Novel method for synthesis of titanium silicalite-1 (TS-1)

ZHOU, Ji-Cheng*,[†](周继承)   WANG, Xiang-Sheng(王祥生)

Open Laboratory of Comprehensive Utilization for Carbon Resource, Dalian University of Technology, Dalian, Liaoning 116012, China

Titanium silicalite-1 (TS-1) was easily synthesized using inorganic silicon and titanium source, tetrapropylammonium bromide (TPABr) or TPAOH as templating molecule, $NH_3 \cdot H_2O$, HDA or TEAOH etc. as base sources. In this system, TPA^+ cations (come from TPABr or TPAOH) served as templating agents to direct the MFI structure. NH_3H_2O, TEAOH or HDA etc. provides the alkalinity necessary for crystallization. X-ray diffraction, UV-Vis, IR spectroscopies, SEM, ^{29}Si MAS NMR showed that the zeolites obtained possessed all the structural characteristics of TS-1, and titanium atoms were introduced into the framework in TS-1. This material was proved to have high crystallinity and high catalytic activity to allyl chloride epoxidation and propylene epoxidation. All the samples synthesized had similar catalytic properties with a standard TS-1 through compared inorganic reactant system with organic synthesis system using propylene epoxidation. The effects of silicon source and $TPABr/SiO_2$ ratio were discussed.

Keywords   Titanium silicalites, TS-1, synthesis, inorganic reactant system, characterization, epoxidation

Introduction

Titanium silicalite-1 (TS-1) has attracted much attention during the last decade because of its remarkable catalytic properties in selective oxidation involving H_2O_2 as the oxidant. Application of Titanium silicalites in catalysis was called as a milestone of 1980s' zeolites catalysis, and the catalytic oxidation process by titanium silicalites molecular sieves was considered as 21st century environment friendly process. The synthesis of TS-1 is the most critical part of its application, and also a key problem. In the original patent,[1] samples were prepared by hydrothermal crystallization of precursor gels containing $Si(OEt)_4$ to supply silicon, tetraethyltitanate, $Ti(OEt)_4$, as the titanium source, tetrapropylammonium hydroxide (TPAOH) solution as the template. However, the synthesis required severe condition ($0\,^{\circ}C$, free from CO_2 or N_2 prevention), particularly, it was critical that no alkali cations be present in the synthesis mixtures, even at ppm levels. It was very difficult to avoid the precipitation of TiO_2 completely during the preparation of the precursor mixture or during the crystallization of the precursor gel, which leads to the presence of extra framework of titanium, even though the procedure was carried out under the severe conditions. Crystallization time is longer (6—30 days),[2] and the quantity of using TPAOH is high ($TPAOH/SiO_2 = 0.45$). The modified method[3] can avoid the precipitation of TiO_2 during the preparation of the precursor mixture, but it still uses the expensive TPAOH, separation of its products is difficult, and crystallization yield is lower(80—90%). Both conventional method and modified one used silicon and titanium organic alkoxides as silicon and titanium sources respectively, only strongly organic base could be used as base. So this system may be called as organic synthesis system (see Fig. 1, schematic representation of TS-1 synthesis).

TS-1 has been synthesized by four different procedures. The first involves the use of silicon and titanium alkoxides e.g. example 1 of Ref. 1. The second method is modified method described in Ref. 3. The third method involves the wetness impregnation of a coprecipitated, amorphous TiO_2-SiO_2[4] or TiO_2-SiO_2 cogel[5] with an aqueous solution of TPAOH. The fourth includes a step

for the formation of peroxytitanates by the reaction of aqueous H_2O_2 with a second aqueous solution containing hydrolysed titanium alkoxides, $e. g.$ example 2 of Ref. 1. Note that in all cases TPAOH is used as a structure-directing agent. Both the third and the fourth methods partly used organic reactants, so they were included in the organic synthesis system.

The experimental results of Thangaraj et al.[6] showed that: TS-1 could be synthesized using TEAOH and TPAOH, but not TMAOH. However its crystallinity was poor using TEAOH as templat, and its sample had not catalytic activity to the hydroxylation of phenol.

In 1993, Mueller et al.[7] reported that TS-1 was synthesized from TPABr (TPAOH) and $NH_3 \cdot H_2O$ system using TPOT and colloidal silicon as titanium and silicon source respectively. In 1996 Tuel[8,9] synthesized TS-1 using TEOS or colloidal silicon as silicon source, TBOT as titanium source, TPABr as templating molecule and C_6DN as base. The catalytic activity of the sample synthesized to hydroxylation of phenol was slightly lower than that of the standard TS-1. Li et al.[10] also synthesized TS-1 by the similar method, using $NH_3 \cdot H_2O$, $BuNH_2$, C_6DN, TEAOH etc. as base. In 1995 Gao et al.[11] synthesized TS-1 using an aqueous solution of $TiCl_3$ as titanium source, the precipitation of TiO_2 could completely avoid during the preparation of the precursor mixture, but it used a large number of expensive TPAOH. (If the presence of an extra framework titanium could be avoided during the preparation has not reported in detail.) Among the researchers above, some used colloidal silicon as silicon source (TPABr as templating molecule) instead of TEOS, Gao et al. used $TiCl_3$ as titanium source instead of titanium organic alkoxides ($e.g.$ TBOT, TEOT, TPOT), partly used inorganic material instead of organic material. All that were included in the organic synthesis system, and still could not completely get rid of limit of organic synthesis system. Although many researchers had made great efforts to solve the synthesis problem of TS-1, but all the results were not satisfactory. It is a meaningful to search a simpler and cheaper process for synthesizing the zeolite TS-1.

In the present study, a new inorganic reactant system (using inorganic reactants) to synthsize titanium silicalite-1 (TS-1) was reported. In this process , TPABr or TPAOH was used as templat molecule and $NH_3 \cdot H_2O$, HDA or TEAOH etc. was used as the base source. The TS-1 synthesized has the same characteristics with the

standard TS-1 characterized by XRD, IR, UV-Vis, ^{29}Si MAS NMR, respectively, and also has high activity to olfine epoxidation involving H_2O_2 as oxidant. It is interesting for basic and applied research on synthesis and catalysis of TS-1.

Experimental

Synthesis, materials and reagents

The TS-1 material was synthesized using colloidal silicon and $TiCl_3$ aqueous solution as the silicon and titanium sources, respectively, TPABr or TPAOH aqueous solution as the templating agent, and $NH_3 \cdot H_2O$ as base. The silicon and titanium compounds could be completely hydrolyzed by weak base, Ti^{3+} ion transfer to Ti^{4+} ion is a step by step process, so this process can completely avoid the precipitation of TiO_2. There is not a stage of alcohol evaporation during the preparation of the precursor mixture, so the operation is handy and the material used for synthesis of TS-1 is cheaper (shown in Fig. 1). A typical gel composition could be described as follows: SiO_2: x TiO_2: y TPABr: z $NH_3 \cdot H_2O$: w H_2O.

Colloidal silica containing 30 wt% SiO_2 (Qingdao ocean chemical plant), $TiCl_3$ aqueous solution (A.R.) (Beijing chemical plant), and $NH_3 \cdot H_2O$ (A.R.) were used in the synthesis process. TPABr was prepared in our own laboratory.

TS-1* sample was synthesized by modified method according to Ref. 3. TS-1** sample was synthesized by the conventional method according to Ref. 1.

Characterization of TS-1

X-ray powder diffraction (XRD) was performed on a shimadzu XD-3A X-ray diffractometer with CuK_α radiation in the 2θ range of 5—40° at a scanning speed of 16°/min.

The framework IR spectra of the calcined sample were recorded on a Nicolet 5DX-FT-IR spectrophotometer in a scanning range of 400—1900 cm^{-1} with KBr spellets containing 1 wt% sample.

Diffuse reflection UV-vis spectra of a calcined sample were determined by a Shimadzu UV-240 spectrometer.

The ^{29}Si MAS NMR (BRUKER, DRX-400 instrument) spectra of the calcined sample were recorded at

400 MHz and referenced to Me₄Si, using spinning rate 4 k and MAS BBO 4 mm probe.

Scanning electron micrographes (SEM) were taken in a JEM-1200 EX instrument (Japan electronic compa-

ny).

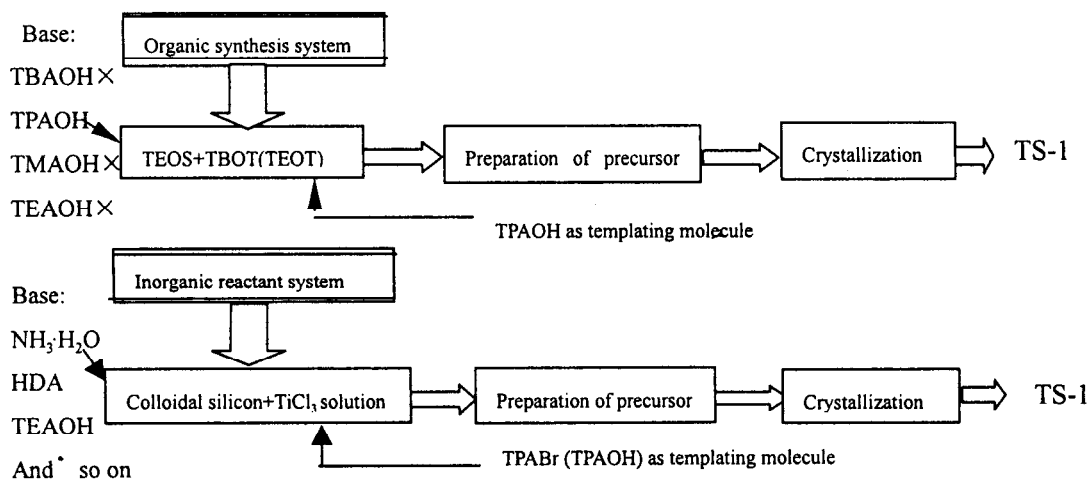An elemental analysis was determined using a Philips PW-1400 X-ray fluorescence spectrometer.

Fig. 1   Schematic representation of TS-1 synthesis by organic and inorganic systems.

Catalytic reaction

The oxidation reactions were proceeded in a batch reactor using propylene and allyl chloride as the organic substrates and aqueous H_2O_2 (30 wt%) as the oxidant. A 400 mL stainless reactor was fitted with a magnetic stirrer and a constant temperature water bath. A typical reaction was carried out as follows: 0.4 g of TS-1 catalysts, 2.0 mL of 30 wt% H_2O_2 aqueous and 31.6 mL of methanol were added into the reactor. At the beginning of reaction propylene was added to the mixture, and propylene pressure was maintained 0.8 MPa, the reaction temperature was 60℃, the reaction time was 2 h. H_2O_2 content was analyzed by iodometric titration and the products were analyzed by Shanghai Analyze Instrument Plant 1102 Gas Chromatography, filled column with polyethylene glycol supported by 101 clay, 4 mm × 4 m. The selectivity and yield were always calculated based on hydrogen peroxide.

Results and disscusion

X-ray diffraction

The X-ray powder patterns synthesized solids

showed all of the reflection characteristic of the MFI-type structure with an orthorhombic symmetry without additional contaminating phases (Fig. 2). The sample peak positions were consistent with those of the standard TS-1 ($2\theta = 7.8, 8.8, 23.2, 23.8, 24.3°$). However, comparison of these patterns to that of the standard TS-1 synthesized with TPAOH following the patent literature revealed important differences in peak intensities, particularly those corresponding to (0k0) reflections. These differences persisted after calcination of the zeolites, indicating that they were not the result of organic molecules within the channels. The systematic increase of (0k0) reflection intensities rather suggests the presence of the preferential planes in the crystals, according to Tuel's opinion (Ref. 8). But at $2\theta = 25.4°$ TiO₂ (anatase) peak was not detected in the X-ray patterns.

Scanning electron microscopy

The scanning electron micrograph (SEM) of TS-1 sample b and c is presented in Fig. 3. SEM pictures show that both samples consist of crystals of uniform size and shape. For the sample synthsized by inorganic reactant system using TPABr and $NH_3 \cdot H_2O$, crystals are in the form of elongated prisms of about 22 × 2.5 × 0.5 μm (see Fig.3). Similarly crystal morphology of TS-1 from

TPABr (TPAOH) and $NH_3 \cdot H_2O$ were observed by Mueller et al.[7] Tuel also reported the similar result. From SEM pictures, almost all crystals are not twinned or perfect morphology. The use of monomeric silica species (TEOS) considerably increases the crystallization rate of the zeolite, thus leading to very small particles of about 0. 2—0. 3 μm. Perhaps large crystal may result from colloidal silicon.

A major difference between TS-1 obtained by the inorganic reactant system and the organic synthesis systems is the very unusual habit of the crystals. Crystals are in the form of very elongated prisms with well-developed planes and very small dimensions along the perpendicular axis with the planes.
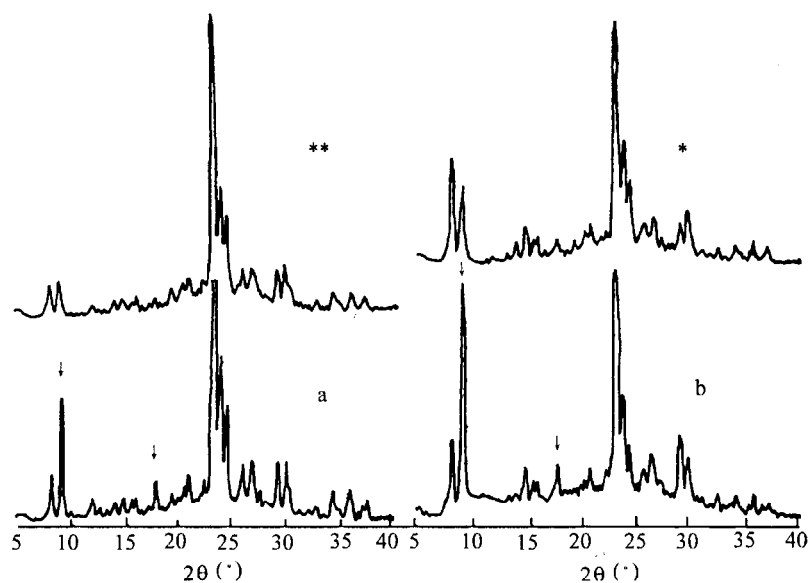
Fig. 2   XRD patterns of samples a, b, * , * * (Samples a and b were synthesized from inorganic reactant system with $TPABr/SiO_2 =$ 0.10, 0. 35, respectively; Sample * was synthesized by modified method, sample * * was synthesized by the conventional method. Samples * and b were calcined).
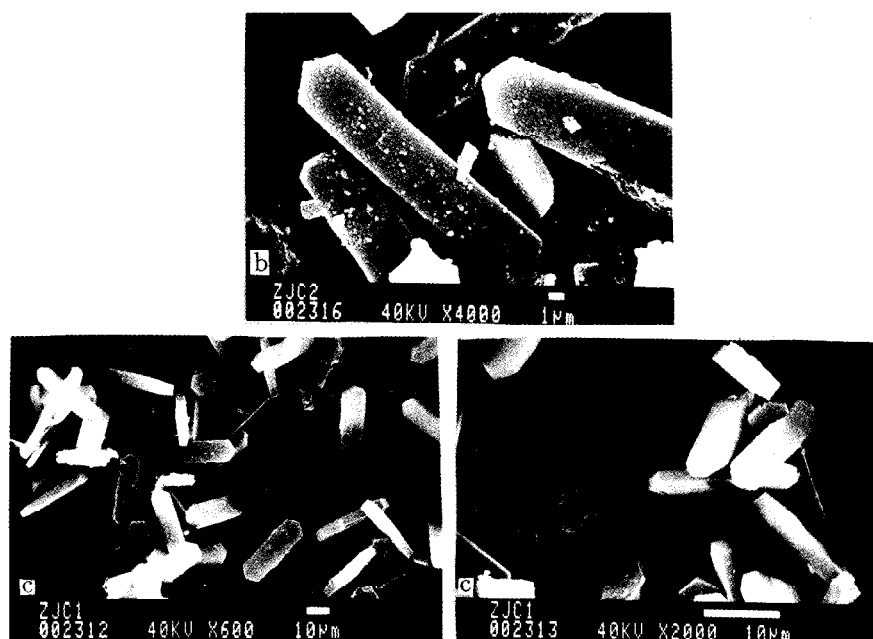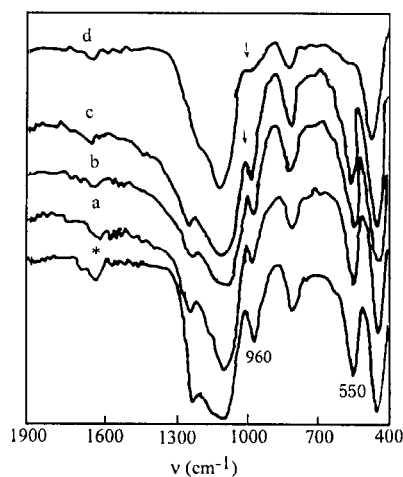

Fig. 3   SEM of samples b and c (sample b: $TPABr/SiO_2 = 0.35$; sample c: $TPABr/SiO_2 = 0.10$).

Infrared spectroscopy

The lattice vibrational bands (400—1900 cm^{-1}) for crystalline samples revealed (i) the presence of a band at 550 cm^{-1}, in addition to that at 450 cm^{-1}, (ii) that the intensity of the band 550 cm^{-1} increases with increasing crystallinity, and (iii) the appearance of a band around 950—970 cm^{-1} on titanium incorporation.

Infrared spectra of calcined samples show an absorption band at 960 cm^{-1}, typical of metal-substituted zeolites. Moreover, the IR band at about 550 cm^{-1}, due to the presence of double rings in the structures, indicates that these samples synthesized have high crystallinity (see Fig. 4 samples * ,a,b,c).
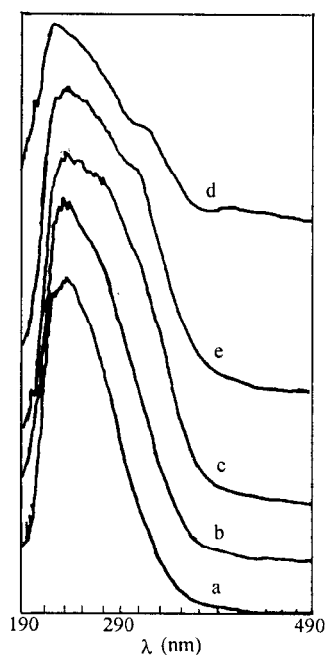

Fig. 4   IR spectra of samples * , a, b, c, and d (Samples a, b and c were synthesized from inorganic reactant system; Samples a, c: TPABr/SiO$_2$ = 0.10; sample b: TPABr/ SiO$_2$ = 0.35; Sample d was synthesized using TEOS as silicon source in inorganic reactant system; sample * was synthesized by modified method).

UV-Vis *spectroscopy*

The presence of the extraframework species could be confirmed by UV-Vis spectroscopy. Samples a, b and c (Fig. 5) show a narrow absorption band at 230 nm, characteristic of isolated tetrahedrally coordinated Ti^{4+} cations. The absorption width increases and the absorption band position shifts as compared with standard TS-1 spectroscopy . This is probably because of the results from colloidal silicon used as silicon source and weak

base (NH$_3$ · H$_2$O) during crystallization. With titanium content in the gel increases, an additional shoulder around 300 nm appears. Geobaldo *et al.*[12] observed a shoulder at about 280 nm in the UV-Vis spectra of hydrated TS-1 samples and thus assigned the shoulder band to isolated hexacoordinated titanium species containing two water molecules in the coordination sphere. According to Blasco *et al.*,[13] this band results from partially condensed hexcoodinated titanium species, thus containing Ti—O—Ti bonds. But it is interesting to note the absence of a well-defined absorption around 330 nm even SiO$_2$/TiO$_2$ = 20 in the gel (sample *). It can thus be concluded that the zeolites do not contain anatase-like oxide species inside the channels. Similar conclusions were reported by different authors.[2,8] The anatase can not be produced in the synthesis of TS-1 from the new inorganic reactant system.

Fig. 5   UV-Vis spectra of samples a, b, c, d and e (Samples a, b, c, d see Fig. 4; Sample e was synthesized from inorganic reactant system using SiO$_2$/TiO$_2$).

Elemental analysis

Molar Ti contents of the TS-1 samples are shown in Table 1. The elemental analysis indicates that the Ti content in TS-1[#] is close to the substitutional limit (2.5% of Ti atoms). UV-Vis spectra indicate that there

is a small amount of TiO_2 (anatase) in TS-1*, but not in TS-1#. The presence of an IR band at 960 cm^{-1} strongly suggests the incorporation of Ti atoms as a framework element. So the studies of IR, UV-Vis spectra and elemental analyses confirm that Ti is incorporated into the framework of silicalite-1.

**Table 1**   Molar Ti content of TS-1 samples

Sample	Ti/(Ti + Si) in gel (%)	Ti/(Ti + Si) in zeolites (%)
TS-1*	1.96	2.85
TS-1#	1.96	2.30

* Sample was synthesized by conventional method.

\# Sample was synthesized by the inorganic reactant system.

^{29}Si MAS NMR

The incorporation of titanium in the MFI framework was also confirmed by ^{29}Si MAS NMR, seeing Fig. 6. With increasing titanium content of the samples, the band (at $\delta = -116$) assigned to the distorted environment of Si bonded with titanium increases in intensity.[6]
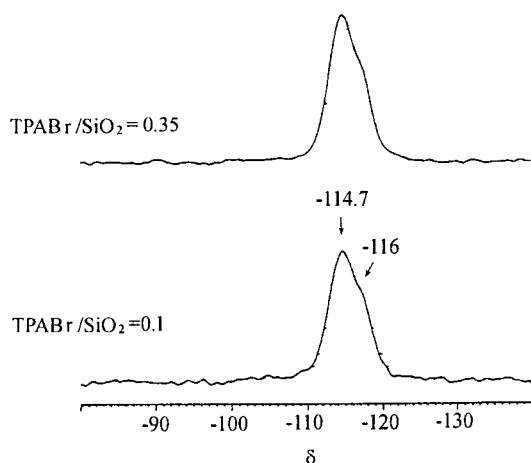
Fig. 6 ^{29}Si MAS NMR of samples b and c.

Effect of ratio TPA$^+$/SiO$_2$

Sample b was synthesized with TPABr/SiO$_2$ = 0.35, samples a and c were synthesized with TPABr/SiO$_2$ = 0.10. Fig. 4 shows that there is no difference between samples b and a or c. Also, UV-Vis spectroscope (see Fig. 5) and ^{29}Si MAS NMR spectroscope (see Fig. 6) show the same results. All samples a, b and c have high crystallinity and pure crystal of TS-1. However, for TPABr/SiO$_2$ = 0.05, XRD patterns show

lower crystallinity, IR spectra also show that characteristic absorption band at 960 cm^{-1} decreases significantly, and absorption band of ZSM-5 characterized at 550 and 1220 cm^{-1} becomes weaker. As long as ratio TPA$^+$/SiO$_2$ was higher than 0.05, high crystalline TS-1 was obtained. The results are consistent with Refs. 6 and 7.

Influence of the silica source

The nature of the silica source greatly influences the morphology of TS-1 crystallites as well as the titanium incorporation. If TEOS was used as silicon source instead of colloidal in the inorganic reactant system, TS-1 had no been synthesized even though evaporating alcohol was carried out for five hours during the preparation of the precursor, and the sample had not activity to epoxidation of allyl chloride. From Fig. 4 IR spectra 550 and 1220 cm^{-1} absorption bands characterized MFI structure were significantly weak. This indicates that the sample has not possessed MFI structure. XRD pattern shows that the sample is amorphous. From Fig. 5 UV-Vis spectra also show that the band of the sample d is weak.

TEOS could hydrolyse only by strong base TPAOH et al., but there were not organic strong base (only NH$_3 \cdot$H$_2$O) in the inorganic reactant system, thus self-assembling MFI structure condition had not matched, while TS-1 could be synthesized in Refs. 5—7 using titanium organic alkoxides as titanium source because they could be easily hydrolyzed.

Catalytic activity

The main interest in TS-1 is its remarkable properties as catalyst in oxidation reaction at low temperature with aqueous H$_2$O$_2$. The results of catalytic epoxidation of allyl chloride show that samples have high catalytic activity. The results of catalytic epoxidation of propylene are shown in Table 2. From these results, all the samples synthesized from inorganic reactant system have high activity. Table 2 shows that the selectivity of propylene oxide is lower for sample c because Na$_2$CO$_3$ aqueous solution has not been added in the reaction system. So far the exact role of sodium ions or other basic compounds are not known. One possible explanation is the neutralization of weakly acidic Si—OH groups, presented on defective TS-1 sites.[14]

Table 2 Catalytic epoxidation of propylene

Catalysts	Gel ratio SiO_2/TiO_2	H_2O_2 conversion $X_{H_2O_2}(\%)$	Selectivity to		
			Propylene oxide ($\%$)	Ether ($\%$)	Glycol ($\%$)
a	50	96.10	88.25	10.83	0.91
b	33	97.75	100	--	--
c	33	90.89	18.92	75.76	5.32
*	50	99.17	100	--	--
* *	50	98.28	74.02	24.26	1.72
e	20	95.29	97.14	2.86	--
TS # 1	33	98.24	89.86	10.14	--
TS # 2	50	97.47	62.36	36.99	--
TS # 3	50	96.60	86.92	9.73	3.35

Experimental conditions: Cat.0.4 g, methanol 25 g, H_2O_2 solution (30 wt%) 2 g, propylene 0.8 MPa, reaction time 2 h, temperature 333 k. Sample * was synthesized by modified method. Sample ** was synthesized by the conventional method. Samples TS # 1,2,3 were synthesized from inorganic reactant system.

Conclusion

We have set up a novel method for synthesis of TS-1, which is a new inorganic reactant system. In contrast to the organic synthesis system, the operation is simplified and materials used are cheaper. In this system, weak base ($NH_3 \cdot H_2O$) can be used as base source, instead of expensive TPAOH, strong base. HDA, TEAOH etc. can also be used as base source.

We have shown that it is possible to synthesize highly crystalline silicalite-1 (TS-1) samples from a new inorganic reactant system. Following this synthesis route, titanium can be incorporated in the silicalite-1 framework without observing the presence of extra framework species. All the samples synthesized possess all the structural characteristics of TS-1 characterized by XRD, UV-Vis, IR, ^{29}Si MAS NMR method. The samples obtained by the inorganic reactant system have shown to be active as catalysts in the epoxidation of propylene and allyl chloride. The activity is the same as that of a standard TS-1.

The samples obtained using TEOS as silica source without MFI structure have not activity to epoxidation of allyl chloride. The strength of base source ($NH_3 \cdot H_2O$, HDA, TEAOH) has no significant effect on the synthesis of TS-1. If TPA^+/SiO_2 ratios are higher than 0.05, the pure TS-1 can be obtained in high yields.

Acknowledgements

References

1. Taramasso, M.; Perego, C.; Notari, B.; U. S. Pat. 4 410 501, 1983[Chem. Abstr., 95, 206272k(1981)].

2. Thangaraj, A.; Eapen, M. J.; Sivasanker, S.; Ratnasamy, R., Zeolites, 12, 943(1992).

3. Thangaraj, A.; Sivasanker, S., J. CHem. Soc., Chem. Commun., 123(1992).

4. Padovan, M.; Leofanti, G.; Roffia, P., Eur. Pat. Appl. 0 311 983, 1989[Chem. Abstr., 110, 175517r(1989)].

5. Uguina, M.A.; Ovejero, G.; Van Grieken, R.; Serrano, D. P.; Camacho, M., J. Chem. Soc., Chem. Commun., 27(1994).

6. Thangaraj, A.; Kumar, R.; Mirajkar, S.P.; Ratnasamy, P., J. Catal., 130, 1(1991).

7. Mueller, U.; Hoelderich, W., Eur. Pat. Appl. 543 247, 1993[Chem. Abstr., 119, 75782r(1993)].

8. Tuel, A., Zeolites, 16, 108(1996).

9. Tuel, A., Stud. Surf. Sci. Catal., 105, 261(1996).

10. Li, C.; Guo, X. W.; Wang, X. S., Synthesis of TS-1 using tetrapropylammonium bromide as template, the proceedings of the Fourth China-Japan-USA symposium on Advanced Adsorption Separation Science and Technology, Guangzhou, 1997, p.69.

11. Gao, H. X.; Suo, J. S.; Li, S. B., J. Chem. Soc., Chem. Commun., 835(1995).

12. Geobaldo, F.; Bordiga, S.; Zecchina, A.; Giamello, E.; Leofanti, G.; Petrini, G., Catal. Lett., 16, 109 (1992).

13. Blasco, T.; Camblor, M. A.; Corma, A.; Perez-Pariente, J., J. Am. Chem. Soc., 115, 11806(1993).

14. Clerici, M.G.; Bellussi, G.; Romano, U., J. Catal., 129, 159(1991).

(SONG, J.P.; LING, J.)