Research Article

Epoxidation of indene and cyclooctene on nanocrystalline anatase titania catalyst

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Nanocrystalline anatase titania samples of different crystallite sizes were prepared by sol gel method using ultrasonication and calcination at different temperatures. The calcined samples were treated with H_2O_2 in order to study the role of surface hydroxyl groups present on titania in generating reactive oxygen species responsible for the epoxidation reaction. The crystallite size of the calcined samples increased from 4 to 18 nm as the calcination temperature increased from 473 to 773 K, respectively. More uniform distribution/dispersion of the nanoparticles (SEM), marginally higher surface area, better thermal stability and phase purity are some of the advantages of preparation of nanocrystalline TiO_2 by using ultrasonication. EPR spectral data on the H_2O_2-treated samples confirmed the presence of superoxide radical species. The two distinct UV bands observed at 400 and 450 nm are assigned to charge transfer of peroxide (O_2^{2-}) to Ti. FT-IR spectral data show that the surface hydroxyl groups are the active sites in the generation of reactive oxygen species. The catalytic activity was evaluated in a series of epoxidation reactions using indene and cyclooctene as substrates and aqueous H_2O_2 as oxidant. The activity was found to decrease with increase in the calcination temperature of the samples, obviously due to an increase in crystallite size and a decrease in surface hydroxyl groups. The nanoparticle titania samples show better conversion and selectivity than the standard titania (Degussa P-25). The kinetic studies revealed that the reaction followed a pseudo first order kinetics in excess of H_2O_2.

KEY WORDS: nanocrystalline anatase titania; superoxide radical on titania; epoxidation of indene; cyclooctene epoxidation.

1. Introduction

The reactive oxygen species on titania is of great interest to researchers for the past three decades. These are not only chemically important but also biologically very interesting [1]. Literature reveals that titanium superoxide species are very stable in aqueous as well as in gel form [2–4]. Its unusual stability has lead to extensive studies on the formation and stabilization of reactive oxygen species on titania during the process of UV irradiation in presence of molecular oxygen [5], redox reactions involving use of hydrogen peroxide and Ti^{3+} salts [6] and on titanium substituted molecular sieves [7–9]. But, very few attempts have been made to explain the formation and stabilization of reactive oxygen species on the surface of anatase TiO_2 [10]. Most commercial samples of titania are a mixture of rutile and anatase phases (for example, Degussa P-25). While surface studies, so far, have mostly focused on rutile, there are some structural differences and the coordination states of Ti^{4+} on the surface between rutile and anatase phases [11]. Experimental surface studies on pure anatase are relatively new and adsorption characteristics of gases on nano particles of anatase titania will be of great interest [12].

Epoxides are valuable intermediates for the synthesis of fine chemicals. These are important precursors in the synthesis of antibiotic and tumor inhibitors. In several asymmetric routes, the epoxides lead to potentially active biological molecules. Titanium in one form or another is an active catalyst for selective epoxidation of many olefins. Titanium substituted zeolites [13,14], mesoporous molecular sieves [14], titanium substituted amorphous silica [15,16], transition metal oxide supported TiO_2 [17] and titanium peroxy solution [18] have been extensively studied. Among cyclic olefins, indene and cyclooctene are usually prepared by oligomerization of simpler olefins. The epoxidation of indene and cyclooctene provides a convenient route to other functional, fine chemicals. These epoxides are relatively stable and hence are good intermediates. The catalytic epoxidation of indene and cyclooctene has, therefore, attracted considerable interest recently [19–22]. Peroxotungstic acids deposited on hydroxyapatite [19], Mn-containing octahedral molecular sieve [21] and Mo-containing organo-inorganic hybrid material [22] have been used as catalysts for the epoxidation. There are no reports to our knowledge on the epoxidation of olefins using titania nanoparticles as catalyst, which is easier to synthesize. In this paper, we report the physicochemical characterization of reactive oxygen species generated on the surface of nanocrystalline anatase titania synthesized by sol gel- ultrasonication technique.

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These titania samples were further explored for the epoxidation of indene and cyclooctene using aqueous hydrogen peroxide as the oxidant.

2. Experimental

2.1. Synthesis

Single-phase anatase titania nanoparticles were synthesized by the sol gel method. 21 mL of titanium ethoxide (0.1 mol) (Aldrich) was mixed with 25 mL of absolute ethanol. To this mixture, 29 mL of water with 4 drops of acetic acid were added under ultrasonication (Sheshin, Japan, 100 V, 30 W, and 38 kHz). The sol gel formed by the hydrolysis process was further ultrasonicated for 30 min [23]. The product was separated by centrifugation, washed with distilled water, dried at 373 K for 24 h (Ti-373) and divided into five parts. These were calcined at 473, 573, 673, 773 and 873 K for 3 h. The calcined samples are designated as Ti-473, Ti-573, Ti-673, Ti-773 and Ti-873, respectively. These calcined samples were characterized and studied for the epoxidation of indene and cyclooctene.

In order to study the reactive oxygen species developed during the reaction after addition of H_2O_2, the calcined samples were treated with an excess of 30% H_2O_2 (Merck). After the treatment, the color of titania changed to yellow and this yellow titania was further filtered, washed thoroughly with water and the filtrate was tested by permanganate ion. These H_2O_2-treated titania samples were dried in a vacuum oven at 313 K for 5 h to remove water.

2.2. Characterization

The powder X-ray diffraction patterns of both the calcined samples and the yellow colored, H_2O_2-treated titania samples were recorded in a Rigaku D-max III VC instrument using Cu Kα radiation and NaI scintillation counter detector. The diffractometer was equipped with a Ni filter and a graphite monochromator. The samples were scanned in the 2θ range of 20–80° at a speed of 1°min^{-1} with 0.02° step. The crystallite size of TiO$_2$ samples was calculated using Debye–Scherrer equation. The FWHM of (101) reflection ($2\theta = 25.3$ °) of anatase was used for the determination of crystallite size. The BET surface area of the samples was calculated from N$_2$ adsorption isotherms at liquid N$_2$ temperature (77 K). The samples Ti-473 and Ti-573 to Ti-773 were evacuated at 473 and 573 K, respectively prior to N$_2$ adsorption. A JEOL-JSM-5200 Scanning Electron Microscope was used to observe the morphology of the particles.

The surface hydroxyl groups on the titania samples were studied by infrared spectroscopy using an SSU-8000 Shimadzu FT-IR spectrophotometer. Self-supporting wafers of similar quantity of samples were taken for IR measurement. The samples calcined at 573, 673 and 773 K were heated at 573 K in N$_2$ atmosphere while the sample calcined at 473 K was heated at 473 K in N$_2$ atmosphere, before recording their IR spectra. The IR spectra of H$_2$O$_2$-treated samples were recorded without heat treatment. The thermal stability of the reactive oxygen species modified titania was investigated by thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) techniques with TG/DTA32 Sieko thermal analyzer. DRUV-Visible spectra of all samples were recorded on a Shimadzu UV-2500PC instrument. Electron spin resonance spectra were recorded on a Bruker EM X-band spectrophotometer operating at 100 kHz field modulation for a typical nanocrystalline titania calcined at 473 K and after addition of 30% H$_2$O$_2$ to just wet the sample. The spectra were recorded at 77 K. A similar EPR measurement was repeated for TiO$_2$ sample P-25 obtained from Degussa.

2.3. Catalytic activity

The epoxidation of indene (Merck) and cyclooctene (Aldrich) was carried out in a batch reactor at 313 K in presence of titania samples, activated at 373 K in air for 12 h prior to the reaction. To 0.50 g of olefin dissolved in 1 g of acetone, 50 mg of the catalyst was added in a round-bottomed flask fitted with a water condenser and a magnetic stirrer (100 rpm). Aqueous H$_2$O$_2$ (30%) was added slowly to the reaction mixture at a substrate to H$_2$O$_2$ mole ratio of 3. The reaction was monitored every 20 min by analyzing aliquots of reaction mixture in a gas chromatograph (HP-5890DN), having a 35 m column of phenyl methyl siloxane as stationary phase and a FID. Ascorbic acid was used as a radical quencher before injection of the sample in GC. The identification of products was done by GC-MS (Shimadzu, GCMS-QP 5000) technique. The kinetic studies were carried out with an excess of H$_2$O$_2$ at 313, 323 and 333 K for the epoxidation of indene.

3. Results and discussion

3.1. Powder XRD and TG-DTA

Synthetic routes for the preparation of titania usually yield amorphous titania, titanium hydroxide or crystalline anatase or rutile phases depending on the experimental conditions and the precursors used. The multiple plots of the powder XRD patterns of the calcined samples and H$_2$O$_2$-treated titania samples are shown in figure 1a and b, respectively. The absence of any peak at $2\theta = 30.8$° (due to the (121) reflection of brookite phase) from a slow step scan of the XRD profile indicates the absence of this impurity phase. The samples are comprised of single anatase phase up to a calcination temperature of 773 K. The broad nature of the peaks
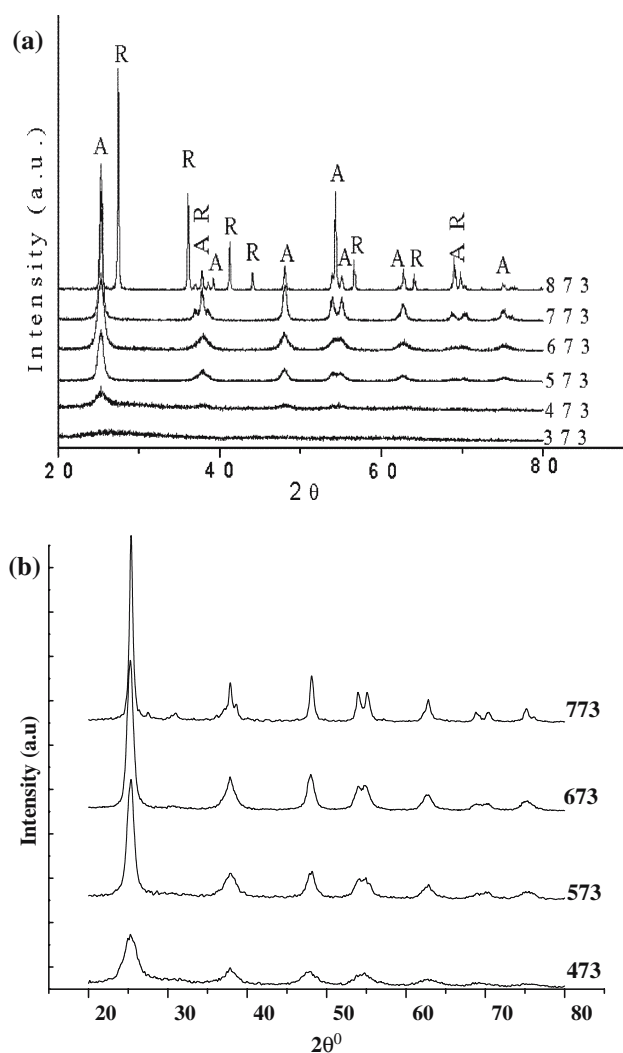
Figure 1. Powder XRD patterns of (a) untreated and (b) H$_2$O$_2$-treated nanocrystalline anatase titania calcined at 473, 573, 673, 773 and 873 K.

confirms the nanocrystalline nature of the sample. Similar XRD patterns of the samples indicate that the structure of the anatase titania remained intact after treatment with H$_2$O$_2$. This observation indicates that the reactive species are confined to the surface of titania. The sample calcined at 873 K shows the formation of rutile phase.

The thermograms of Ti-473 and the H$_2$O$_2$ treated sample are shown in figure 2a. The TG curve shows a weight loss of 11.9% up to 773 K, which could be due to the surface adsorbed water and hydroxyl groups. The endothermic peak at 330 K in the DTA curve confirms that the weight loss is due to the desorption of adsorbed water. The weight loss between 673 and 773 K is more prominent (4.6% of the total weight loss), which is due to the dissociation of surface hydroxyl groups. A tiny exothermic peak at around 860 K can be ascribed to the transformation of anatase to rutile, which is supported by the XRD pattern of the sample calcined at 873 K.

The TG curve of H$_2$O$_2$-treated anatase titania shows similar behavior as that of untreated one, but the exothermic peak in DTA at 632 K shows the loss of reactive oxygen from the surface of titania, which is absent in Ti-473 sample (figure 2b) [4].

Typical SEM micrograph (figure 3) of a sample calcined at 573 K shows that the particles are spherical in nature, more uniform in size and less aggregated. Larger particles are seen, which are likely to be aggregates of smaller particles. The BET surface areas of titania samples calcined at 473, 573, 673 and 773 K are 168, 91, 67 and 23 m^2 g^{-1}, respectively.

3.2. EPR measurement

The sample Ti-473 after treatment with H$_2$O$_2$ shows an intense EPR signal of paramagnetic oxygen radical with characteristic g_x, g_y, and g_z values, which are 2.025, 2.011 and 2.0034, respectively and in rhombic symmetry (figure 4a). The observed g values of superoxide radical agree well with those reported earlier [2–4]. The signal recorded at 77 K is quite sharp. Degussa P-25 sample shows a similar signal (figure 4b) but the intensities of two signals differ considerably.

3.3. Infrared spectral measurements

The FT-IR spectra of the untreated samples (figure 5a) show a broad band at around 900 cm^{-1}, which is due to the bending vibrations of Ti–O–Ti [24]. The absorption of the surface hydroxyl groups in the IR region on anatase titania is strongly dependent on the synthesis procedure and particle size [25]. The Ti-473 sample shows a broad band in 3400–3750 cm^{-1} region, which is indicative of the physically adsorbed water as well as hydroxyl groups on different faces of anatase crystal. Ti-573 sample shows a weak band at 3569 cm^{-1}, due to the stretching vibrations of physically adsorbed water on the surface. The intensity of this peak decreases with calcination temperature of the sample and finally disappears in Ti-773 sample. Two bands, one at 3660 cm^{-1} and another in the 3720 to 3724 cm^{-1} region show the presence of two types of hydroxyl groups in titania [26,27].

The band due to the hydroxyl groups, which was observed in 3400 and 3750 cm^{-1} region, disappeared on treatment of the sample with H$_2$O$_2$ (figure 5b). The surface hydroxyl groups are the active centers for the formation of superoxide as observed earlier [10]. The H$_2$O$_2$-treated Ti-473 and Ti-773 samples showed another band at 970–950 cm^{-1} due to the O–O stretching of peroxide radical [28]. H$_2$O$_2$ interacts with hydroxyl groups on surface of anatase to generate peroxide (O$_2^{2-}$) or hydroperoxide (OOH) species, which normally cannot be distinguished by IR studies. In superoxides, O–O stretching band appears in the region, 1075–1125 cm^{-1} in end-on structure [28], whereas our samples show a broad band in the region, 970–950 cm^{-1}.
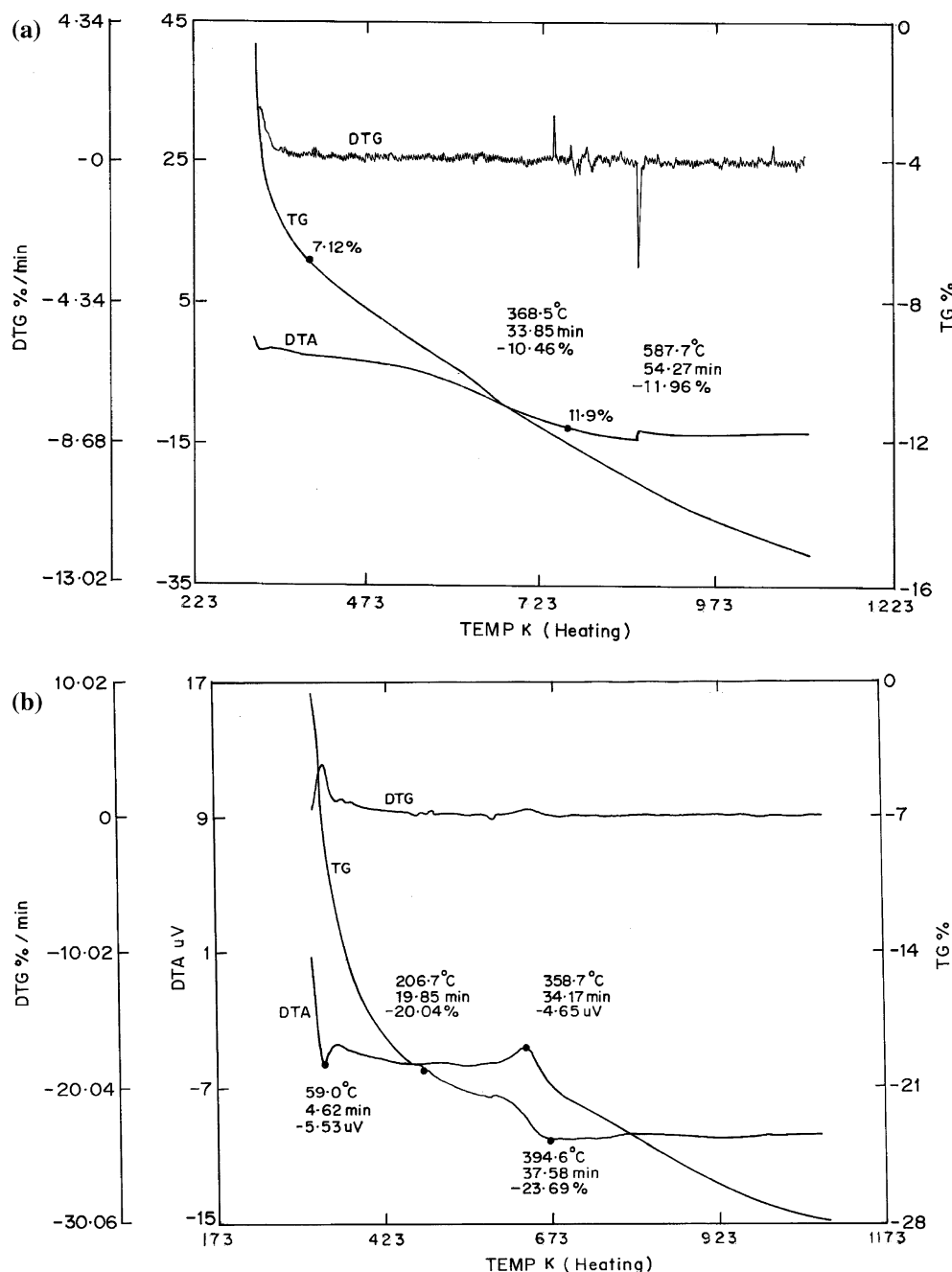
Figure 2. TG, DTG and DTA profiles of (a) untreated and (b) H_2O_2 -treated Ti-473 sample.

However, EPR studies confirm the presence of super-oxide radical, which is observed at lower temperatures. The observed O–O stretching frequency is in the range of peroxide rather than superoxide. The lowering of frequency is due to various reasons reported earlier [9], where superoxide is converted into peroxide at room temperature. At room temperature, peroxide and hydroperoxide species are present on the surface of nanocrystalline anatase titania which are responsible for the epoxidation activity. However, the presence of superoxide in small concentrations at the reaction con-ditions cannot be ruled out [10].

3.4. UV–Visible spectroscopy

The diffuse reflectance UV–Visible spectra (in Kubelka–Munk units) of samples calcined at 473, 573 and 673 K are shown in figure 6a–c, respectively. A clear difference can be observed between untreated and H_2O_2-treated samples (figure 6a and e). The maxima at $\sim$225 nm seen in all the H_2O_2 treated samples is absent in the untreated samples. A change in the hydration state changes the coordination around titanium [29] and hence, this band is likely to be due to the presence of tetrahedrally coordinated titanium. The band at
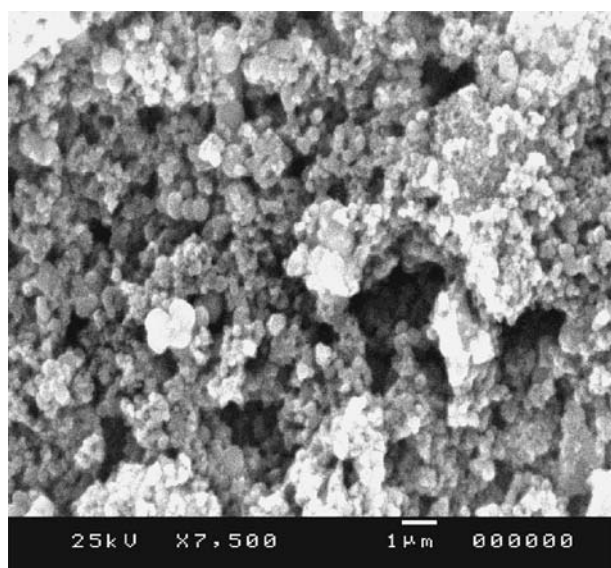
Figure 3. Scanning Electron Micrograph of anatase titania calcined at 573 K.

~310 nm observed in all samples matched with the band edge of anatase titania nanoparticles [14]. The spectra of the H_2O_2-treated Ti-473 and Ti-573 samples were deconvoluted and two distinct bands are observed in the
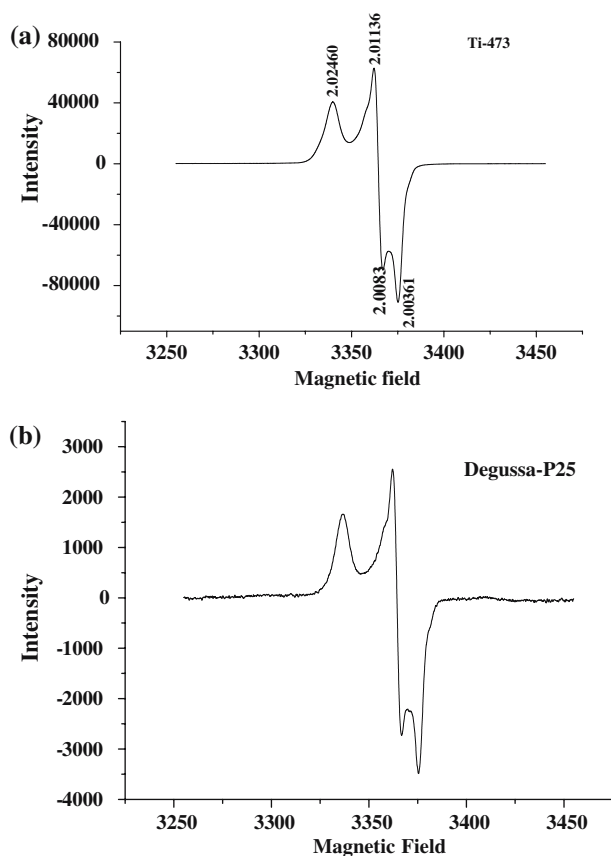

Figure 4. EPR spectra of H_2O_2-treated (a) Ti-473 sample and (b) Degussa P-25.
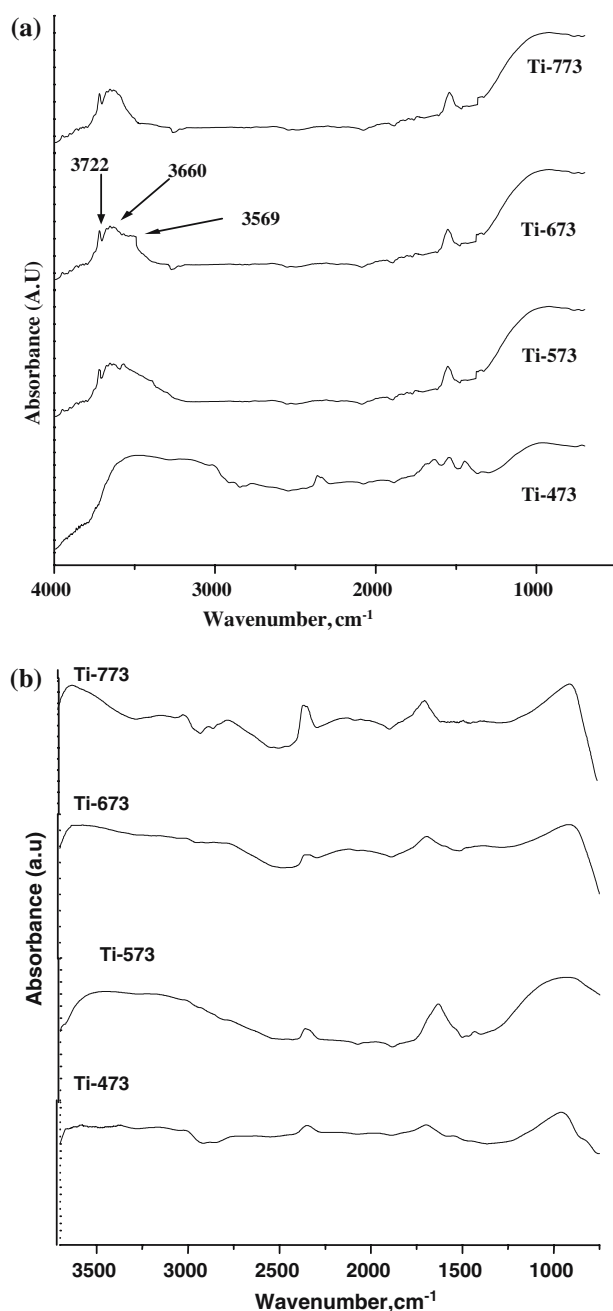

Figure 5. FT-IR spectra of (a) untreated Ti-473, Ti-573, Ti-673 and Ti-773 samples and (b) after treatment with H_2O_2.

visible region at ~400 and ~450 nm (Figure 6d and e). These bands are assigned to charge transfer of O_2^{2-} to Ti. There are two transitions possible in ligand to metal charge transfer [10,28], one is a strong $(\sigma-\sigma^*)$ transition and the other is weaker $(\pi-\sigma^*)$ transition, irrespective of the structure of peroxide. The UV–Visible spectra of untreated Ti-673 sample and the corresponding H_2O_2 treated sample are almost similar. This is an indication that the reactive oxygen species might have formed in very low concentrations. This low concentration is due to a decrease in the surface hydroxyl concentration of the samples with increasing temperature of calcination,
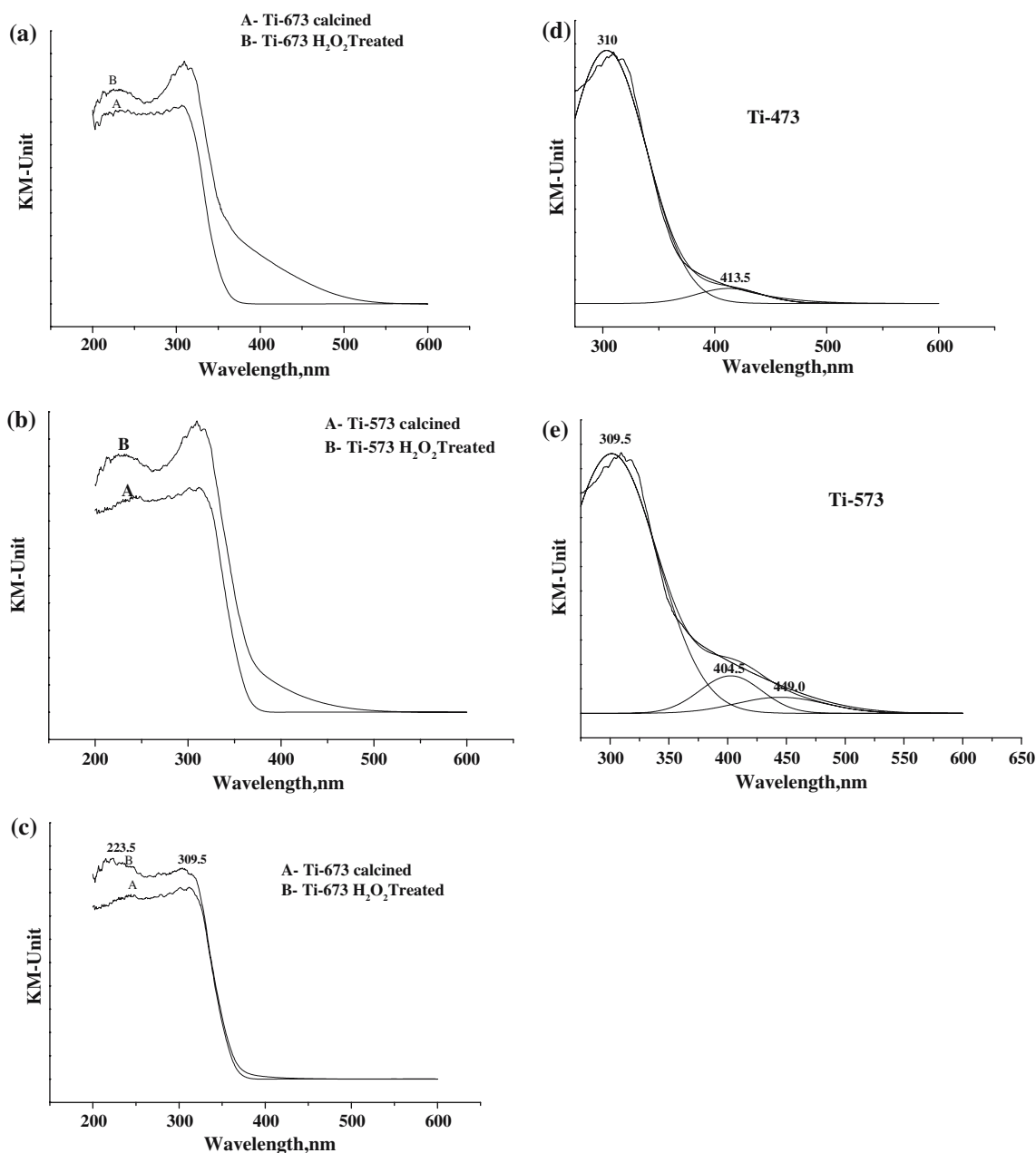
Figure 6. DRUV-Vis spectra of calcined and H_2O_2-treated titania samples: (a) Ti-473; (b) Ti-573 and (c) Ti-673 samples. The deconvoluted spectra of calcined and H_2O_2-treated titania samples: (d) Ti-473 and (e) Ti-573.

since the hydroxyl groups are the active centers for the formation of reactive oxygen.

3.5. Catalytic activity

The epoxidation of indene and cyclooctene leads to the formation of various products but the selectivity to one of the products, *viz.*, the epoxide is of great importance for the chemical industry. The results obtained on the epoxidation of indene and cyclooctene as substrates with aqueous H_2O_2 are summarized in tables 1 and 2, respectively. The highest activity in terms

of conversion of indene and cyclooctene under the reaction conditions is seen for the Ti-473 sample (27.5 wt% and 13.8 wt%, respectively). Due to the smaller crystallite size of Ti-473 ($\sim$4 nm), the reactive oxygen species developed at reaction conditions are readily accessible to the olefin, which leads to a higher conversion than the other catalysts as well as the standard Degussa P-25 sample. Apparently, the crystallite size of the nanoparticles plays an important role in the reaction. The conversion of indene and cyclooctene decreases rather sharply as the crystallite size increases from 4 nm to 18 nm for Ti-473 to Ti-773 samples,

Table 1
Catalytic activity of anatase titania nanoparticles in the oxidation of indene using aqueous hydrogen peroxide[a] and acetone as solvent

Catalyst	Conversion wt%	TOF[b] h^{-1}	Initial rate mmole g^{-1} s^{-1}	Product distribution, wt%	
				Indene oxide	Indanone
Ti-473	27.5	2.56	1.74	97.9	2
Ti-573	11.4	0.91	1.22	96.1	3.9
Ti-673	5.7	0.72	0.86	94.3	5.7
Ti-773	1.5	0.66	–	93.6	6.4
Desussa-P25	1.1	–	–	94.8	5.2

[a]Reaction conditions : Temp. = 313 K; Batch reactor; indene/oxidant (mole/mole) = 3:1; indene/acetone (wt/wt) = 2; Reaction time = 15 h; catalyst = 10 wt% of the substrate.
[b]Turn over frequency = moles of substrate converted per moles of titania present in the given catalyst per h.

Table 2
Catalytic activity of anatase titania nanoparticles in oxidation of cyclooctene using aqueous hydrogen peroxide[a] and acetone as solvent

Catalyst	Conversion wt%	TOF[b]h^{-1}	Initial rate mmole g^{-1} s^{-1}	Product distribution, wt%	
				Epoxide	Others
Ti-473	13.8	1.07	1.09	91.0	8.9
Ti-573	8.4	0.62	0.86	83.1	18.1
Ti-673	4.9	0.33	0.41	85.8	14.0
Ti-773	3.5	0.23	–	86.2	14.9
Desussa-P25	Nil	–	–	–	–

[a]Reaction conditions: Temp. = 328 K; cyclooctene/oxidant (mole/mole) = 3:1; cyclooctene/acetone (wt/wt) = 2; Reaction time = 15 h; catalyst = 10 wt% of the substrate.
[b]Turn over frequency = moles of substrate converted per moles of titania present in the given catalyst per h.

respectively (figure 7a). For the smaller crystallites of titania, a higher external surface area is obvious. Hence, the decrease in conversion is an effect of the lower surface area with increasing crystallite size of the samples. The initial rates presented in table 1, normalized to specific BET surface area give very similar values, indicating that the differences in the catalytic activity is related to the surface area effect. It is also noted that the number of exposed surface hydroxyl groups on the samples is directly related to the surface area. Hence, the higher activity of Ti-473 is due to a larger exposed surface area resulting from very small (nano sized) crystallites of titania. This leads to a higher concentration of surface hydroxyl groups that generate more reactive oxygen species in presence of H$_2$O$_2$. The selectivity of epoxide varied from 94 to 98% and 86 to 91% in the series of catalysts (tables 1 and 2). The selectivity for epoxide is fairly independent of the conversion levels and the crystallite size of titania.

In effect, based on a higher exposed surface area of smaller crystallites, the number of surface OH groups should be higher. The number of hydroxyl groups per unit surface area calculated from the ν_{OH} intensity in the IR spectrum (relative values among the samples studied) showed that the surface of Ti-473 has maximum number of surface hydroxyl groups (figure 7b). After the addition of H$_2$O$_2$, apart from the surface hydroxyl groups

the physically adsorbed water might be taking part in the formation of reactive oxygen species. But, the role of adsorbed water is not well understood. The reactive oxygen species generated on the surface of nanoparticles of titania are responsible for the higher activity observed. Bulk titania, such as Degussa P-25 has a much larger crystallite size (a very low surface area) as compared to sol gel derived nanocrystalline anatase titania and hence inactive in this reaction.

In our earlier studies, we found that the sample Ti-473 was quite active in the epoxidation of styrene and cyclohexene [30].

3.6. Kinetic studies

The kinetic plots of the epoxidation of indene and cyclooctene at 313 K in terms of the concentrations of the substrates as a function of time at a substrate to H$_2$O$_2$ mole ratio of 3 are given in figure 8. A small quantity of nanoparticles of titania (10% of the substrate concentration) was employed in the reaction medium under well-stirred conditions. Any variation in the speed of mixing (stirring speed) did not influence the conversions and hence the reaction is truly under kinetic regime. The rate equation can be written as,

$$\text{rate} = -d[S]/dt = k[S]^{\alpha}[H_2O_2]^{\beta}$$
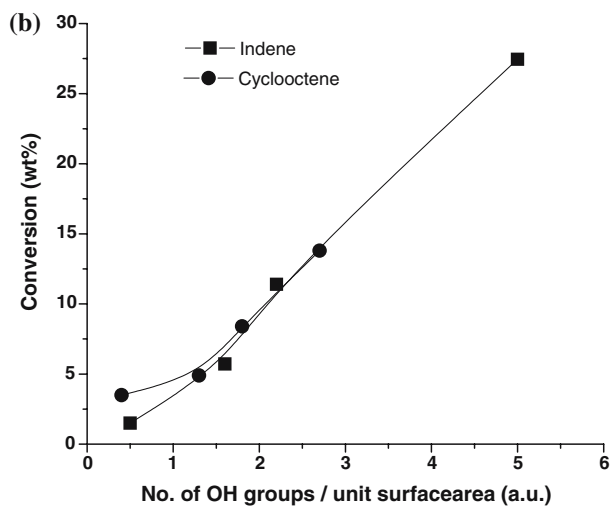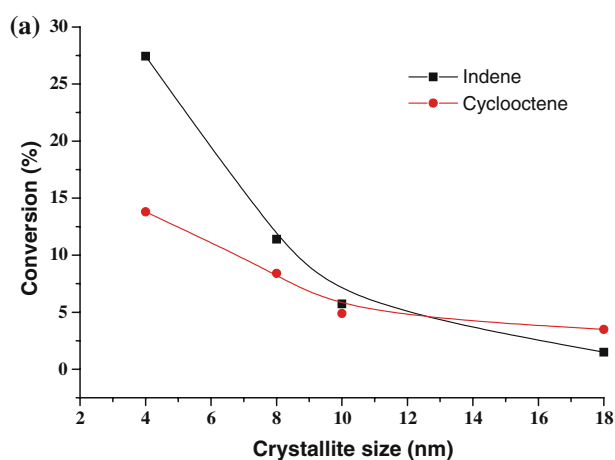
(a)

(b)

Figure 7. (a) Influence of crystallite size and (b) surface hydroxyl groups of anatase titania on the epoxidation of indene and cyclooctene.
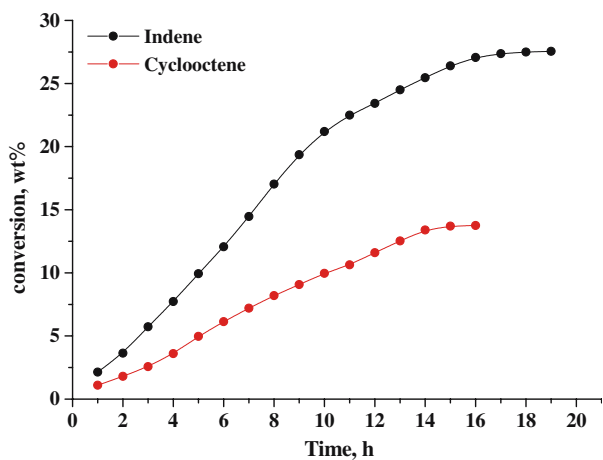

Figure 8. Kinetics of epoxidation of indene and cyclooctene at 313 K on Ti-473 sample carried out at a substrate to H_2O_2 mole ratio of 3.
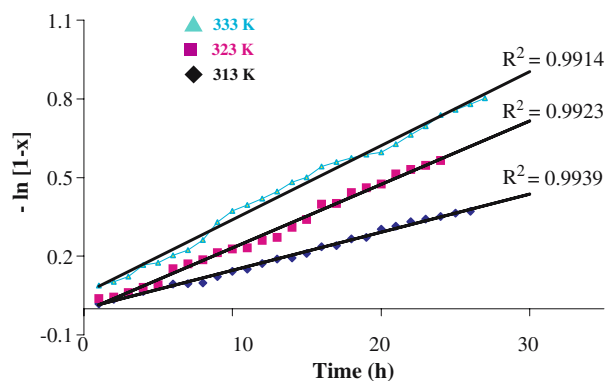

Figure 9. Pseudo first order kinetic plot for the epoxidation of indene on Ti-473 sample in excess of H_2O_2 at three different temperatures.

where [S] stands for the concentration of indene or cyclooctene, α, the order of reaction with respect to olefin, β is the order of reaction with respect to H_2O_2 and k is a rate constant. In excess H_2O_2,

$$rate = k[S]^{\alpha}$$

If $\alpha = 1$ then the characteristic plot of a first order reaction $-\ln(1-x) = k't$ (where x is the conversion of the substrate) with respect to time should be linear. The reaction carried out with indene at three different temperatures in excess concentrations of H_2O_2 is plotted with respect to time. The plot shows a straight line passing through origin (figure 9), which indicates that the formation of epoxide is a first order reaction with respect to indene.

4. Conclusions

Nanocrystalline particles of pure anatase titanium dioxide without any impurity of brookite phase were prepared by sol-gel method under ultrasonication at ambient temperatures. The average crystallite size increased from 4 to 18 nm as the calcination temperature increased. SEM shows a uniform distribution of nanoparticles. The BET surface area was found to decrease from 168 to 23 m^2 g^{-1} with an increase in calcination temperature from 473 to 773 K, respectively. The titania nanoparticles treated with H_2O_2 shows the generation of three types of reactive oxygen species. At low temperature, a superoxide species is prominent and is identified by EPR spectroscopy. Superoxide may be one of the major products of the decomposition of H_2O_2. At room temperature, the superoxide decomposed to peroxide, which is identified by IR spectroscopy. Although the hydroperoxide (OOH) or reversibly adsorbed H_2O_2 could not be identified, their presence cannot be ruled out. The surface hydroxyl groups act as reaction centers for the formation of reactive oxygen

species. Peroxide and hydroperoxide species generated on the surface of nanocrystalline titania are responsible for the epoxidation of indene and cyclooctene. The crystallite size of titania and the associated number of surface hydroxyl groups influence the epoxidation activity significantly. A high selectivity of epoxides (98 and 91 %) has been observed for both the substrates.

Acknowledgments

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