

# Propylene epoxidation with hydrogen peroxide catalyzed by molecular sieves containing framework titanium

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## Abstract

The catalytic epoxidation of propylene with aqueous hydrogen peroxide over four Ti-containing silicates, namely titanium silicalite (TS-1), a  $\text{TiO}_2\text{-SiO}_2$  xerogel, Ti-MCM-41, and a  $\text{TiCl}_4$ -modified HZSM-5 zeolite has been investigated. It was found that only the crystalline molecular sieve TS-1 and the  $\text{TiCl}_4$  modified HZSM-5 zeolite were active, whereas the  $\text{TiO}_2\text{-SiO}_2$  xerogel and the mesoporous Ti-MCM-41 were almost inactive. The structure of these Ti-containing silica materials plays an important role in determining their catalytic performances. Shape-selectivity and the hydrophobic nature of the material are the two most important factors. In the presence of TS-1, propylene oxide was the predominant product, whereas propylene diol and its mono-methyl ethers were formed with a  $\text{TiCl}_4$  modified HZSM-5. It is suggested that the acidity of catalyst is a crucial factor in determining product selectivity. Propylene diol and the mono-methyl ethers are produced by further reactions of propylene oxide with  $\text{H}_2\text{O}$  and methanol. The oxirane ring opening reactions are catalyzed on acid sites. The  $\text{H}_2\text{O}_2$  turnover frequency based on the titanium content increased while the selectivity to propylene oxide decreased with an increase of the Si/Ti ratio in TS-1 catalyst. The influence of  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  ratio in the solvent as well as the reaction temperature on the title reaction and the regeneration of deactivated catalyst have also been investigated. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Propylene epoxidation; Hydrogen peroxide; Titanium silicalite-1 (TS-1)

## 1. Introduction

Propylene oxide is an important industrial intermediate which has traditionally been produced by the epoxidation of propylene with hydroperoxides or epichlorohydrin. In this process, environmentally hazardous chemicals such as chlorine or *t*-butylhydroperoxide are used as oxidants and various by-products are produced stoichiometrically [1,2]. Much recent effort has been devoted to search for more environmental

friendly processes. Yamanaka et al. [3] reported that propylene could be directly epoxidized by oxygen in solution containing  $\text{EuCl}_3$ , acetic acid, and zinc. A heterogeneously catalyzed process for the direct epoxidation of propylene with oxygen in the gas phase has also been reported [4–6]. Propylene oxide can also be produced by an electrocatalytic method [7] or by the microbial epoxidation of propylene [8,9]. These new routes are very interesting as they avoid the use of environmentally hazardous oxidants. Recently, titanium-containing redox materials are attracting much attention. Titanium ions incor-

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porated into certain silica matrices are active and selective catalysts for the epoxidation of various alkenes [10–14]. Especially, titanium silicalite-1 (TS-1) zeolite and variously modified TS-1 have been shown to be active for propylene epoxidation with  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  [15–18]. With methanol or a methanol/water mixture as the solvent, TS-1 catalyzed the epoxidation of propylene by  $\text{H}_2\text{O}_2$  with a high rate. The yield is quantitative with respect to  $\text{H}_2\text{O}_2$ , and the selectivity to propylene oxide is very high (> 96%) [15]. The use of  $\text{H}_2\text{O}_2$  as oxidizing agent is attractive to the chemical industry because it leaves no side products besides of water. Therefore, this process has potential industrial application and deserves more studies.

Here, we report new investigations of the ability of titanium ions incorporated into silica samples with different structures (TS-1,  $\text{TiO}_2$ - $\text{SiO}_2$  xerogel, Ti-MCM-41 and a titanium modified HZSM-5 zeolite) to catalyze the propylene epoxidation using  $\text{H}_2\text{O}_2$  as oxidant. The differences of these samples in the activity and selectivity have been correlated with their structures. The effect of the Si/Ti ratio in TS-1 zeolite, the role of acidic sites as well as the influence of the reaction conditions have been studied in detail.

## 2. Experimental

### 2.1. Preparation of catalysts

#### 2.1.1. TS-1 zeolites

TS-1 zeolites with Si/Ti molar ratios from 24 to 70 were synthesized according to Taramasso et al. [19]. Tetrapropylammonium hydroxide (TPAOH) was prepared from tetrapropylammonium bromide (TPABr) by batchwise exchange with a Duolite A113 resin (BDH). The concentration of the aqueous TPAOH solution was about 20 wt.%. In all preparations, a  $\text{TPA}^+/\text{SiO}_2$  ratio of 0.46 and a  $\text{H}_2\text{O}/\text{SiO}_2$  ratio of 35 were employed. In a typical preparation, 19.2 g of tetraorthosilicate

Table 1  
Si/Ti molar ratio in the synthesis mixture and the final solid product

Sample	Si/Ti in synthesis mixture	Si/Ti in final product
TS-1 (1)	24	16.9
TS-1 (2)	41	35.6
TS-1 (3)	62	54.5
TS-1 (4)	70	65.3

(TEOS, Merck) were mixed with 0.54 g of tetrapropylorthotitanate (TPOT, Merck) at 0°C and stirred for half an hour. Then 30 ml of aqueous TPAOH solution was slowly added while stirring continued for another half an hour. It was then heated to 60°C and held at this temperature for 2 h to hydrolyze the silicate and titanate. The obtained clear gel was then transferred to a Teflon-lined stainless-steel autoclave and heated in an oven at 175°C under autogeneous pressure for 2 days. After cooling the autoclave to room temperature, the resulting mixture was filtered, washed with plenty of deionized water, dried at 120°C overnight and finally calcined at 540°C for 6 h. The Si/Ti molar ratios in the synthesis mixtures and those in the final products are given in Table 1.

#### 2.1.2. $\text{TiO}_2$ - $\text{SiO}_2$ xerogel

A total of 0.54 g of TPOT in 5 ml of 2-propanol was mixed with 9.6 g of TEOS in 10 ml ethanol and stirred at 40°C for 6 h. The solution was then heated at 60°C for 4 h. About 15 ml deionized  $\text{H}_2\text{O}$  was added during this time to compensate for the evaporation loss. At last, the gel mixture was dried at 110°C for 24 h and calcined at 540°C for 6 h. The Si/Ti molar ratio in this mixture was 24.2.

#### 2.1.3. Ti-MCM-41 mesoporous material

A total of 14.4 g of TEOS was mixed with 0.27 g of TPOT at 0°C and stirred for half an hour. Then the templating agent, 62 ml of 25 wt.% aqueous solution of cetyltrimethylammonium hydroxide, was added dropwise while stirring continued. The mixture was heated to 80°C and kept at this temperature for 1 h. It was then

transferred into a Teflon-lined stainless steel autoclave and heated at 100°C for 2 days under autogenous pressure. After it had cooled down to room temperature, the resulting mixture was filtered, washed with plenty of deionized water, dried at 120°C overnight and finally calcined at 540°C for 6 h. The heating rate in the calcination step was 1°C/min. The Si/Ti molar ratio in the final product was 68.3.

#### 2.1.4. $TiCl_4$ modified HZSM-5 zeolite

A  $TiCl_4$ -modified HZSM-5 zeolite sample was prepared according to Refs. [20,21]. Commercial HZSM-5 ( $SiO_2/Al_2O_3$  ratio 50, PQ) was dealuminated by treating it with aqueous 1 M HCl solution at 60°C for four times. By this treatment, the  $SiO_2/Al_2O_3$  ratio increased to 240. The partially dealuminated HZSM-5 (0.5 g) was heated at 450°C for 10 h in a tubular reactor under a flow of  $N_2$  (flow rate 30 ml/min). The flushing gas was then switched to  $N_2$  which had been saturated with  $TiCl_4$  at room temperature. The gas mixture was kept flowing for 2 h. Finally, the sample was heated in a flow of oxygen at 500°C for 4 h. The final titanium content in this sample was 0.91 wt.% (corresponding to a Si/Ti of 86) as determined by ICP.

## 2.2. Characterization of catalysts

IR spectra using the KBr pellet technique were recorded on a Bio-Rad FTS 165 FT-IR spectrometer with a resolution of  $4\text{ cm}^{-1}$ . The UV absorption of solid samples was measured using a Shimadzu UV-240 spectrometer. A Philips PW 1729 X-ray diffractometer was used to analyze the XRD pattern. Water sorption capacity of the solid sample was measured with a Dupont 9900 DTA-TG instrument. Prior to DTA-TG measurements, the samples were immersed into distilled water for 4 h. They were then filtered off and dried at ambient temperature for 2 days.

Temperature-programmed desorption (TPD) of ammonia and the decomposition of titanium-

peroxide were performed using a quadrupole mass spectrometer (HIDEN) connected to a computer for data acquisition. For ammonia desorption studies, the sample was heated in a flow of helium at 450°C for 2 h. After cooling to room temperature, a mixture of helium and ammonia (2:1) gas was passed through the solid sample for 30 min for ammonia adsorption. The flushing gas was then switched to pure helium and the TPD was carried out after the physisorbed ammonia was completely purged off. The heating rate in the desorption process was 8°C/min. The signal at 17 amu was used to trace ammonia desorption. For titanium-peroxide decomposition studies, the titanium-containing sample was first treated with  $H_2O_2$  aqueous solution (35 wt.%). The white powder became light yellow, indicating the formation of a titanium-peroxide [13]. The solid was recovered by filtration, followed by evacuation using a mechanical pump to remove adsorbed water in the sample. The dried solid remained yellow. This implied that the peroxide species was still present. The titanium-peroxide was decomposed at a heating rate of 8°C/min under a He flow. The signal at  $m/e$  32 was used to monitor the formation of oxygen during the heating process.

## 2.3. Epoxidation of propylene

A total of 0.2 g of catalyst was added to 20 ml of methanol in a three-neck flask equipped with gas inlet and outlet tubes and a septum port for sample withdrawal. Propylene was bubbled through the suspension which was stirred at room temperature. A saturated propylene solution, containing about 1.5 wt.% of propylene, was obtained after about 2 h. The epoxidation reaction was started by injecting 2 ml of 35 wt.%  $H_2O_2$  aqueous solution into the reaction mixture. Samples were removed from the reaction mixture at 10, 30, 60 and 120 min and analyzed by GC (Porapark Q; FID detector). The various reaction products were identified by GC/MS. The consumption of  $H_2O_2$  was monitored by volumetric titration with 0.1 N

$\text{Na}_2\text{S}_2\text{O}_3$  as described in Ref. [22]. The selectivity of  $\text{H}_2\text{O}_2$  to propylene oxide was 100% in all cases except where indicated otherwise. Therefore, throughout this study, the turnover frequency (TOF) of  $\text{H}_2\text{O}_2$  is used to represent the reaction rate. This turnover frequency which in most of the cases is equal to that of propylene, is defined as number of moles of  $\text{H}_2\text{O}_2$  converted per mole of titanium in the catalyst per minute.

### 3. Results and discussion

#### 3.1. Influence of catalyst structure on the epoxidation of propylene with $\text{H}_2\text{O}_2$

The structures of various silica samples with incorporated titanium, TS-1,  $\text{TiO}_2\text{-SiO}_2$  xerogel and Ti-MCM-41 have been characterized by XRD, framework IR, UV absorption as well as BET surface area and pore size distribution measurements. The XRD pattern confirms that TS-1 possessed the MFI structure similar to ZSM-5 zeolite, whereas the  $\text{TiO}_2\text{-SiO}_2$  xerogel

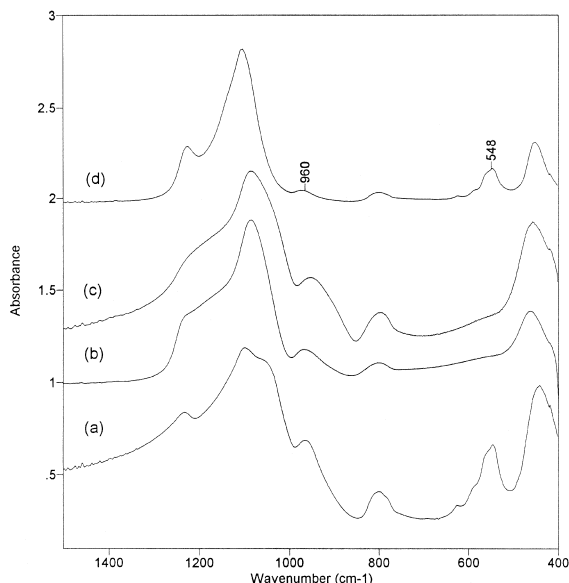


Fig. 1. FT-IR spectra of (a) TS-1 (sample 3), (b) Ti-MCM-41, (c)  $\text{TiO}_2\text{-SiO}_2$  xerogel and (d) Ti/HZSM-5.

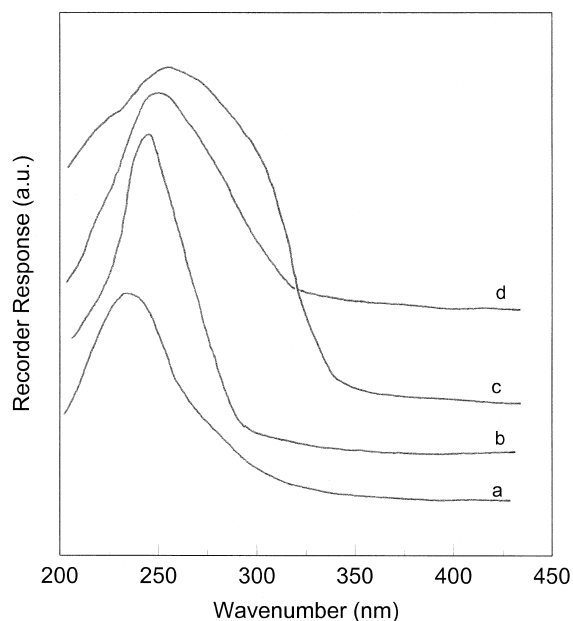


Fig. 2. UV absorption spectra of (a) TS-1 (sample 3), (b) Ti-MCM-41, (c)  $\text{TiO}_2\text{-SiO}_2$  xerogel and (d) Ti/HZSM-5.

was amorphous. A pronounced step in the  $\text{N}_2$  adsorption isotherm indicates that the Ti-MCM-41 sample was mesoporous with a narrow pore diameter distribution at about 31 Å. From the  $t$ -plot analysis of the  $\text{N}_2$  adsorption isotherms, a pore diameter of about 5.5 Å was determined for TS-1, while that of the  $\text{TiO}_2\text{-SiO}_2$  xerogel was about 4.1 Å (Table 1). The IR spectra (Fig. 1) show a peak at  $960\text{ cm}^{-1}$  for all samples. This absorption has generally been assigned to the O-Si stretching vibration associated with the incorporation of titanium species into silica lattice [23]. The appearance of the IR peak at  $960\text{ cm}^{-1}$  as well as the absence of a separated  $\text{TiO}_2$  phase in the XRD pattern indicate that the titanium was well-dispersed in the silica lattice for all samples.

Fig. 2 gives the UV absorption spectra of the samples. The spectra of TS-1 and Ti-MCM-41 consist of a single relatively narrow absorption band at about 236 and 245 nm, respectively. The  $\text{TiO}_2\text{-SiO}_2$  xerogel shows a much broader band in the range of 230–340 nm. The appearance of the band below 230 nm and the absence

of any absorption above 330 nm for TS-1 and Ti-MCM-41 indicates that the titanium in these two samples is in tetrahedral coordination in the framework [24–30]. The broad band with an absorption edge above 300 nm for the TiO<sub>2</sub>–SiO<sub>2</sub> xerogel implies that the titanium environment in this sample was different from that in TS-1 and Ti-MCM-41. Possibly the titanium species were not uniformly dispersed, and some octahedral titanium species might be present.

TS-1 showed the highest activity for propylene epoxidation with H<sub>2</sub>O<sub>2</sub> whereas both the mesoporous Ti-MCM-41 and the TiO<sub>2</sub>–SiO<sub>2</sub> xerogel were almost inactive (Table 2). One possible explanation for this difference can be made based upon the differences of their pore structures. The TiO<sub>2</sub>–SiO<sub>2</sub> xerogel does not possess uniform channels, and the majority of its pores is too small for the epoxidation reaction to take place in the pores. Therefore, only surface titanium sites are accessible to both reactants at the same time. The average pore diameter of TS-1 is about 5.5 Å, and that of Ti-MCM-41 is about 31 Å. The sizes of the reactant and reaction intermediate are close to the pore size of TS-1. Furthermore, TS-1 has intersecting uniform channels which facilitate the access of the reactants to the active sites. The propylene epoxidation reaction is greatly affected by this special pore structure. The relatively long residence time inside the intersecting channels enhances the opportunity for propylene to interact with the active Ti–OOH species. This is why TS-1 shows shape-selectivity. The low activity of the mesoporous Ti-MCM-41 was unexpected. However, it had already been re-

ported that mesoporous materials showed lower activity toward reactions involving only small molecules as compared to TS-1 [31–33]. The pores of Ti-MCM-41 are probably too big to show any shape effect. For reactions involving only small molecules, the environment inside a pore will not be much different from that at the surface.

Clerici et al. [15] attributed the high activity of TS-1 to its hydrophobic properties. That is, TS-1 preferentially adsorbs the less polar molecules H<sub>2</sub>O<sub>2</sub> and propylene, and rejects water and methanol from its pore space. It has been reported that the hydrophobic characteristics of zeolite can be evaluated by measurements of water sorption [34]. Samples which hardly adsorb water when immersed in water are hydrophobic. It can be seen from the thermal analysis (Fig. 3) that TS-1 retains the smallest amount of water while Ti-MCM-41 and TiO<sub>2</sub>–SiO<sub>2</sub> xerogel absorb a large amount of water and retain it to a higher temperature. If the active titanium ion is surrounded by adsorbed water molecules, the access of reactant molecules to the titanium species will be inhibited, resulting in a poor catalytic activity. TS-1 is strongly hydrophobic. Therefore, the active sites in TS-1 cannot be blocked by water molecules, but are readily accessible to the less polar reactants. It is thus concluded that the hydrophobic property is important to this reaction.

The intensity of the 960 cm<sup>-1</sup> IR band after treating with aqueous H<sub>2</sub>O<sub>2</sub> solution contains information on the interaction between hydrogen peroxide and the Ti-site. For TS-1, the

Table 2  
Properties of various Ti-containing catalysts for the epoxidation of propylene with H<sub>2</sub>O<sub>2</sub>

Sample	Si/Ti ratio	BET surface area (m <sup>2</sup> /g)	Pore diameter (Å)	TOF <sup>a</sup> of H <sub>2</sub> O <sub>2</sub> (mol/mol Ti min)
TiO <sub>2</sub> –SiO <sub>2</sub> xerogel	24.2	236	4.1	0.01
TS-1 (3)	54.5	348	5.5	4.91
Ti-MCM-41	68.3	1218	31	0.01

<sup>a</sup>Reaction conditions: 0.2 g catalyst, 20 ml methanol containing 1.5 wt.% propylene, room temperature, 2 ml 35 wt.% H<sub>2</sub>O<sub>2</sub> aqueous solution.

Data were obtained after reaction for 1 h.

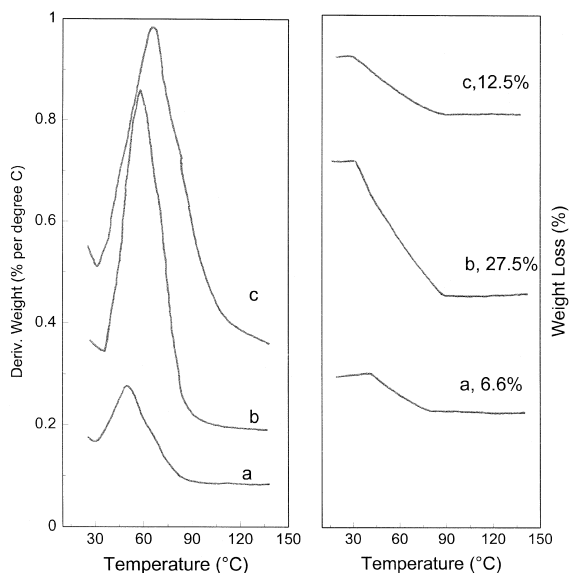


Fig. 3. DTA (right) and TG (left) spectra of water-treated (a) TS-1 (sample 3), (b) Ti-MCM-41 and (c) TiO<sub>2</sub>-SiO<sub>2</sub> xerogel.

intensity of the 960 cm<sup>-1</sup> peak was much affected by interaction with H<sub>2</sub>O<sub>2</sub> (Fig. 4), whereas there was no significant change for Ti-MCM-41 and TiO<sub>2</sub>-SiO<sub>2</sub> xerogel (not shown). A color change from white to light yellow for all three samples during treatment with aqueous H<sub>2</sub>O<sub>2</sub> solution is an indication for the formation of the titanium peroxide species. However, the fact that only for TS-1, the 960 cm<sup>-1</sup> peak was significantly attenuated implies that the titanium species in TS-1 interacted much stronger with H<sub>2</sub>O<sub>2</sub> than it did in the other samples. The UV spectrum of TS-1 also changed significantly when treated with aqueous H<sub>2</sub>O<sub>2</sub>. The ligand-to-metal charge transfer band shifted from 236 nm to 250 nm, which is similar to the influence of water [25,26,30]. In addition, a new band with an absorption edge above 300 nm, indicating the formation of titanium peroxide, appeared [35]. Therefore, the nature of the titanium peroxide species in TS-1 seems to be different from that formed in the other materials. To obtain more information, temperature-programmed decomposition (TPDE) was applied, and the evolution of di-oxygen from the decomposition of titanium peroxide was moni-

tored as a function of temperature. The TPDE spectra are shown in Fig. 5. The fact that oxygen was released from all the samples substantiates the existence of a titanium peroxide species in all three titanium-containing materials. However, differences were observed with respect to the size of the oxygen signal and the stability of the peroxide. For Ti-MCM-41, only one very weak oxygen signal peak was recorded at about 140°C. The titanium peroxide species in this material is obviously unstable and may have decomposed partially during the drying process. Oxygen evolved from the titanium peroxide species which formed with the TiO<sub>2</sub>-SiO<sub>2</sub> xerogel in a very broad peak with maximum at 130°C and a shoulder in the range of 150–300°C. This is an indication of the heterogeneity of the titanium species in this non-crystalline material. TS-1 gave only one sharp peak at about 130°C. This indicates that only one type of titanium peroxide species was formed throughout this sample. This species seems to be responsible for the high activity of TS-1 toward propylene epoxidation.

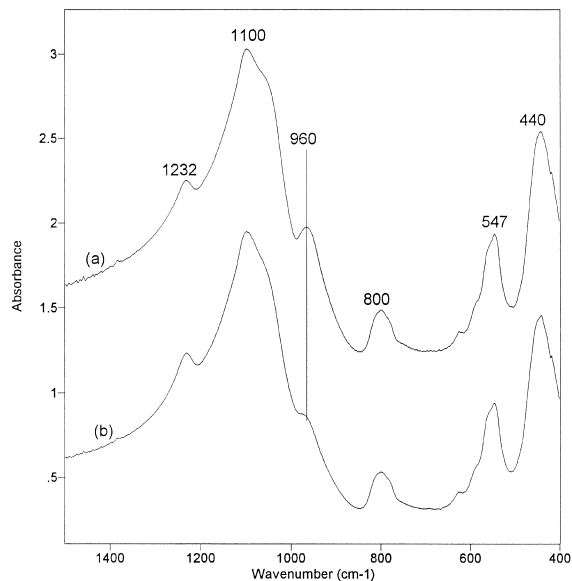


Fig. 4. Effect of H<sub>2</sub>O<sub>2</sub> treatment on the IR spectrum of TS-1(3) zeolite. (a) Fresh TS-1 (sample 3) and (b) H<sub>2</sub>O<sub>2</sub> treated TS-1 (sample 3).

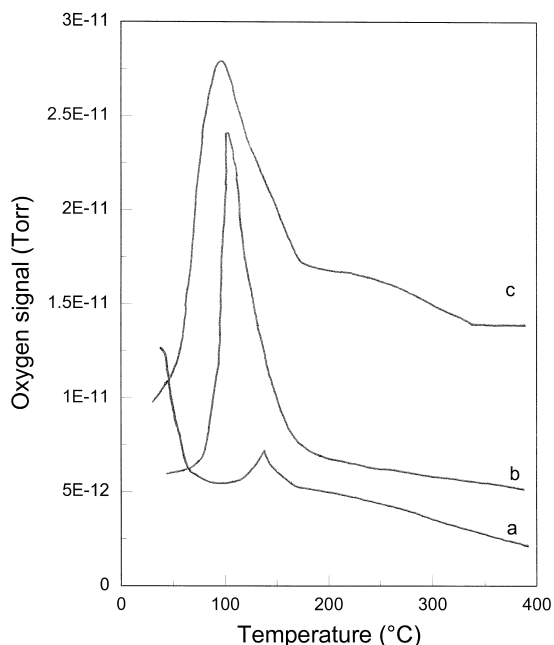


Fig. 5. Temperature-programmed decomposition spectra of titanium-peroxide species formed from the interaction of (a) Ti-MCM-41, (b) TS-1 (sample 3) and (c)  $\text{TiO}_2$ - $\text{SiO}_2$  xerogel with  $\text{H}_2\text{O}_2$ .

### 3.2. Effect of Si/Ti ratio in TS-1 zeolite

Neither pure  $\text{TiO}_2$  nor  $\text{SiO}_2$  shows any activity toward propylene epoxidation with  $\text{H}_2\text{O}_2$ . It has been reported that extra-framework Ti species appear in TS-1 samples when the titanium content reaches 1.5 ~ 2.0 wt.% [36]. Therefore, it is important to ensure that all the titanium is incorporated into the framework and that no separate  $\text{TiO}_2$  phase forms. In this work, a TS-1 sample with a Si/Ti ratio of 35.6 (~ 2.2 wt.% Ti) was successfully synthesized without the presence of  $\text{TiO}_2$  particles as shown by UV absorption and XRD measurements. However, when the titanium content was further increased, a segregated  $\text{TiO}_2$  phase did indeed appear [35].

Fig. 6 shows the influence of the Si/Ti ratio in TS-1 on propylene epoxidation. The  $\text{H}_2\text{O}_2$  turnover frequency based on the total number of titanium in TS-1 decreased slowly with the decrease of Si/Ti ratio in the range of 36–65,

then sharper when Si/Ti was lower than 36. The selectivity for propylene oxide decreased with increasing Si/Ti ratio. Significant amounts of propylene diol and its mono-methyl ethers were produced at a high Si/Ti ratio. The near-edge structure of the X-ray absorption (XANES) had been measured for TS-1 samples with different Si/Ti ratios [37]. These measurements showed that the number of tetrahedral titanium sites increases with increasing Si/Ti ratio. A recent theoretical calculation in support of experimental results obtained with model compounds showed that alkenes preferentially attack the oxygen closest to titanium in  $\text{HOO-Ti}(\text{OSiH}_3)_3(\text{MeOH})$  and  $\text{HOO-TiL}_3(\text{MeOH})$  in TS-1 [38]. It thus can be concluded that the tetrahedrally coordinated titanium species in the framework is the active center for the epoxidation reaction. The decrease of the turnover frequency at higher Ti substitution is possibly the result of the presence of a non-framework titanium species. This titanium species cannot form

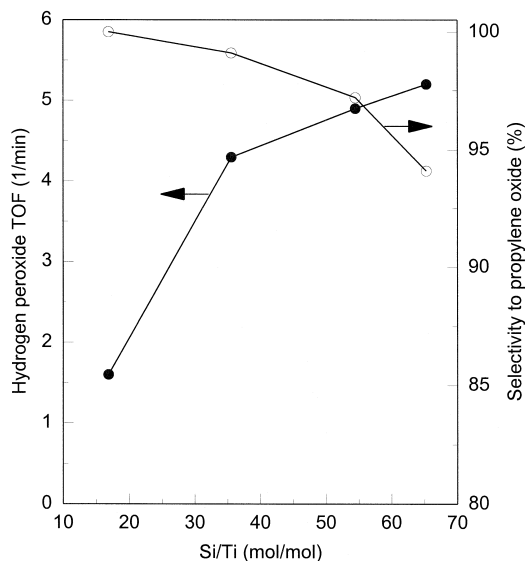


Fig. 6. Effect of Si/Ti ratio in TS-1 on propylene epoxidation. Reaction conditions: 0.2 g catalyst, 20 ml methanol, 2 ml 35 wt.%  $\text{H}_2\text{O}_2$  aqueous solution, room temperature; batch reactor, 1 h reaction time (●) TOF of  $\text{H}_2\text{O}_2$ , (○) selectivity for propylene oxide. The by-products were propylene glycol and its mono-methyl ethers.

the active peroxo-titanium species needed for epoxidation [39]. Therefore, the TOF based on the total titanium in TS-1 decreased with the increase of titanium content, especially when the Si/Ti ratio was lower than 36. The slight decrease of TOF with a decrease of the Si/Ti ratio from 65 to 36 is possibly caused by a lower dispersion of the titanium in the lattice at a higher titanium content, although it was observed that all the titanium species were in the tetrahedral form. It is known from IR studies that the amount of OH groups in TS-1 increases with an increase of the Si/Ti ratio [27]. The increase in OH-groups or Lewis acid sites of the TS-1 catalyst is probably responsible for the drop of epoxide selectivity with increasing of Si/Ti ratio [28,29]. Propylene glycol and its mono-methyl ethers are the products of further reactions of propylene oxide with H<sub>2</sub>O and methanol; the solvolysis of propylene epoxide is catalyzed by the acidic sites of the catalyst. This conclusion will be further substantiated later in this study. It can be seen that the optimal Si/Ti ratio in TS-1 zeolite for propylene epoxidation will be in the range of 36 to 55. A further increase of the Si/Ti ratio can increase the TOF, but it lowers the selectivity for propylene epoxide as well as the overall reaction turnover number based on catalyst weight.

### 3.3. Conversion of propylene in the presence of a TiCl<sub>4</sub> modified HZSM-5 zeolite

The dependence of the selectivity on Si/Ti ratio has been explained with the acidic property of the TS-1 catalyst. A catalyst with more acidic sites shows poorer selectivity to propylene oxide. In order to further demonstrate the role of surface acidity in propylene epoxidation, a more acidic catalyst was prepared from a partially dealuminated HZSM-5. Titanium was incorporated from the gas phase using TiCl<sub>4</sub> as precursor. The IR peak at 960 cm<sup>-1</sup> and the narrow UV band at 255 nm indicate that the titanium had been incorporated into the HZSM-5 zeolite framework (Figs. 1 and 2).

Fig. 7 compares NH<sub>3</sub>-TPD spectra obtained with the dealuminated HZSM-5, Ti/HZSM-5 and TS-1 zeolite. The TS-1 zeolite shows only one desorption peak at 120°C which can be ascribed to the desorption of weakly adsorbed NH<sub>3</sub>. This means that only one kind of weak acidic sites, possibly silanol groups, is present in TS-1. For both the dealuminated HZSM-5 and Ti/HZSM-5, another peak appears in the range of 300–400°C in addition to the low temperature peak at 120°C. This desorption peak at high temperature indicates the presence of strong acidic sites in these samples.

The catalytic performance of this more acidic Ti/HZSM-5 sample is shown in Fig. 8. The initial H<sub>2</sub>O<sub>2</sub> conversion, expressed as turnover frequency, was comparable to that of TS-1. However, the activity dropped very fast and the product distribution was quite different from that of TS-1. It is possible that only part of the titanium was incorporated into the HZSM-5 framework. The remaining titanium species exists inside the pores as extra-framework species.

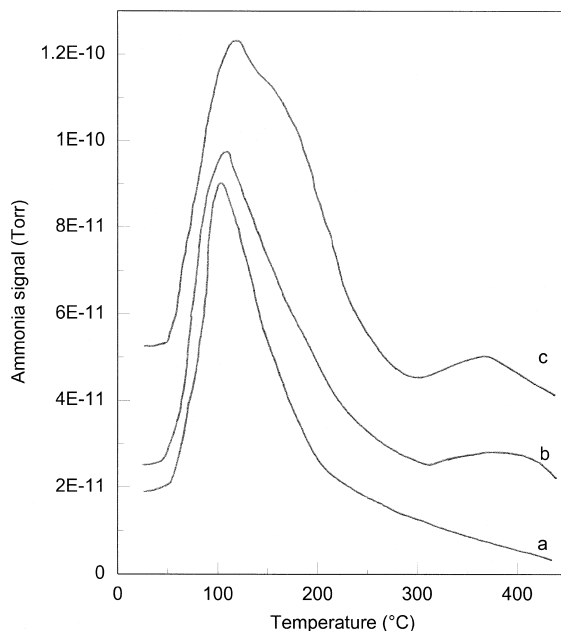


Fig. 7. NH<sub>3</sub>-TPD spectra from (a) TS-1 (sample 3), (b) Ti/HZSM-5 and (c) dealuminated HZSM-5.



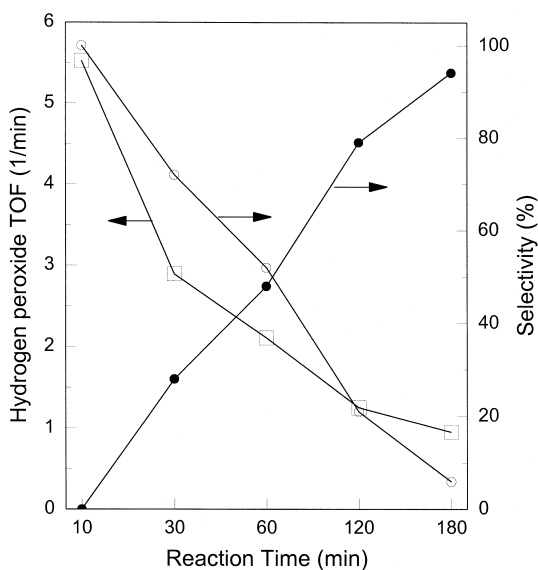


Fig. 8. Catalytic performance of a Ti-modified HZSM-5 catalyst for propylene epoxidation as a function of reaction time. (□) TOF of H<sub>2</sub>O<sub>2</sub>, (○) selectivity to propylene epoxide, (●) selectivity to propylene glycol and its mono-methyl ethers. Reaction conditions were the same as those in Fig. 6.

This assumption is supported by the evidence that the 960 cm<sup>-1</sup> peak in the IR spectrum was very weak (Fig. 1). The residual aluminum species in the sample may also be responsible for the difference in the reaction pathway. This aluminum makes this sample more hydrophilic and more acidic than TS-1. As a result, the reaction rate is lower, and the product distribution quite different [40,41]. At the beginning of the reaction with Ti/HZSM-5, only propylene oxide is produced. However, with increasing reaction time, the selectivity for propylene oxide decreases while the selectivity for propylene diol and its mono-methyl ethers increases. Finally, only propylene diol and its mono-methyl

ethers are found, and propylene oxide has completely disappeared. Propylene oxide obviously undergoes further solvolysis reactions which are catalyzed by acidic sites. It has indeed been reported that the selectivity towards propylene oxide can be enhanced by treatment of TS-1 catalyst with a base [15,42].

### 3.4. Influence of reaction conditions on propylene epoxidation with TS-1 catalyst

#### 3.4.1. Influence of reaction temperature

Reaction temperature plays an important role in the catalytic performance. Table 3 summarizes the results on propylene epoxidation at different reaction temperatures. It was observed that upon increasing the temperature, the reaction rate was slightly accelerated. However, the selectivity to propylene oxide decreased. Furthermore, decomposition of H<sub>2</sub>O<sub>2</sub> was observed when the temperature was above 40°C. The low apparent activation energy of 15 kJ mol<sup>-1</sup> indicates that the reaction rate is limited by pore diffusion. The decrease of propylene oxide selectivity is the result of the accelerated solvolysis of the epoxide at higher temperature.

#### 3.4.2. Influence of CH<sub>3</sub>OH / H<sub>2</sub>O ratio

It has been proven that methanol is the best solvent and water inhibits the reaction [15,42]. However, the presence of water cannot be avoided in this reaction. It comes from the oxidant aqueous H<sub>2</sub>O<sub>2</sub> solution and the by-product of H<sub>2</sub>O<sub>2</sub>. It can be seen that the CH<sub>3</sub>OH/H<sub>2</sub>O volume ratio (we did not con-

Table 3

Influence of reaction temperature on propylene epoxidation with H<sub>2</sub>O<sub>2</sub> catalyzed by TS-1 (sample 3)<sup>a</sup>

T (°C)	TOF of H <sub>2</sub> O <sub>2</sub> (min <sup>-1</sup> )	Selectivity to epoxide (%)	Selectivity to diol and ethers (%)	H <sub>2</sub> O <sub>2</sub> selectivity (%)
0	2.6	100	0	100
25	4.9	97.7	2.3	100
40	6.2	95.1	4.9	92

<sup>a</sup>Except for temperature, the reaction conditions were as in Table 2. TOF and selectivity determined after 1 h of reaction.

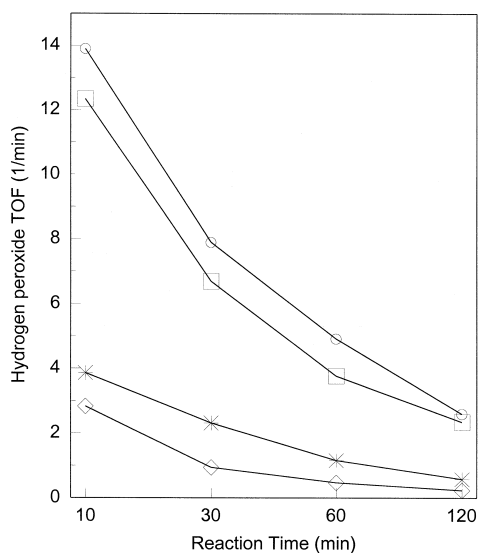


Fig. 9. Influence of the water content in the solvent on the reaction rate as a function of reaction time. CH<sub>3</sub>OH/H<sub>2</sub>O ratio: (O) 20/0, (□) 10/10, (S) 2/18, (\*) 0/20. Other reaction conditions were the same as those in Fig. 6.

sider the water produced from the reaction of H<sub>2</sub>O<sub>2</sub>) exerted a significant influence on this reaction (Fig. 9). The highest reaction rate was obtained when using pure methanol as solvent. Generally, the smaller the amount of H<sub>2</sub>O in the solvent, the higher was the reaction rate. It is interesting that a high reaction rate could still be achieved even with a solvent containing 50% of water. This means that this reaction can be carried out with a dilute H<sub>2</sub>O<sub>2</sub> aqueous solution. However, with the further increase of H<sub>2</sub>O content in the solvent, the reaction rate decreased significantly, and the reaction hardly proceeded in pure water. The low reaction rate may simply be the consequence of the low solubility of propylene in water. It is interesting that the CH<sub>3</sub>OH/H<sub>2</sub>O ratio did not show much influence on the product selectivity. It seems that the product selectivity is mainly dependent on the catalyst acidity and reaction temperature.

### 3.5. Regeneration of deactivated TS-1 catalyst

Although the dissolved propylene can be completely converted in the presence of an ex-

cess amount of H<sub>2</sub>O<sub>2</sub> in a batch reactor, its limited solubility makes it more desirable to work with a continuous flow of propylene. Unfortunately, we observed that in most of the cases, the reaction ceased within 2 h of reaction irrespective of the amount of the H<sub>2</sub>O<sub>2</sub> the reaction mixture. In order to find out whether the deactivation was permanent or reversible, a number of experiments were carried out where the used catalyst was re-evaluated after different treatments. Some results are shown in Fig. 10.

With an excess amount of H<sub>2</sub>O<sub>2</sub> in the reaction mixture, an initial amount of propylene was completely converted. Propylene was then bubbled through the solution again in order to make use of the remaining H<sub>2</sub>O<sub>2</sub>. However, no significant increase in H<sub>2</sub>O<sub>2</sub> conversion was observed. In order to investigate whether this was caused by the inhibiting effect of the product, the reaction mixture was centrifuged when the reaction ceased, and the catalyst was separated from the liquid. The collected catalyst was put

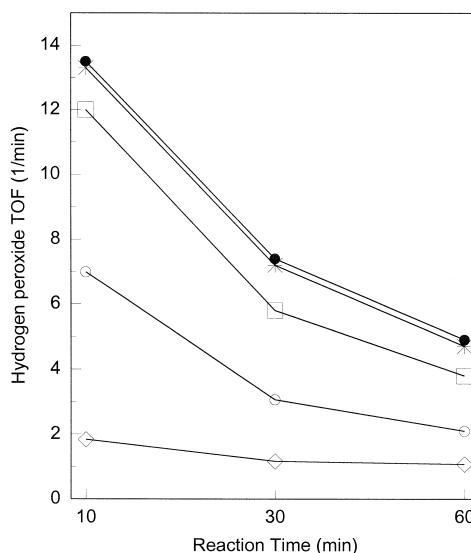


Fig. 10. Effect of treatments of the deactivated TS-1 zeolites on propylene epoxidation. (●) Fresh, (\*) calcined at 500°C after 1 cycle of reaction, (□) five times re-calcined at 500°C after five cycles of reaction, (O) dried at 110°C after one cycle of reaction, (◇) washed with methanol after one cycle of reaction. Reaction conditions as in Fig. 6.

into a fresh reaction mixture. Still, the conversion of propylene was negligible. It was obvious that the catalyst was deactivated. When the used catalyst was washed with pure methanol at room temperature and used again, it remained inactive. Drying the deactivated catalyst at 110°C for 2 h restored the activity partially, but it remained lower than that of the fresh catalyst. Heating at 110°C can only remove the contaminating organic compounds which are weakly adsorbed on the catalyst surface or in the pores. More strongly held molecules, possibly the propylene oxide oligomers, can only be removed by high temperature calcination or refluxing with dilute hydrogen peroxide [42].

In fact, the catalytic activity was restored by calcination of the deactivated catalyst at 500°C for 5 h. Even after five recycles of operation and regeneration, the catalyst was still very active. However, a slight decrease of TOF was observed. Subsequent analysis of the titanium content showed a loss of about 10% of titanium in TS-1 (3) after five recycles of reaction and regeneration. This titanium loss can account for the decrease of catalytic activity of TS-1. The TOF calculated on the basis of the remaining titanium was almost the same as that of the fresh catalyst. It seems that polar molecules like  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{OH}$ , promote titanium leaching by interacting with the framework tetrahedral titanium species to form the octahedral coordinated titanium peroxide species [39] which is active for propylene epoxidation. There is a possibility that this titanium species breaks away from the bulk and moves into the solution, and thus causes the leaching of titanium. Indeed, IR study showed that there was a minor decrease of the intensity of the  $960\text{ cm}^{-1}$  IR peak in the regenerated catalyst as compared to the fresh one after normalization the peak at  $800\text{ cm}^{-1}$ . This strongly supports the conclusion that titanium leaches from TS-1 framework during reaction. Nevertheless, the structure of TS-1 did not change as evidenced by the UV absorption and XRD spectra, which were almost identical to those of the fresh sample.

#### 4. Conclusions

The structure of Ti-containing silica material is a crucial factor in determining its catalytic performance toward propylene epoxidation with aqueous  $\text{H}_2\text{O}_2$ . The shape selectivity as well as the hydrophobic interaction are the most important factors. Only materials with intersecting channels (MFI structure) and a pore diameter of about 6 Å such as TS-1 and the Ti-modified ZSM-5 are active whereas  $\text{TiO}_2\text{-SiO}_2$  xerogel and mesoporous Ti-MCM-41 are almost inactive for this reaction. The low activity of the  $\text{TiO}_2\text{-SiO}_2$  xerogel and Ti-MCM-41 is possibly due to their pore sizes and hydrophilic properties. The activity of TS-1 catalysts depends on the number of framework tetrahedral titanium species while the selectivity to propylene oxide is largely affected by the catalyst acidity. The  $\text{H}_2\text{O}_2$  turnover frequency, based on the titanium in the catalyst, decreased slightly when the Si/Ti ratio in TS-1 was above 36. However, a significant drop was observed when it was below 36. The selectivity to propylene oxide decreased with the increase of Si/Ti ratio. The by-products of this reaction, propylene glycol and its mono-methyl ethers, are produced from the solvolysis of propylene epoxide, which is catalyzed by the acidic sites of catalyst. Increasing the reaction temperature will enhance the reaction rate but will sacrifice the selectivity for propylene oxide. The catalyst is deactivated by the deposition of propylene oxide oligomers inside the zeolite pores. The deactivated catalyst can be regenerated by calcination in air at 500°C. Titanium leaching was observed when the catalyst was repeatedly used.

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## References

- [1] R.A. Sheldon, *J. Mol. Catal.* 7 (1980) 107.
- [2] G. Strukul, *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Kluwer Academic Publishers, Dordrecht, 1992.
- [3] I. Yamanaka, K. Nakagaki, K. Otsuka, *J. Chem. Soc., Chem. Commun.* (1995) 185.
- [4] H. Yoshida, T. Tanaka, M. Yamamoto, T. Funabiki, S. Yoshida, *J. Chem. Soc., Chem. Commun.* (1996) 2125.
- [5] F. Blatter, H. Sun, H. Frei, *Catal. Lett.* 35 (1995) 1.
- [6] T. Tanaka, M. Ooe, T. Funabiki, S. Yoshida, *J. Chem. Soc., Faraday Trans. 1* 82 (1986) 35.
- [7] K. Otsuka, T. Ushiyama, I. Yamanaka, K. Ebitani, *J. Catal.* 157 (1995) 450.
- [8] G.A. Kovalenko, V.D. Sokolovskii, *Biotechnol. Bioeng.* 39 (1992) 522.
- [9] C.T. How, *Appl. Microbiol. Biotechnol.* 19 (1980) 1.
- [10] B. Notari, *Stud. Surf. Sci. Catal.* 37 (1988) 413.
- [11] B. Notari, *Stud. Surf. Sci. Catal.* 60 (1990) 343.
- [12] B. Notari, *Stud. Surf. Sci. Catal.* 67 (1991) 243.
- [13] D.R.C. Huybrechts, L.D. Bruycker, P.A. Jacobs, *Nature* 345 (1990) 240.
- [14] M.G. Clerici, P. Ingallina, *J. Catal.* 140 (1993) 71.
- [15] M.G. Clerici, G. Bellussi, U. Romano, *J. Catal.* 129 (1991) 159.
- [16] R.L. Burwell, *Chemtracts-Inorg. Chem.* 3 (1991) 344.
- [17] L.Y. Nemeth, T.P. Malloy, R.R. Jones, US Patent 5354875, 1994.
- [18] P. Ingallina, M.G. Clerici, L. Rossi, G. Bellussi, *Stud. Surf. Sci. Catal.* 92 (1995) 31.
- [19] M. Taramasso, G. Perego, B. Notari, US Patent 4410501, 1983.
- [20] B. Kraushaar, J.H.C. Hooff, *Catal. Lett.* 1 (1988) 81.
- [21] P.J. Kooyman, P. Waal, P.A.J. Verdaasdonk, K.C. Jansen, H. Bekkum, *Catal. Lett.* 13 (1992) 229.
- [22] R.M. Hanson, K.B. Sharpless, *J. Org. Chem.* 51 (1986) 1922.
- [23] K.S. Smirnov, B. Graaf, *Microporous Mater.* 7 (1996) 133.
- [24] A. Keshavaraja, V. Ramaswamy, H.S. Soni, P. Ratnasamy, *J. Catal.* 157 (1995) 501.
- [25] A. Zecchina, G. Spoto, S. Bordiga, A. Ferrero, G. Petrini, G. Leofanti, M. Padovan, in: P.A. Jacobs et al. (Eds.), *Zeolite Chemistry and Catalysis*, Elsevier, Amsterdam, 1991, p. 251.
- [26] A. Zecchina, S. Bordiga, C. Lamberti, G. Ricchiardi, D. Scarano, G. Petrini, G. Leofanti, M. Mantegazza, *Catal. Today* 32 (1996) 97.
- [27] D.R.C. Huybrechts, L.D. Bruycker, P.A. Jacobs, *J. Mol. Catal.* 71 (1992) 129.
- [28] J.S. Reddy, A. Sayari, *Appl. Catal. A: General* 128 (1995) 231.
- [29] S. Imamura, T. Nakai, K. Utani, H. Kanai, *J. Catal.* 161 (1996) 495.
- [30] D.T. On, L.L. Noc, L. Bonneviot, *J. Chem. Soc., Chem. Commun.* (1996) 299.
- [31] A. Corma, M.A. Cambor, P. Estevo, A. Martinez, J. Pérez-Pariente, *J. Catal.* 145 (1994) 151.
- [32] J.S. Reddy, A. Sayari, *Appl. Catal. A: General* 128 (1995) 231.
- [33] W.F. Maier, J.A. Martens, S. Klein, J. Heilmann, R. Parton, K. Verduyck, P.A. Jacobs, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 180.
- [34] T. Kawai, K. Tsutsumi, *Colloid Polym. Sci.* 270 (1992) 711.
- [35] L.Y. Chen, S. Jaenicke, G.K. Chuah, H.G. Ang, *J. Electron Spectrosc. Relat. Phenom.* 82 (1996) 203.
- [36] L.L. Noc, D.T. On, S. Solomykina, B. Echchahed, F. Beland, C.C. Moulin, L. Bonneviot, *Stud. Surf. Sci. Catal.* 101 (1996) 611.
- [37] S. Imamura, T. Nakai, H. Kanai, T. Ito, *Catal. Lett.* 28 (1994) 277.
- [38] M. Neurock, L.E. Manzer, *J. Chem. Soc., Chem. Commun.* (1996) 1133.
- [39] E.P. Talsi, D.E. Babushkin, *J. Mol. Catal. A: Chem.* 106 (1996) 179.
- [40] D.T. On, M.P. Kapoor, S. Kaliaguine, *J. Chem. Soc., Chem. Commun.* (1996) 1161.
- [41] A. Corma, P. Esteve, A. Martinez, *J. Catal.* 161 (1996) 11.
- [42] G.F. Thiele, E. Roland, *J. Mol. Catal. A: Chem.* 117 (1997) 351.