

TARTARIC ACID TEMPLATED SYNTHESIS OF MESOPOROUS Ti-INCORPORATED SILICA AND ITS CATALYTIC ACTIVITY FOR THE RING-OPENING POLYMERIZATION OF ϵ -CAPROLACTONE*

Jie-bin Pang^a, Chang-ming Dong^a, Kun-yuan Qiu^{a**} and Yen Wei^{b**}

^aDepartment of Polymer Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

^bDepartment of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104, USA

Abstract Ti-incorporated mesoporous silica materials with pore diameters of 3–4 nm have been prepared *via* the co-hydrolysis and co-condensation reactions, that is the sol-gel reactions, of titanium (IV) tetrabutoxide and tetraethyl orthosilicate in the presence of tartaric acid as template, followed by extraction with ethanol to remove the template molecules. The materials were characterized in detail by Fourier transform infrared spectroscopy, nitrogen adsorption-desorption test, powder X-ray diffraction, transmission electron microscopy and X-ray energy dispersive spectroscopy. The results indicate that the Ti-containing silica materials have large specific surface areas (*ca.* 1200 m² g⁻¹) and pore volumes (*ca.* 0.900 cm³ g⁻¹). The mesoporosity arises from disordered interconnecting channels or pores. The Ti-incorporated silicas exhibit catalytic activity for the ring-opening polymerization of ϵ -caprolactone, otherwise, the pure mesoporous silica material shows no catalytic activity under the identical conditions.

Keywords Mesoporous material, Ti-incorporated silica, ϵ -Caprolactone, Ring-opening polymerization, Sol-gel reactions

INTRODUCTION

Titanium silicate is a kind of effective molecular sieve catalyst for the selective oxidation of alkanes, the hydroxylation of phenol and the epoxidation of alkenes in the presence of H₂O₂^[1]. However, the range of substrates that can be oxidized is greatly restricted due to the relatively small pore size of the inorganic framework. The exciting discovery of the novel hexagonal mesoporous silica molecular sieves offers promising opportunities for the preparation of catalytic active materials with larger-pores (mesopores)^[2]. Therefore, mesoporous titanium-incorporated materials Ti-MCM-41^[3–7], Ti-HMS^[5, 6], Ti-MSU^[8] and Ti-SBA-15^[9] have been prepared *via* ionic or neutral surfactant templated pathway, and these materials show excellent catalytic activity and selectivity when bulky substrates are involved^[3–7]. Mesoporous titanium phosphate molecular sieves^[10] with ion-exchange capacity have recently been prepared. To date, transition-metal substituted mesoporous silica and its catalytic application has been one of the main focuses in the field of mesoporous material study^[11–14].

Recently, nonsurfactant organic compounds have been employed as template to prepare silica^[15–21], titania^[22], alumina^[23] and polymer-modified silica^[24–26] mesoporous materials with randomly interconnecting worm-like pores. This new method has such advantages as facility, the fact that it proceeds under ambient conditions, versatility, as well as affording monolithic and transparent mesoporous silica^[17] and Ti-incorporated silica^[27] materials. The three-dimensional pore structure of the materials might have significant benefits in

* This work was supported by the National Natural Science Foundation of China (No. 29874002), and the Outstanding Young Scientist Award from the National Natural Science Foundation of China (No. 29825504).

** Corresponding authors: Kun-yuan Qiu (丘坤元), E-mail: kyqiu@chem.pku.edu.cn; Yen Wei, E-mail: weiyen@drexel.edu
Received September 7, 2001; Revised October 12, 2001; Accepted November 9, 2001

practical catalytic applications by reducing the possibility of pore blockage^[8]. Mesoporous materials Al-MCM-41^[28] and Sn-HMS^[29] have been employed as catalyst for the ring-opening polymerization of lactones and lactide, respectively. In this article, the synthesis of mesoporous Ti-incorporated silica materials and the ring-opening polymerization of ϵ -caprolactone (CL) catalyzed by this kind of mesoporous material are reported.

EXPERIMENTAL

Synthesis of Mesoporous Materials

The synthetic procedures were similar to that given in our previous publications^[17, 18], except that titanium(IV) tetrabutoxide (TBT) (Aldrich, 99%) was employed. In a typical synthesis (*e.g.* for TA60-ST40), 10 mL of TEOS (Acros Organics, 98%) was prehydrolyzed with deionized H₂O in ethanol using HCl as catalyst (at TEOS:HCl:H₂O:EtOH molar ratios of 1:0.01:4:3) at about 345 K for 5 h. Upon being cooled to room temperature, the prehydrolyzed solution was added to a definite amount (*i.e.* 9 mL) of 0.45 g mL⁻¹ aqueous solution of tartaric acid (TA) under stirring to afford a homogeneous solution. Then, a calculated amount (*i.e.* 3.9 mL) of 10 V% TBT ethanol solution was added dropwise to the above mixture in a beaker. After stirring for about 10 min, the beaker was sealed with a cellophane film with several small pin holes to allow slow evaporation of the solvent and reaction by-products. The transparent template-containing disks were obtained after gelling and drying for over two months at room temperature. The dried disks appeared slightly yellowish when the Si/Ti molar ratio was less than 40. The samples were ground into fine powders and extracted with ethanol for 3 days in a Soxhlet apparatus under ambient pressure. Upon being dried in a vacuum oven at about 353 K for *ca.* 3 h, the porous materials were obtained.

Characterization of Mesoporous Materials

The surface area, pore volume, pore diameter and pore size distribution of the silica samples as small pieces after the solvent extraction were determined by nitrogen adsorption-desorption isotherm measurement at 77 K on a Micromeritics ASAP2010 analyzer. The sample was degassed at 473 K and below 1.33 Pa for more than 3 h before each measurement. The powder X-ray diffraction (XRD) pattern was recorded on a Rigaku DMAX2400 instrument using Cu K α radiation ($\lambda = 0.15418$ nm, 40 kV, 100 mA) at scanning rates of 1° min⁻¹ in the 2θ range of 0.6–10° and of 8° min⁻¹ in the ranges of 10–60°. Morphologies of the porous samples were examined on a JEOL JEM-200CX transmission electron microscope (TEM), which was attached on an EDAX 9100/60 X-ray energy dispersive spectrometer (EDS) for microphase composition analysis. The accelerating voltage was 200 kV, and the samples were prepared by dipping an ethanol suspension of finely ground sample powders onto a Cu grid coated with a holey C film.

Ring-opening Polymerization of ϵ -Caprolactone

For the bulk ring-opening polymerization of CL (Acros Organics, 98%, purified by distillation from CaH₂ before use), 0.05 g of mesoporous material catalyst was added to 1 mL of CL in a glass tube. A control sample was prepared without any catalyst. After four freeze-thaw cycles degassing, the tube was filled with pure nitrogen, sealed and then kept in an oil bath at 383 K to initiate the polymerization. After reaction for 55 h, the tube was cooled to stop the polymerization, and then it was subjected to high-speed centrifugation. The upper solution was removed and directly subjected to ¹H-nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) measurements to determine the conversion of CL to poly(ϵ -caprolactone) (PCL), the average molecular weight (M_n) and the molecular weight distribution (MWD) of PCL. The ¹H-NMR measurement was performed on a Varian VXR-200 spectrometer, or a Bruker ARX-400 spectrometer, where CDCl₃ was used as solvent and tetramethylsilane (TMS) was used as internal standard. GPC was performed at 308 K on a Waters 515 instrument using THF as eluent at a flow rate of 1.0 mL min⁻¹. The column set consisted of three Styragel columns: HT2, HT3 and HT4. The molecular weight calibration curve was obtained by using standard polystyrenes.

RESULTS AND DISCUSSION

Structure and Morphology of Mesoporous Ti-incorporated Silica

The removal of the TA template compounds from the sol-gel composite was monitored by FT-IR analysis^[27]. The FT-IR spectra of Ti-incorporated silica samples before and after ethanol extraction show that the absorption band at about 1738 cm^{-1} which is assigned to the C=O stretching vibration of TA molecules, disappears after the extraction with ethanol, indicating the complete removal of the template. The absorption band at 1636 cm^{-1} is attributed to the O—H vibration of H_2O molecules adsorbed by the samples and KBr substrate. The spectrum of the mesoporous sample after the extraction with ethanol closely resembles that of Ti-MCM41^[3, 4]. The band observed around 960 cm^{-1} can be attributed to the Si—O—Ti group and Si—OH group^[3, 4].

Table 1 summarizes the physicochemical characteristics of the Ti-incorporated porous silicas after the removal of TA template from the sol-gel composite. It can be seen that mesoporous materials with different Si/Ti molar ratios, *i.e.* 100, 80, 40, 20, were obtained. The samples prepared with TA content higher than 50 wt % show large specific surface areas (*ca.* 1200 $\text{m}^2 \text{g}^{-1}$), pore volumes (*ca.* 0.900 $\text{cm}^3 \text{g}^{-1}$) as well as pore diameters of *ca.* 3.0–4.0 nm. At a fixed Si/Ti molar ratio (*i.e.* 40), the pore volume and diameter tend to rise as the TA content increases. From the *t*-plot analysis the contributions from micropores to the measured surface areas and pore volumes are negligible at TA content higher than 50 wt%. The control sample TA0-ST80 prepared without TA template is dominantly microporous; its nitrogen adsorption-desorption isotherms are typically reversible type I isotherms^[30].

Table 1. Physicochemical properties of the Ti-incorporated mesoporous silica materials with different Si/Ti molar ratios

Sample code	TA content ^a (wt%)	Si/Ti molar ratio ^b	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ^c ($\text{cm}^3 \text{g}^{-1}$)	Pore diameter ^d (nm)	Micropore ^e	
						Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)
TA50-ST100	50	100	1166	0.933	3.5	—	—
TA0-ST80	0	80	473	0.229	<2.0	396	0.183
TA50-ST80	50	80	1193	0.942	3.5	—	—
TA30-ST40	30	40	1034	0.525	2.6	250	0.105
TA40-ST40	40	40	1145	0.663	2.7	47	0.005
TA50-ST40	50	40	1194	0.889	3.4	—	—
TA60-ST40	60	40	1153	1.283	4.2	—	—
TA50-ST20	50	20	1249	0.920	3.2	—	—
TA60-ST20	60	20	1195	1.288	4.1	—	—

^a TA = tartaric acid, the designed template content is calculated from $\text{TA}/(\text{SiO}_2 + \text{TA})$ based on the feed composition under the assumption that TEOS is completely transformed into SiO_2 .

^b Designed Si/Ti molar ratio is calculated from the feed composition.

^c Single point total pore volume at the relative pressure of *ca.* 0.995.

^d Average pore diameter calculated by BJH analysis from the adsorption branch of the isotherms.

^e The surface area and pore volume of micropores were obtained by *t*-plot analysis using Harkins-Jura equation.

The Ti-incorporated samples prepared with TA content higher than 50 wt% generally exhibit type IV isotherms with type H2 hysteresis^[30], which are given by many mesoporous industrial adsorbents^[30]. Figure 1 exemplifies the nitrogen adsorption-desorption isotherms for the samples with Si/Ti molar ratios of 40 and different template contents. It can be seen that the isotherms for the samples TA50-ST40 and TA60-ST40 are type IV isotherms with type H2 hysteresis^[30], which are similar to that of the reported mesoporous silicas^[15–21]. However, the samples TA30-ST40, TA40-ST40 show reversible type I isotherms^[30]. As the template concentration is increased from 30 to 60 wt%, the final (*i.e.* $P/P_0 = 1$) nitrogen volume adsorbed increases significantly, indicating that the pore volume becomes greater. The regularity agrees well with that for porous pure silicas prepared via a nonsurfactant pathway^[15–21]. However, it is noticeable that the Ti-incorporation leads to slight decrease of the pore volume and pore diameter in comparison with the silica porous materials via the TA-templated pathway^[18].

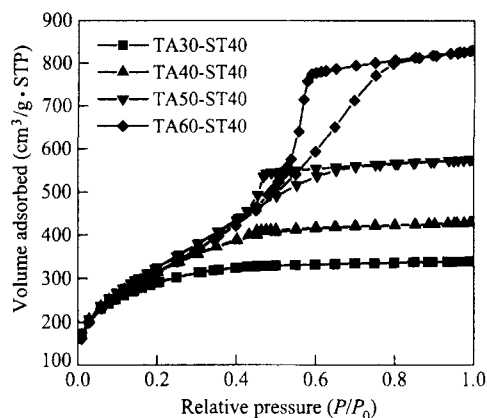


Fig. 1 Nitrogen adsorption-desorption isotherms of samples TA30-ST40, TA40-ST40, TA50-ST40 and TA60-ST40

The powder XRD patterns of the mesoporous samples generally show a diffraction peak in the small-angle range. The XRD patterns for the samples prepared with Si/Ti molar ratios of 40 and different template contents are shown in Fig. 2. It is shown that the intensity of the diffraction peaks in the small-angle range (Fig. 2a) rises with the increase of TA content, indicating the improvement of mesoporosity. The broadness of the single peak and the absence of additional higher degree peaks suggest that these samples lack long-range hexagonal ordering of the structure^[31], which is similar to the XRD pattern of Ti-HMS^[5]. The XRD patterns for the samples were also recorded in the large-angle range of 10–60°, as exemplified in Fig. 2(b) for the sample TA60-ST40. It is shown that there is only a weak and typical amorphous halo around the 2θ value of 23°, indicating the amorphous nature of the sol-gel Ti-substituted silica matrix^[15]. The pattern exhibits no diffraction peaks corresponding to anatase phase, which were generally observed for mesoporous sol-gel titania^[22].

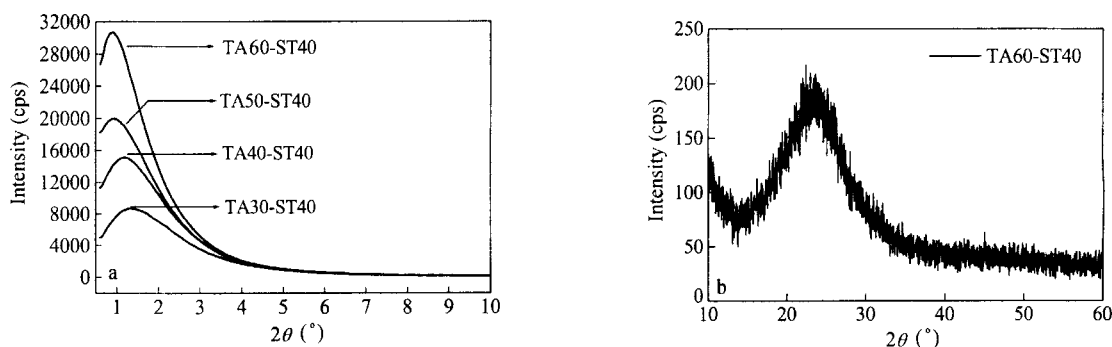


Fig. 2 Powder XRD pattern at small-angle range (a) of the samples TA30-ST40, TA40-ST40, TA50-ST40 and TA60-ST40 in powder form and the powder XRD pattern in the large-angle range (b) of the sample TA60-ST40

Figure 3 exemplifies the TEM image of the mesoporous sample TA60-ST40 after the removal of template and it shows numerous wormlike interconnected channels or pores that are disordered in arrangements, which closely resemble that of the mesoporous titanasilicate obtained via the cationic surfactant templated route^[7]. The framework-confined mesoporosity is clearly revealed. The pore diameters are mostly about 4.5 nm, which is comparable to the average pore diameter (e.g. 4.2 nm) obtained from nitrogen sorption measurements.

To ascertain the incorporation of Ti into the mesoporous silica framework, the samples were subjected to microphase composition analysis via EDS. Figure 4 shows the EDS pattern of the sample TA60-ST20. The TiK α radiation is obviously detected, verifying the Ti incorporation into the framework. The quantitative analysis

results are summarized in Table 2. It can be seen that the Ti incorporation content can be varied from 0.73 to 4.32 atomic (at.) %. The observed values are close to the designed ones. At a fixed designed value, the observed Ti content decreases slightly as the TA content increases.

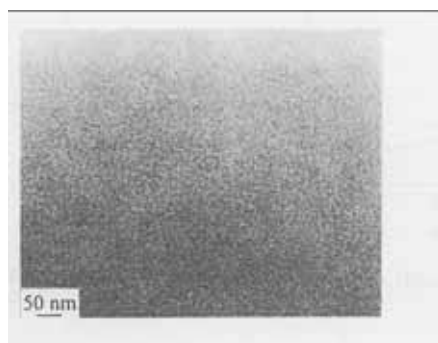


Fig. 3 TEM image of the sample TA60-ST40

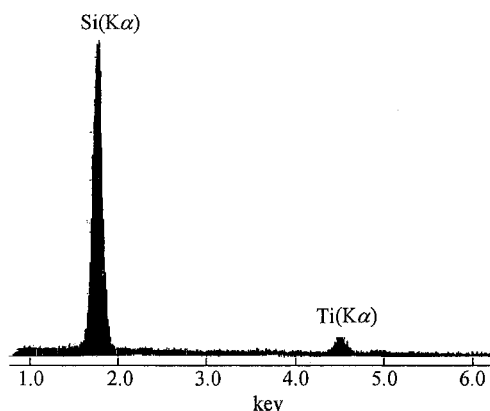


Fig. 4 EDS pattern of the sample TA60-ST20

Table 2. Microphase composition according to EDS analysis of the Ti-incorporated mesoporous silica materials with different Si/Ti molar ratios

Sample code		TA50-ST100	TA50-ST80	TA30-ST40	TA50-ST40	TA60-ST40	TA50-ST20	TA60-ST20
Ti/(Ti+Si)	Calculated ^a	0.99	1.23	2.44	2.44	2.44	4.76	4.76
(at. %)	Observed	0.73	0.99	2.50	1.82	1.54	4.32	3.51

^a The designed Ti content is calculated from the feed composition.

Catalytic Activity of Mesoporous Ti-incorporated Silica in Ring-opening Polymerization of CL

To determine the catalytic activity of the Ti site in the silica framework, the ring-opening polymerization of CL was conducted in the presence of the Ti-incorporated mesoporous silica. As shown in Table 3, the ring-opening polymerization of CL can be catalyzed by Ti-incorporated mesoporous silica. The increasing Ti content and pore diameter can raise the catalytic activity. However, no polymerization was observed without catalyst or in the presence of pure mesoporous silica material, such as TA50 prepared with 50 wt% of TA as template. The results also show that PCLs with narrow molecular weight distributions (MWD = 1.10) are obtained from Ti-incorporated mesoporous silica. This might arise from the steric hindrance of mesoporous structure, which will constrain the propagating polymeric chain and then minimize the “back-biting” and intermolecular transesterification reactions^[28, 29]. A representative GPC curve for PCL catalyzed by TA60-ST20 is given in Fig. 5.

Table 3. Ring-opening polymerization of CL catalyzed by Ti-incorporated mesoporous silica materials^a

Catalyst	Blank ^b	TA-50 ^c	TA50-ST100	TA30-ST40	TA60-ST40	TA50-ST20	TA60-ST20
Pore diameter (nm)	—	4.6	3.5	2.6	4.2	3.2	4.1
Ti content (at.%)	—	0	0.73	2.50	1.54	4.32	3.51
Conversion (%) ^d	0	0	17	22	30	27	32
M_n^e	—	—	1640	1680	2010	1980	2040
M_n^f	—	—	1040	—	1270	—	1500
M_w/M_n^e	—	—	1.06	1.06	1.09	1.09	1.11

^a Reaction condition: 50 mg catalyst; 1 mL CL; 383 K; 55 h; bulk; ^b No catalyst was used; ^c Pure silica mesoporous material prepared with 50 wt% of TA as template; ^d Calculated based on the integral intensities at the chemical shifts of $\delta = 4.25$ and 4.06 from ¹H-NMR measurement on a Varian VXR-200 spectrometer, scanning frequency at 200 MHz; ^e Determined by GPC; ^f Calculated based on the integral intensities at the chemical shifts of $\delta = 4.06$ and 3.65 from ¹H-NMR measurement on a Bruker ARX-400 spectrometer, scanning frequency at 400 MHz.

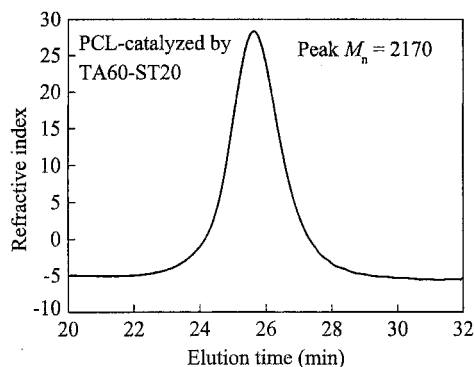
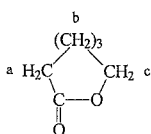


Fig. 5 GPC curve of the poly(ϵ -caprolactone) sample catalyzed by TA60-ST20

CL:



PCL:

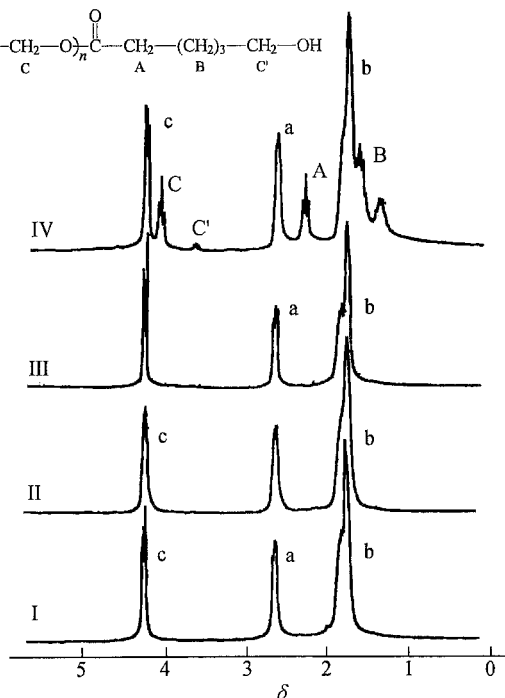
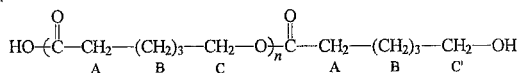


Fig. 6 ^1H -NMR spectra of the monomer CL (I), polymerization mixture without catalyst (II), as well as that catalyzed by TA-50 (III) and TA60-ST20 (IV), respectively

Figure 6 gives the ^1H -NMR spectra of the monomer CL (I), the polymerization mixture without catalyst (II), as well as that catalyzed by TA-50 (III) and TA60-ST20 (IV), respectively. It is shown that spectra II and III are nearly identical to I, indicating that no polymerization occurred without catalyst or with pure silica mesoporous material. Otherwise, the spectrum IV shows several additional peaks corresponding to the protons of PCL. Especially, the chemical shift at 3.65 is observed corresponding to the protons of $-\text{CH}_2-$ linked to the terminal

hydroxy. This result convincingly indicates that the Ti-incorporated mesoporous silica is catalytically active for the ring-opening polymerization of CL. Unlike such conventional catalysts as stannous octoate^[32] or aluminum alkoxide^[33] for ring-opening polymerization of lactones or lactides, the lower M_n of PCL is obtained with the Ti-incorporated mesoporous silica heterogeneous catalyst. Further studies are in progress in our laboratory to increase the catalytic activity of the mesoporous materials for the ring-opening polymerization of lactones or lactides.

CONCLUSIONS

Tartaric acid has been successfully employed as a template to prepare mesoporous Ti-incorporated silica materials through the sol-gel process of tetraethyl orthosilicate and titanium(IV) tetrabutoxide. The materials with desired Si/Ti molar ratios of 100-20 exhibit large specific surface areas of $1200 \text{ m}^2 \text{ g}^{-1}$ and pore volumes of $0.900 \text{ cm}^3 \text{ g}^{-1}$. The XRD and TEM analyses suggest that the materials exhibit interconnecting worm-like channels or pores with disordered channel arrangements. The mesoporous Ti-incorporated silica can catalyzed the ring-opening polymerization of ϵ -caprolactone and poly(ϵ -caprolactone)s with narrow polydispersities are obtained.

ACKNOWLEDGEMENT The authors greatly appreciate Prof. X. H. Chen (Institute of Materials Science, Tsinghua University) for her friendly assistance with the TEM measurements.

REFERENCES

- 1 Zhou, J.C. and Wang, X.S., *Progress in Chemistry*, 1998, 10: 381
- 2 Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartuli, J.C. and Beck, J.S., *Nature*, 1992, 359: 710
- 3 Corma, A., Navarro, M.T. and Perez-Pariente, J., *Chem. Commun.*, 1994: 147
- 4 Blasco, T., Corma, A., Navarro M.T. and Perez-Pariente, J., *J. Catal.*, 1995, 156: 65
- 5 Tanev, P. T., Chibwe, M. and Pinnavaia, T.J., *Nature*, 1994, 368: 321
- 6 Zhang, W., Froba, M., Wang, J., Tanev, P.T., Wong, J. and Pinnavaia, T.J., *J. Am. Chem. Soc.*, 1996, 118: 9164
- 7 Haskouri, J.E., Cabrera, S., Gutierrez, M., Beltran-Porter, A., Beltran-Porter, D., Marcos, M.D. and Amoros, P., *Chem. Commun.*, 2001: 309
- 8 Bagshaw, S.A., Renzo, F.D. and Fajula, F., *Chem. Commun.*, 1996: 2209
- 9 Luan, Z., Maes, E.M., Van der Heide, P.A.W., Zhan, D., Czernuszewica, R.S. and Keven, L., *Chem. Mater.*, 1999, 11: 3680
- 10 Bhaumik, A. and Inagaki, S., *J. Am. Chem. Soc.*, 2001, 123: 691
- 11 Ying, J.Y., Mehnert, C.P. and Wong, M.S., *Angew. Chem. Int. Ed.*, 1999, 38: 56 and references therein.
- 12 Ciesla, U. and Schuth, F., *Microporous and Mesoporous Mater.*, 1999, 27: 131 and references therein.
- 13 Mizuno, N., Hatayama, H., Uchida, S. and Taguchi, A., *Chem. Mater.*, 2001, 13: 179
- 14 Dai, L.X., Tabata, K., Suzuki, E. and Tatsumi, T., *Chem. Mater.*, 2001, 13: 208
- 15 Wei, Y., Jin, D., Ding, T., Shih, W.H., Liu, X., Cheng, S.Z.D. and Fu, Q., *Adv. Mater.*, 1998, 3: 313
- 16 Wei, Y., Xu, J., Dong, H., Dong, J.H., Qiu, K.Y. and Jansen-Varnum, S.A., *Chem. Mater.*, 1999, 11: 2023
- 17 Pang, J.B., Qiu, K.Y., Wei, Y., Lei X. J. and Liu, Z. F., *Chem. Commun.*, 2000: 477
- 18 Pang, J.B., Qiu, K.Y. and Wei, Y., *J. Non-Cryst. Solids*, 2001, 283: 101
- 19 Pang, J.B., Qiu, K.Y., Xu, J., Wei, Y. and Chen, J., *J. Inorg. Organomet. Polymers*, 2000, 10: 39
- 20 Pang, J.B., Qiu, K.Y. and Wei, Y., *Chinese J. Chem.*, 2000, 18: 693
- 21 Pang, J.B., Qiu, K.Y. and Wei, Y., *Microporous and Mesoporous Mater.*, 2000, 40: 299
- 22 Zheng, J.Y., Qiu, K.Y., Feng, Q., Xu, J. and Wei, Y., *Mol. Cryst. Liq. Cryst.*, 2000, 354: 183
- 23 Liu, X., Wei, Y., Jin, D. and Shih, W. H., *Mater. Lett.*, 2000, 42: 143
- 24 Wei, Y., Feng, Q., Xu, J., Dong, H., Qiu, K.Y., Jansen, S.A., Yin, R. and Ong, K.K., *Adv. Mater.*, 2000, 12: 1448

- 25 Feng, Q., Xu, J., Dong, H., Li, S. and Wei, Y., *J. Mater. Chem.*, 2000, 10: 2490
- 26 Pang, J. B., Qiu K.Y. and Wei, Y., *Chinese J. Polym. Sci.*, 2000, 18: 469
- 27 Pang, J.P., Qiu, K.Y. and Wei, Y., *Chinese J. Chem.*, 2001, 19: 2001
- 28 Kageyama, K., Ogino, S., Aida, T. and Tatsumi, T., *Macromolecules*, 1998, 31: 4069
- 29 Abdel-Fattah, T.M. and Pinnavaia, T.J., *Chem. Commun.*, 1996, 665
- 30 Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J. and Siemieniowska, T., *Pure Appl. Chem.*, 1985, 57: 603
- 31 Tanev, P.T. and Pinnavaia, T.J., *Science*, 1995, 267: 865
- 32 Pensec, S., Leroy, M., Akkouche, H. and Spassky, N., *Polym. Bull.*, 2000, 45: 373
- 33 Barakat, I., Dubois, P., Grandfils, C. and Jerome, R., *J. Polym. Sci., Part A: Polym. Chem.*, 2001, 39: 294