}_2@\text{SiO}_2$ in which titanium tends to bond with $\text{Si}(\text{OH})_2(\text{OSi})_2$ to make it stable in tetrahedral form. Considering that the tetrahedral titanium was considered the most active species in epoxidation of alkene, it can be concluded that a high epoxidation activity of $\text{TiO}_2@\text{SiO}_2$ particle was related to the modification of the local environment of titanium surface species by attachment of silica nanoparticles.

Acknowledgments

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