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Epoxidation of propylene with dilute H_2O_2 over titanium silicalite containing trace aluminum

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Titanium silicalite (TS-1) was successfully synthesized by using TPABr as the template and silica sol as silicon source in a 100 l stainless steel autoclave. IR, XRD, UV–vis, elemental analysis, and ^{27}Al and ^{31}P MAS NMR were used to characterize the synthesized products. The results show that the synthesized material has an MFI structure with high crystallinity and large crystal size and two kinds of titanium species. Trace aluminum in silica sol is also incorporated into the zeolite framework. The synthesized TS-1 exhibits high activity in the epoxidation of propylene with dilute H_2O_2 with high selectivity to methyl mono-ethers and low selectivity to propylene oxide (PO). The low selectivity toward PO is due to the residual acidity onto TS-1. The selectivity of PO can reach up to 90% through adjusting the pH of the reaction mixture. Extra amounts of base decrease the H_2O_2 utilization and the H_2O_2 conversion. However, in over acid-treated TS-1 in which part removal of extra-framework titanium takes place, the utilization of H_2O_2 is quite different: for the low Si/Ti ratio of TS-1, the H_2O_2 utilization increases. But the utilization of H_2O_2 does not change for the high Si/Ti ratio TS-1. Thermal analysis shows that the as-synthesized TS-1 exhibits high activity and thermal stability in the calcined range 540–900 °C.

KEY WORDS: titanium silicalites; aluminum-containing TS-1; TPABr; propylene; epoxidation; thermal stability; acid treatment.

1. Introduction

Titanium silicalite (TS-1) was first synthesized by Taramasso *et al.* [1] using tetraethyl orthosilicalite (TEOS), tetraethyl orthotitanate (TEOT) and tetrapropylammonium hydroxide (TPAOH) as the silicon source, titanium source and the template, respectively. Because of its specific catalytic oxidation properties, TS-1 became a hot topic in the domain of catalysis [2]. The expensive TPAOH makes TS-1 synthesis rather costly, and, therefore, restrains its industrial application. The key issue is to synthesize TS-1 with cheaper templates. There are many reports on the synthesis of TS-1 using TPABr to replace TPAOH [3–5]. However, the synthesized TS-1 contains trace amounts of aluminum in the framework due to the use of silica sols as silicon sources. The incorporation of trivalent metal ions such as in TS-1 (Al–TS-1 [6–8]) enables it to have both oxidation and acidic properties. This may further enlarge the use of these aluminotitanium silicalites as a catalyst. Van Grieken *et al.* [9] reported the synthesis of MTBE from isobutene using Al–TS-1 as the catalyst. A bifunctional material, Al–TS-1, is capable of catalyzing the liquid-phase oxidation of isobutene with H_2O_2 and subsequently the etherification with methanol. Ovejero *et al.* [10] reported the synthesis of Al–TS-1 by wetness impregnation of amorphous Al_2O_3–TiO_2–SiO_2 solids prepared by the sol-gel method. Thangaraj *et al.* [11] demonstrated the simultaneous incorporation of Al and Ti in the MFI structure by XRD, IR, ^{27}Si and ^{27}Al MAS NMR techniques. However, the incorporation of Al in TS-1 is not in favor of oxidation of organic substrates with H_2O_2. As early as 1990, Thangaraj *et al.* [12] found that the incorporation of Al in TS-1 led to a decrease in the activity of TS-1 for the oxidation of benzene to phenol. Bellussi *et al.* [13] reported epoxidation of butylene results over Al–TS-1 and found that acidity affects oxidation activity and selectivity. Glycol selectivity increases with decrease in the H_2O_2 conversion rate. The reason that the H_2O_2 conversion decreases may be that the slow diffusion of glycols from the Al–TS-1 channels hinders the diffusion of H_2O_2 and the olefins. Huybrechts *et al.* [14] reported on the oxidation of 1-octene and phenol over TS-1 synthesized by using a silica sol as silicon source, and proposed that the low selectivity was ascribed to the presence of traces of acidity. This acidity is related to impurity levels of trivalent ions (Al and Fe), which were introduced during the hydrothermal synthesis, as confirmed by chemical analysis. However, there is no report on epoxidation of propylene over TS-1 containing trace amounts of aluminum. In this paper, the synthesis of titanium silicalite containing

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trace aluminum is presented, and the catalytic properties of the synthesized TS-1 are investigated in detail.

2. Experimental

Titanium silicalites (TS-1) were prepared by using colloidal silica (30 wt%) and tetrabutylorthotitanate (TBOT) as silicon and titanium sources, respectively, and using TPABr (to replace TPAOH) and *n*-butylamine as the template and the base, respectively [15]. The gel was transferred into a 100 l autoclave and heated for 3–5 days at 160–180 °C; the slurry was then filtered, washed with distilled water and dried at 100 °C in static air.

The Si/Ti ratio of the TS-1 was determined by a Bruker SRS 3400 XRF spectrometer. X-ray diffraction patterns were obtained on a D/max-2400 diffractometer using Cu K_α radiation. Relative crystallinity of samples was calculated by comparing the sum of the peak intensities at 23.1°, 23.3°, 23.8°, 24.0° and 24.50° on the basis of TS-1 sample calcined at 540 °C (100%). Framework IR spectra were recorded on an FT-5DX spectrometer. Zeolite samples were ground with KBr and pressed into thin wafers. ^{27}Al solid-state MAS NMR spectra were recorded on a Bruker DRX 400 spectrometer at room temperature using a relaxation delay of 2 s, a contact time of 2 ms and a spinning frequency of 4–6 kHz. Solid-state ^{31}P NMR of the probe molecule trimethylphosphine was used to characterize the acidity of TS-1 with a special device for on-line treatment of zeolite samples [16]. TS-1 was heated up to 673 K in vacuum for dehydration and exposed to trimethylphosphine-saturated vapor at room temperature for 30 min and then evacuated for a while to remove weakly adsorbed species on the surface. After treatment, the sample was loaded *in situ* into an NMR rotor, sealed and transferred to the spectrometer without exposure to air. UV–vis measurements were performed on a Shimadzu UV-240 by using the diffuse reflectance technique in the range 190–490 nm, and freshly-prepared silicalite was used as the reference.

Epoxidation of propylene was carried out in a stainless-steel autoclave reactor, 0.4 g of calcined catalyst, 2.0 ml of ~30% H_2O_2 and 31.6 ml of methanol were first fed into the reactor and then propylene was charged at a constant pressure (0.4 MPa). The reactor was heated to 60 °C for 60–90 min under magnetic agitation. The residual H_2O_2 after reaction was checked by iodometric titration. The reaction products were analyzed by GC-8A gas chromatography with a flame ionization detector (FID) and a capillary column (40.0 m × 0.25 mm) containing polyethylene glycol 20 M as the stationary phase. Propylene oxide (PO) was the main product, while propylene glycol (PU) and its mono-methyl ethers (MME) were the by-products. The results of the reaction were reported according to the literature [5].

The acid treatment of titanium silicalite was carried out by adopting the following conditions: the temperature was 80 °C; the ratio of TS-1 to acid solution (2 mol/l HNO_3) was 1 : 20 g/ml.

3. Results and discussion

3.1. Characterization of TS-1 containing trace aluminum

The XRD pattern of the sample shows the characteristic of MFI-type structure, and no peaks attributable to impurities (anatase or rutile) are revealed in the spectra of TS-1. The IR spectrum of the sample exhibits a distinct band at 960 cm^{-1}, which is attributed to the incorporation of titanium into the framework. The UV–vis spectrum of the sample exhibits two peaks at about 220 and 270 nm; the former is attributed to tetra-coordination of titanium and the latter is attributed to hexa-coordination of titanium [5]. The ^{27}Al MAS NMR spectrum of TS-1-C (figure 1) shows that only a line at 52.5 ppm assigned to tetrahedral coordinated aluminum and no 0 ppm non-framework aluminum signal is observed in TS-1. This shows that trace aluminum (the ratio of SiO_2 to Al_2O_3 is about 500–700) existing in the silica sol precursor is incorporated into the framework completely. The ^{31}P MAS NMR spectra shown in figure 2 display a resonance at −4.1 ppm which has been well characterized and is assigned to a $[(CH_3)_3P{-}H]^+$ complex arising from interaction of $(CH_3)_3P$ with Brønsted acid sites in the zeolite. The peak at −33.6 ppm is attributed

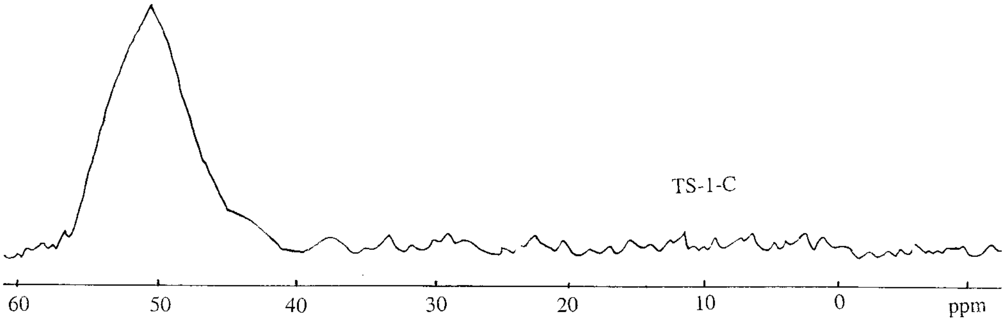

Figure 1. ^{27}Al MAS NMR spectrum of TS-1 containing trace aluminum.

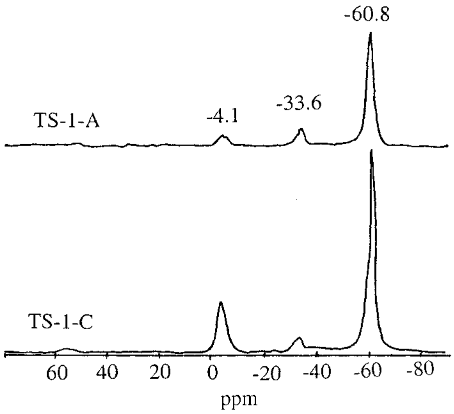

Figure 2. ^{31}P MAS NMR spectra of $(CH_3)_3P$ in TS-1.

to Lewis-bound trimethylphosphine, and the higher-shielding peak at −60.8 ppm is related to the physisorbed phosphine [17]. By quantitatively comparing these two curves in figure 2, we can conclude that there are more Brønsted acid sites in sample TS-1-C containing trace aluminum than TS-1-A.

3.2. *Epoxidation of propylene over TS-1 containing trace aluminum*

Table 1 lists the elemental composition of titanium silicalites with different amounts of aluminum. From the table it can be seen that aluminum in TS-1-A cannot be detected by XRF, while TS-1-C synthesized in a 100 l autoclave contains 0.24% of aluminum, whose molar ratio of SiO_2/Al_2O_3 reaches 672.

The calcined samples TS-1-A and TS-1-B exhibit high selectivity for PO in the epoxidation of propylene with dilute H_2O_2, while sample TS-1-C containing trace aluminum exhibits high activity and low selectivity for PO. The low selectivity of PO is attributed to the acidity of TS-1 from trace aluminum and silicon hydroxyls. In order to improve the selectivity toward PO, a base can be used to neutralize the residual acidity in the TS-1. In this experiment, Na_2CO_3 was used as the neutralizer, when the amount of Na_2CO_3 increases from 0 μmol/g Cat; the selectivity to PO increases to about 90% from about 5%. However, an extra amount of basic substance (>52.5 μmol/g Cat) will make the conversion and the utilization of H_2O_2 decrease, and further deactivate TS-1. This can be explained as follows: in the epoxidation of propylene, a five-member cyclic active species structure (figure 3), which is formed by a titanium hydroperoxo moiety Ti–OOH and a protic molecule ROH at Ti sites, is proposed by Clerici and Ingallina [18]. The stable five-member intermediate species can activate the oxygen atom of H_2O_2, then transfer the oxygen atom to the organic substrate. When an extra amount of Na_2CO_3 is added to the reaction mixture, exchange reactions between species II with metal salts produce anionic derivatives with reduced electrophilic power. Maximum and minimum concentrations of species II are achieved in acidic and basic solutions, respectively. Thus, excess amounts of basic substances will lead to a decrease in the concentration of species II and make the conversion of H_2O_2 decrease. The decomposition of H_2O_2 in a basic medium will lead to low utilization of H_2O_2.

Table 1

Elemental analysis of titanium silicalites with different amounts of aluminum[a]

Sample	SiO_2 (wt%)	TiO_2 (wt%)	Al_2O_3 (wt%)	SiO_2/TiO_2 (molar ratio)	SiO_2/Al_2O_3 (molar ratio)
TS-1-A	95.02	3.725	0	34.0	∞
TS-1-B	95.40	4.21	0.034	30.2	4770
TS-1-C	94.80	3.75	0.24	33.7	672

[a] TS-1-A was synthesized by using TPAOH as the template and $Si(OC_2H_5)_4$ as silicon source, while both TS-1-B and TS-1-C were synthesized by using TPABr as the template and silicon sol as silicon source. During all the syntheses, $Ti(OC_4H_9)_4$ was used as titanium source. TS-1-C was synthesized in a 100 l autoclave. During the synthesis of TS-1-B, the silica sol was pretreated to remove aluminum.

One-half gram TS-1-C was impregnated with different amounts of Na_2CO_3 solution. After drying at 120 °C for 3 h and calcining at 540 °C for 5 h, the samples were characterized by IR. The IR spectra of TS-1-C with different amounts of basic additive show that the intensity of the peak at about 960 cm^{-1} does not decrease with an increase in the amount of basic additive. There is no relationship between epoxidation properties and the intensity of the peak at about 960 cm^{-1}. The ^{31}P MAS NMR spectra in figure 4 show that peak intensity at −4.1 ppm decreases with the increase in the amount of basic additive. This demonstrates that the treatment of TS-1 with a basic additive neutralizes the Brønsted acidity onto the TS-1 surface, restrains the open-ring reaction of PO with methanol, and increases the selectivity to PO. This is in agreement with the results listed in table 2.

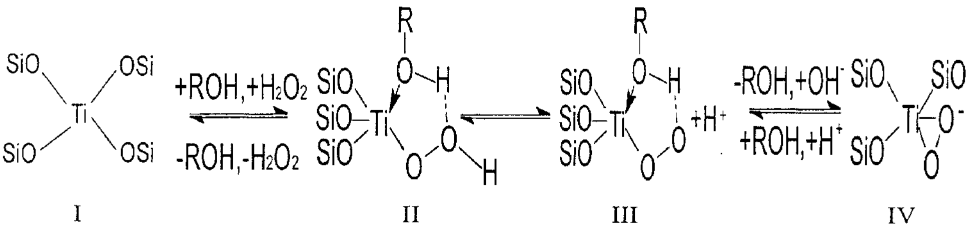

Figure 3. Catalytic scheme of titanium silicalite reported by Clerici and Ingallina [18].

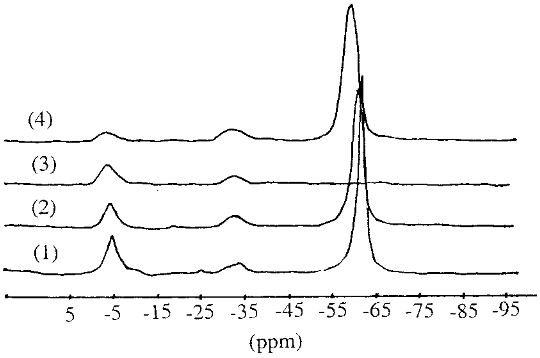

Figure 4. ^{31}P spectra of TS-1-C with different amounts of basic additive (μmol/g Cat): (1) 0, (2) 12.5, (3) 35, (4) 87.5.

3.3. Acid treatment of TS-1 containing trace aluminum

In the epoxidation of propylene with dilute H_2O_2 over TS-1, trace amounts of aluminum existing in the framework will result in drastic decreases in PO selectivities. Attempts were made to remove framework aluminum by acid treatment of TS-1. The results are listed in table 3. It can be seen that after acid treatment the amount of TiO_2 decreases and the amount of aluminum increases slightly. ^{27}Al MAS NMR shows that the signal of framework aluminum does not decrease after acid treatment and there is no signal from non-framework aluminum. Thus, the increase in the amount of aluminum measured by XRF belongs to instrument error in the measurement. This shows that trace aluminum is not removed, but part of the TiO_2 is removed after acid treatment. Acid treatment makes the utilization of H_2O_2 increase for the sample with low Si/Ti ratio of TS-1 (sample 1 and 3 in table 3), but the utilization of H_2O_2 is kept at a constant level for the sample with a high Si/Ti ratio (sample 5 in table 3) after acid treatment. Figures 5 and 6 are UV–vis and IR spectra of TS-1 samples 5 and 6, respectively. It can be seen that the intensity of the peak at about 270 mm decreases after acid treatment but, in the IR spectrum of the sample,

Table 2
Epoxidation of propylene with dilute H_2O_2 over titanium silicalites with different amounts of aluminum

Sample	Amount of Na_2CO_3 added (μmol/g Cat)	$X_{H_2O_2}$ (%)	$U_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)
TS-1-A	0	98.1	92.8	95.3	4.7
TS-1-B	0	97.6	92.4	89.6	10.4
TS-1-C	0	98.5	96.4	5.1	91.9
TS-1-C	5	99.3	95.4	41.9	54.7
TS-1-C	12.5	99.2	95.9	54.3	43.2
TS-1-C	17.5	97.6	91.2	70.8	29.2
TS-1-C	35	98.4	92.6	78.2	21.8
TS-1-C	52.5	97.9	89.1	90.7	9.3
TS-1-C	87.5	87.8	87.0	93.9	6.1

Reaction conditions: temperature: 60 °C; time: 90 min; H_2O_2 concentration: 0.741 mol/l; propylene pressure: 0.4 MPa; catalyst amount: 11.9 g/l; solvent: methanol.

Table 3
Epoxidation of propylene over TS-1 before and after acid treatment

Sample	Acid treatment	SiO_2/TiO_2 (molar ratio)	SiO_2/Al_2O_3 (molar ratio)	$X_{H_2O_2}$ (%)	$U_{H_2O_2}$ (%)	S_{PO} (%)
1	No	12.8	561	90.3	78.1	96.4
2	Yes	13.2	498	95.1	90.9	96.1
3	No	14.6	562	94.1	80.8	90.8
4	Yes	38.6	475	95.6	100	90.9
5	No	27.3	617	93.8	93.2	93.0
6	Yes	30.9	522	93.8	94.7	93.0

Reaction conditions: temperature: 60 °C; time: 90 min; H_2O_2 concentration: 0.741 mol/l; propylene pressure: 0.4 MPa; catalyst amount: 11.9 g/l; the neutralizer: Na_2CO_3 solvent: methanol. Acid-treatment conditions: temperature: 80 °C; ratio of TS-1 to acid solution (2 mol/l HNO_3): 1 : 20 g/ml; time: 2 h.

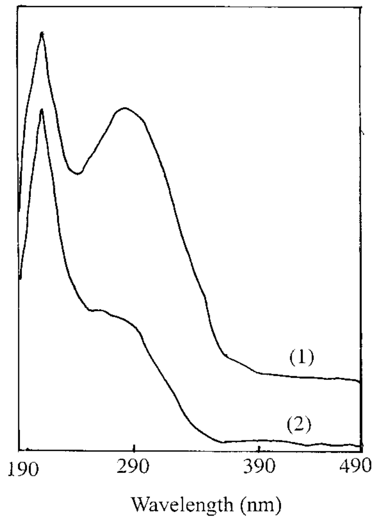

Figure 5. UV–vis spectra of TS-1 samples 5 and 6: (1) sample 5, (2) sample 6.

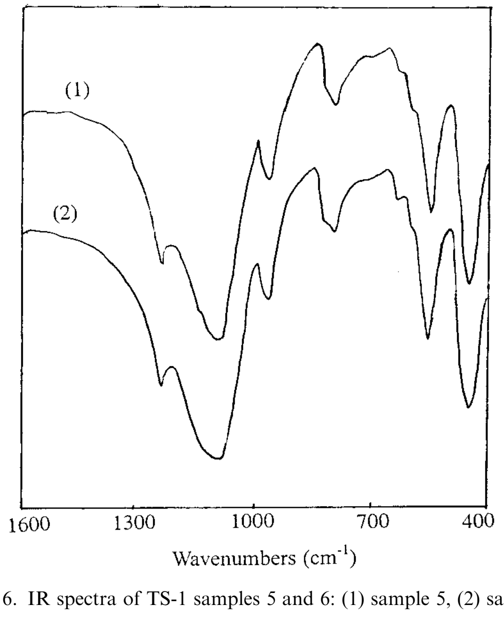

Figure 6. IR spectra of TS-1 samples 5 and 6: (1) sample 5, (2) sample 6.

Table 4
Thermal stability of TS-1-C

Calcination temperature (°C)	Relative crystallinity (%)	$X_{H_2O_2}$ (%)	$U_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)
540	100	96.7	91.0	89.8	10.2
650	97	93.1	87.4	91.8	8.2
750	94	88.7	87.5	91.4	8.6
900	91	90.4	93.1	90.0	10.0
1000	90	77.6	86.7	91.8	8.2
1100	81	52.3	89.5	91.7	8.3
1200	50	15.9	100	95.6	4.4
1300	α-Cristobalite	0	–	–	–

the intensity of 960 cm^{-1} does not decrease. This shows that titanium dioxide is removed as extra-framework titanium.

It can be assumed that there are two kinds of extra-framework titanium existing in the samples. One type improves the decomposition of H_2O_2; the other does not improve either the decomposition or the epoxidation, and the latter is thought to be a kind of inactive titanium species.

3.4. Thermal stability of TS-1 containing trace aluminum

Experimental results of thermal stability (table 4 and figure 7) show that the crystallinity decreases with increasing calcination temperatures. When the calcination temperature is above 1000 °C, the crystallinity of the TS-1 sample decreases drastically. When TS-1 is calcined at 1300 °C, the structure of TS-1 collapses and is converted into α-cristobalite. When the calcination temperature is above 900 °, the conversion of H_2O_2 decreases drastically.

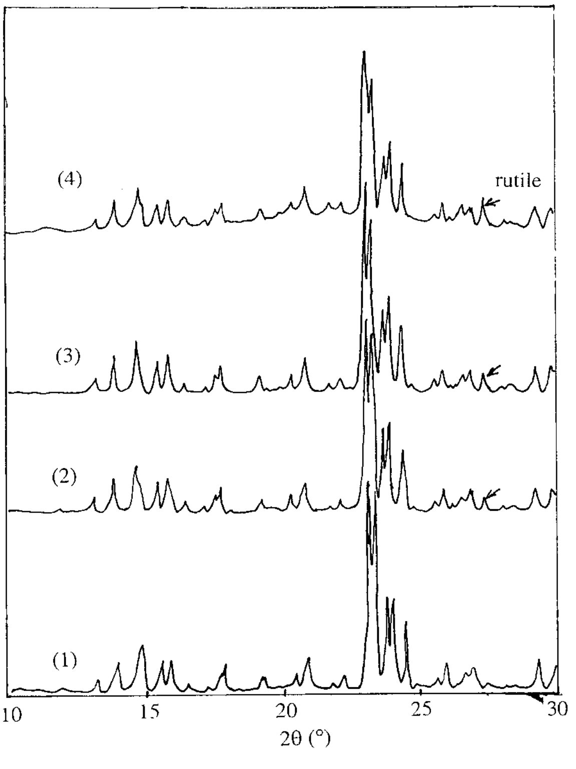

Figure 7. XRD spectra of TS-1-C molecular sieves after calcination at different temperatures: (1) 540 °C, (2) 1000 °C, (3) 1100 °C and (4) 1200 °C.

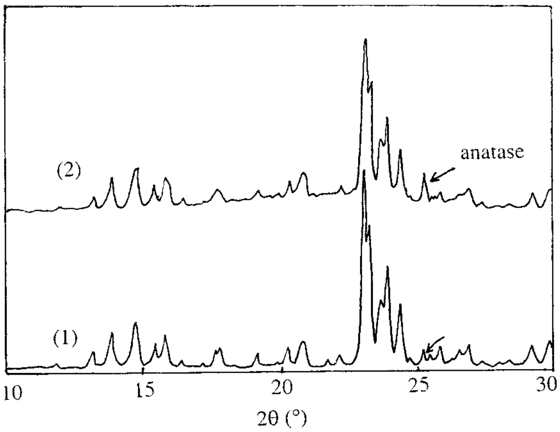

Figure 8. XRD spectra of TS-1-A molecular sieves after calcination at different temperatures: (1) 900 °C and (2) 1200 °C.

Although the TS-1 sample has about 90% crystallinity (TS-1 sample calcined at 1000 °C), the conversion of H_2O_2 decreases to 77.6%, and it is evident that there is inconsistency between the crystallinity and the catalytic properties of TS-1. Moreover, according to XRD spectra of TS-1 calcined at different temperatures, it can be seen that the extra-framework titanium is converted into rutile during calcination (figure 7). However, the TS-1 synthesized by using TPAOH as the template was calcined at high temperature, and the extra-framework Ti is still in the form of anatase (figure 8). The reason may be that trace aluminum existing in the TS-1 improves the formation of rutile.

4. Conclusions

Titanium silicalites (TS-1) containing trace aluminum were synthesized by using TPABr as the template. In the epoxidation of propylene with dilute H_2O_2, trace aluminum existing in the TS-1 framework makes the selectivity to PO decrease. Proper amounts of a basic substance can be used to increase the selectivity to PO. However, an extra amount of basic substance will make the conversion and the utilization of H_2O_2 decrease. Acid treatment can remove part of the extra-framework TiO_2, but cannot remove trace aluminum. Trace aluminum in TS-1 has little influence on the thermal stability of TS-1, but improves the formation of rutile.

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