Zurückziehung

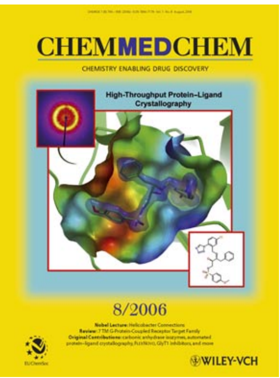
Design and Size Control of Uniform Zeolite Nanocrystals Synthesized in Adjustable Confined Voids Formed by Recyclable Monodisperse Polymer Spheres

X. Yang, Y. Feng, G. Tian, Y. Du, X. Ge, Y. Di, Y. Zhang, B. Sun, F.-S. Xiao* **2619–2624**

Angew. Chem. **2005**, *117*

DOI 10.1002/ange.200462187

Nach der Veröffentlichung bemerkten die Autoren, dass einige TEM-Bilder dieser Zuschrift falsche Maßstäbe enthalten. Die aus diesen Bildern abgeleiteten Partikelgrößen sind somit inkorrekt, und die Folgerungen aus diesen Daten unrichtig. Daher ziehen alle Autoren die Zuschrift zurück und entschuldigen sich bei den Lesern der *Angewandten Chemie* für die fehlerhaften Angaben.



Zeolite Nanocrystals

Design and Size Control of Uniform Zeolite Nanocrystals Synthesized in Adjustable Confined Voids Formed by Recyclable Monodisperse Polymer Spheres**

*Xiaoyu Yang, Yefei Feng, Ge Tian, Yunchen Du, Xin Ge, Yan Di, Yonglai Zhang, Bo Sun, and Feng-Shou Xiao**

Zeolite nanocrystals have attracted much attention because of their potential uses as active catalysts, effective membranes, low-*k* thin films, and model systems for fundamental studies of zeolite crystal growth.[1–16] For most of these applications, dispersible zeolite nanocrystals with controlled and uniform size are preferred.[1–20]

There are a number of examples of the preparation of zeolite nanocrystals.[21–32] For example, zeolite nanocrystals with small size and narrow distribution could be prepared by control of synthetic gel composition or crystallization temperature/time.[21–25] Addition of organic templates to synthetic gels can effectively reduce the size of the zeolites.[7,8,12–14,26–30] Space-confined synthesis by means of carbon black can be used to prepare zeolite nanocrystals, the sizes of which are generally controlled by the various types of carbon black.[31] Thermoreversible polymer hydrogels are novel media for the synthesis of zeolite nanocrystals, and the polymer hydrogels are recyclable.[32] However, design and size control of uniform zeolite nanocrystals is still not easy owing to the complexity of their synthesis and limitations of various synthetic routes.

Recently, uniform and monodisperse polymer spheres were synthesized, and there are voids between these polymer spheres in aqueous media.[33] Interestingly, these confined voids can be simply adjusted by the solid content and diameter of the polymer spheres. The adjustable confined voids formed by polymer spheres could potentially serve as micro- or nanoreactors for controlling zeolite growth. Moreover, these polymer spheres are stable in the temperature range 0–160 °C,[34] which is suitable for the synthesis of most types of zeolites. Furthermore, these polymer spheres can easily be transformed into polymer chains dissolved in an

---

[*] X. Yang, Y. Feng, G. Tian, Y. Du, X. Ge, Y. Di, Y. Zhang, B. Sun, Prof. F.-S. Xiao
Department of Chemistry & Key Laboratory of Inorganic Synthesis and Preparative Chemistry
Jilin University, Changchun 130012 (China)
Fax: (+86) 431-567-1974
E-mail: fsxiao@mail.jlu.edu.cn

[**] We thank Dr. U. Müller of BASF as well as Prof. B. Yang, Prof. Z.-C. Cui, Prof. D.-Z. Jiang, K. Zhang, H.-Y. Jia, M.-J. Li, J.-Y. Fang, H.-T. Li, and Dr. X. Chen of Jilin University for helpful suggestions and discussions. This work is supported by the NSFC (20373018, 20233030, and 20121103), BASF, the CNPC, the National High Technology Research and Development Program of China (863 Program), the State Basic Research Project (973 Program), and the Ministry of Education of China.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200462187

appropriate solvent, and the polymer chains can be transformed back into polymer spheres by evaporation of the solvent,[35,36] which allows convenient recycling of polymer spheres in zeolite synthesis.

Herein we report a simple route for the design and size control of uniform zeolite nanocrystals synthesized in confined voids formed by polymer spheres. Interestingly, the size (60–500 nm) of zeolite nanocrystals observed experimentally is in good agreement with that estimated from theoretical calculations. Moreover, the polymer spheres could be recycled during the synthesis of zeolite nanocrystals, which is an environmentally benign procedure. The general synthetic procedure is illustrated in Figure 1.

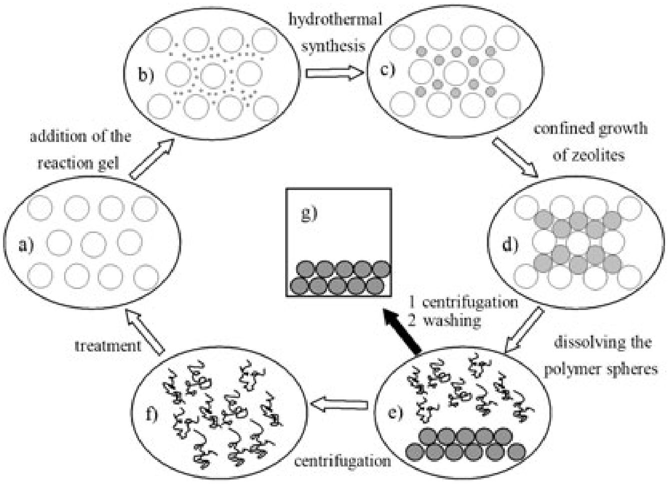


Figure 1. Schematic representation of the synthesis of zeolite nanocrystals in confined voids formed by polymer spheres: a) the emulsion with monodisperse polymer spheres, b) the aluminosilicate and titanosilicate gels are homogenously mixed with the emulsion, c) crystallization of zeolite nanocrystals, d) confined growth of zeolite nanocrystals in the voids controls the final size of the zeolite nanocrystals, e) the polymer spheres are dissolved to give a mixture of zeolite nanocrystals and polymer solution, f) separation of the polymer solution from the zeolite nanocrystals by centrifugation and washing, g) isolated zeolite nanocrystals, and (f)→(a) the solution of polymer chains is transformed into polymer spheres by evaporation of the solvent.

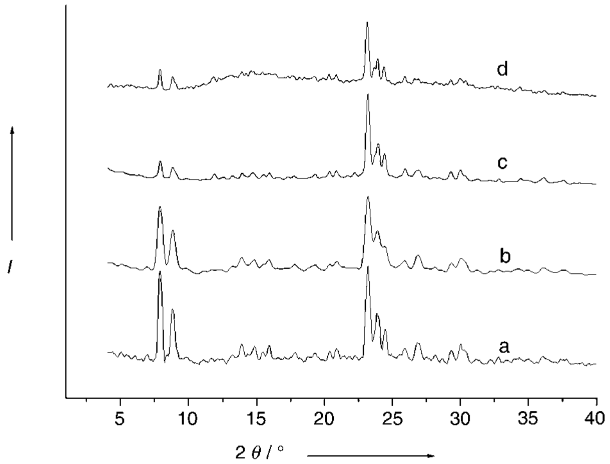


Figure 2. XRD patterns of nanosized a) ZSM-5(1.5), b) ZSM-5(3), c) ZSM-5(6), and d) ZSM-5(7.5) zeolites.

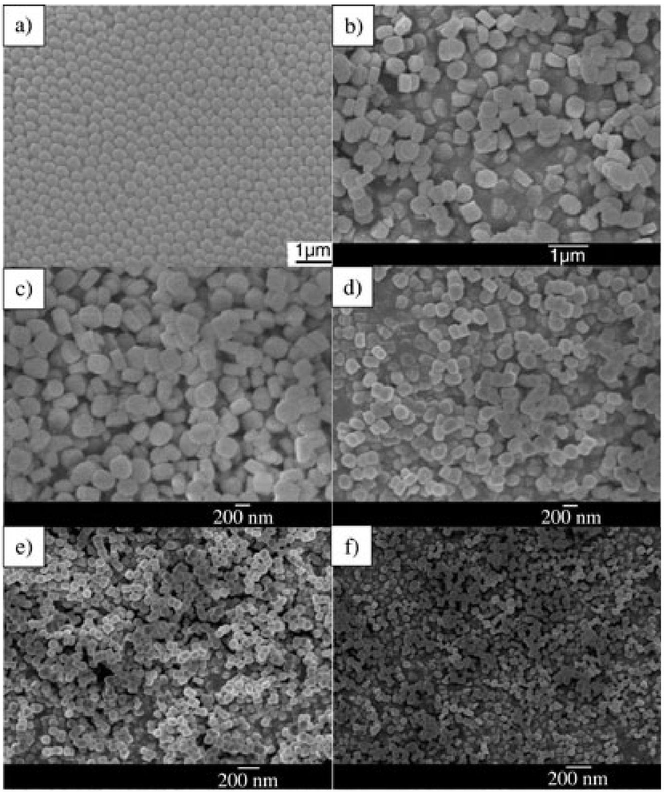


Figure 3. Field-emission SEM images of a) polymer nanospheres b) ZSM-5(1.5–500), c) ZSM-5(1.5), d) ZSM-5(3), e) ZSM-5(6), and f) ZSM-5(7.5) zeolites.

Figure 2 shows X-ray diffraction (XRD) patterns of ZSM-5 nanocrystals synthesized with various contents of polymer spheres. Notably, the XRD peaks of all samples are characteristic of ZSM-5 crystals, but the peaks become progressively weaker with increasing content of polymer spheres in the synthesis. This indicates that the size of the zeolite nanocrystals decreases with the increasing content of polymer spheres.

Figure 3 shows scanning electron microscopy (SEM) images of polymer spheres and ZSM-5 nanocrystals synthesized at various contents and diameters of polymer spheres. The zeolites have crystal sizes of around 60–500 nm (Figure 3b–f), and each zeolite sample has an almost uniform crystal size. For example, when the content of polymer spheres with a diameter of 340 ± 20 nm in the synthesis (see the Experimental Section) is 7.5 g, ZSM-5(7.5) has a crystal size of around 60 nm (Figure 3 f), and when the content of the same polymer spheres is 1.5 g in the synthesis, ZSM-5(1.5) has a size of about 340 nm (Figure 3c). A content of polymer spheres with a diameter of 500 ± 30 nm of 1.5 g results in ZSM-5(1.5–500) with a size of around 500 nm (Figure 3b), and a content of the same polymer spheres of 3.0 g leads to ZSM-5(3–500) with a size of about 300 nm (see the Supporting Information). More importantly, the polymer spheres used for the synthesis of zeolite nanocrystals could be recycled.[36] (For an example of an SEM image of monodisperse polymer spheres (≈350 nm) synthesized from recovered polymer chains, see the Supporting Information).

Furthermore, transmission electron microscopy (TEM) studies of these zeolite samples confirm that they have uniform nanocrystals with high crystallinity. For example, a TEM image of ZSM-5(1.5) shows very uniform nanocrystals (see the Supporting Information).

Figure 4 shows N_2 adsorption/desorption isotherms of calcined ZSM-5 samples, and textural parameters are presented in Table 1. Notably, the samples exhibit a steep rise followed by flat curves at low partial pressures that are typical Langmuir curves. These results are reasonably assigned to complete filling of the micropores with N_2. Additionally, the samples also show quite narrow hysteretic uptakes at high partial pressures, which are assigned to mesopores formed by the aggregation of ZSM-5 nanocrystals. Interestingly, the BET surface area of the samples is relatively high compared with that of conventional ZSM-5 samples (Table 1). This further supports the fact that the zeolite ZSM-5 nanocrystals have small crystal sizes.

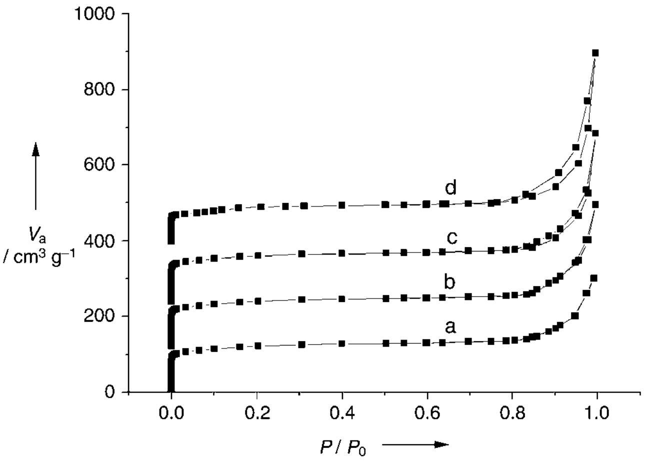


Figure 4. N_2 adsorption/desorption isotherms of nanosized a) ZSM-5(1.5), b) ZSM-5(3), c) ZSM-5(6), and d) ZSM-5(7.5) zeolites. Isotherms b), c), and d) are offset by 100, 220, and 390 $cm^3 g^{-1}$, respectively, along the vertical axis for clarity.

Table 1: Calculated and experimental size of zeolite nanocrystals synthesized in confined voids formed by polymer spheres.

Sample	Polymer content [g]	Exptl crystal size [nm][a]	Calcd crystal size [nm][b]	BET surface area [$m^2 g^{-1}$]
ZSM-5(1.5)	1.5	340 ± 30	340 ± 20	489
ZSM-5(3)	3.0	200 ± 20	200 ± 12	496
ZSM-5(6)	6.0	90 ± 8	89 ± 4	516
ZSM-5(7.5)	7.5	60 ± 6	58 ± 4	521
ZSM-5(1.5–500)	1.5	500 ± 40	500 ± 30	438
ZSM-5(3–500)	3.0	300 ± 30	294 ± 18	490

[a] Experimental crystal size was measured by SEM. [b] Calculated crystal size = $2R_v$ (R_v is calculated by the equation $R_v = [2.29\,M_T^{-1/3} - 1]\,R_p$, in which M_T = polymer content and R_p = radius of a polymer sphere).

The synthesis of ZSM-5 nanocrystals of various sizes should be attributed directly to the use of various contents of polymer spheres because during synthesis all other parameters, such as temperature, time, template, pH value, and composition, are completely the same. Therefore, we suggest that the ZSM-5 nanocrystals crystallize in the confined voids, and the size of ZSM-5 nanocrystals should depend on that of the confined voids, which could be adjusted by the content of polymer spheres in the synthesis. The model of adjustable confined voids is proposed in Figure 5 (confined voids are simplified as spherelike and polymer spheres are considered as hard, inflexible, and relatively actionless balls in the solution). According to this model, the relationship between the radius of a confined void R_v, the radius of a polymer sphere R_p, and the total weight of polymer spheres M_T is given by Equation (1).

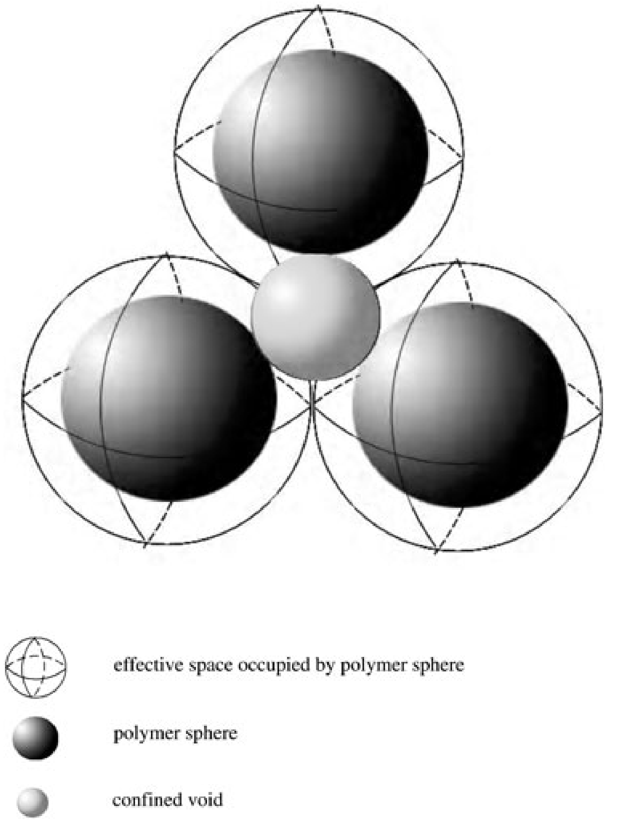


Figure 5. Proposed model of confined voids for crystallization of zeolite nanocrystals.

$$R_v \approx [2.29\,M_T^{-1/3} - 1]\,R_p\text{[37]} \qquad (1)$$

Clearly, the radius of the confined voids depends on the content and radius of the polymer spheres, and the confined voids can be designed and size-controlled by means of these parameters of the polymer spheres in the synthesis of zeolites. Figure 6 shows the good agreement between the size of zeolite nanocrystals calculated by Equation (1) and the experimental size of zeolite nanocrystals measured by SEM. This indicates that the size of zeolite nanocrystals can be simply designed and controlled by means of the adjustable voids formed by monodisperse polymer spheres.

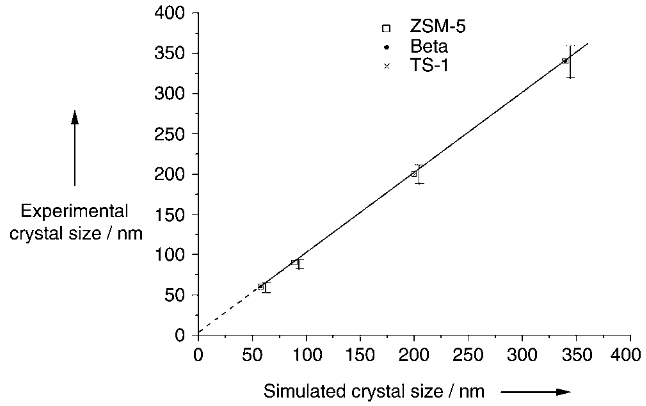


Figure 6. Plots of experimental crystal size of zeolite nanocrystals observed by SEM versus the simulated crystal size of zeolite nanocrystals estimated by a mathematical model of the confined voids (Figure 5 and the Supporting Information).

The synthesis of zeolite nanocrystals in confined voids is not limited to ZSM-5; zeolites such as A, X, Y, L, MOR, β, and TS-1 can also be synthesized. For example, samples of zeolite β with sizes of about 340 and 60 nm were synthesized at contents of polymer spheres of 1.5 and 7.5 g, respectively (Figure 7), and zeolite TS-1 with a size of around 200 nm was obtained at a content of polymer spheres of 3.0 g (see the Supporting Information). The strategy reported herein provides a unique, effective, and potentially general approach for the synthesis of zeolite nanocrystals and the other nanocrystals with controllable size under hydrothermal conditions.

Experimental Section

The monodisperse polymer spheres were supplied by BASF, and zeolite nanocrystals with various sizes were synthesized with varying contents of the polymer spheres.

Typical synthesis of ZSM-5 nanocrystals: 1) Aluminosilicate gel was prepared by mixing aqueous tetrapropylammonium hydroxide (TPAOH) solution (25%; 5 mL) with H_2O (5 mL), followed by addition of 0.3 g of $Al_2(SO_4)_3\cdot 18H_2O$ (0.3 g) and tetraethyl orthosilicate (TEOS; 5 mL) with stirring ($Al_2O_3/SiO_2/TPAOH/C_2H_5OH/H_2O$ molar ratio of 1.0:30:8:120:1500). The mixture was then aged at 140 °C for 3 h to form the aluminosilicate gel. 2) An emulsion (5 mL) containing 1.5, 3, 6, or 7.5 g of the polymer spheres with an average size of around 340 nm was mixed with the aluminosilicate gel (containing 60 mmol of SiO_2, 5 mL) obtained in step 1. The mixture was stirred at room temperature for 4 h, then transferred into an autoclave for further reaction at 140 °C for 96 h. 3) The crystallized product was treated with ethyl acetate, followed by washing by water, centrifugation, drying, and ultrasonic redispersion in water until the polymer was completely washed away. The final products are denoted ZSM-5(1.5), ZSM-5(3), ZSM-5(6), and ZSM-5(7.5), in which the number in parentheses is the content of polymer spheres in the synthesis. 4) The calcined samples were heated at 550 °C for 4 h to remove the TPA^+ template

Zeolite β(1.5) and β(7.5) samples were synthesized with polymer spheres (1.5 and 7.5 g) with a diameter of about 340 nm at a molar ratio of $Al_2O_3/SiO_2/TEAOH/H_2O$ of 1.0:60:25:800, and TS-1(3) was prepared with polymer spheres (3.0 g) with a diameter of about 200 nm at a molar ratio of $TiO_2/SiO_2/TPAOH/C_2H_5OH/H_2O$ of 1.0:30:8:120:375. Similarly, samples of ZSM-5(1.5–500), ZSM-5(3.0–500), and β(7.5–500) (see the Supporting Information) were synthesized with polymer spheres (1.5, 3.0, and 7.5 g) with a diameter of around 500 ± 30 nm.

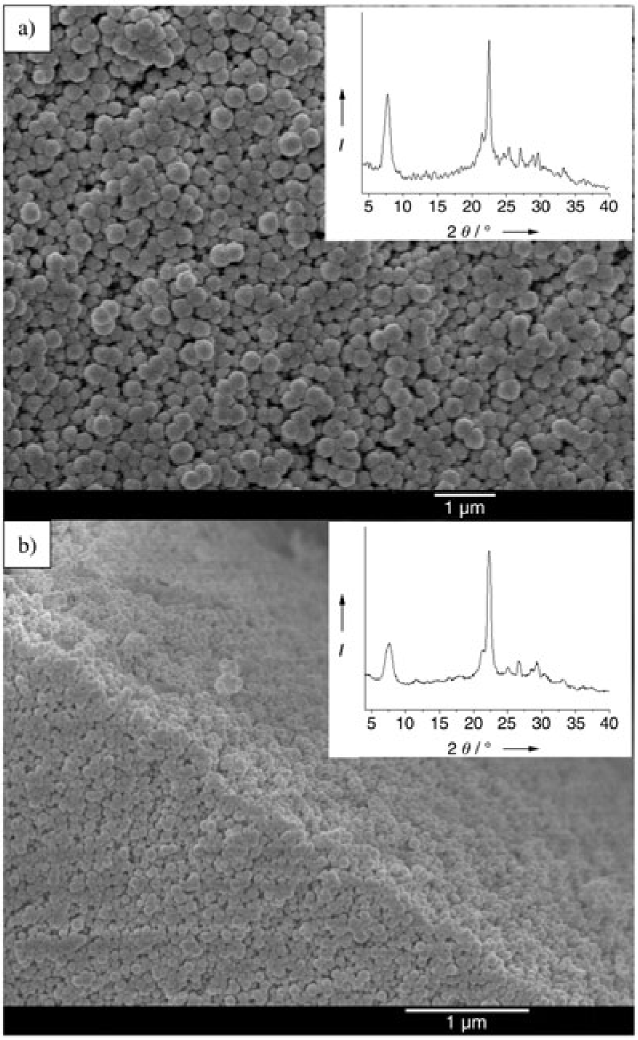


Figure 7. Field-emission SEM images and XRD patterns (inset) of nanosized a) β(1.5) and b) β(7.5) zeolites.

XRD patterns were obtained on a Siemens D5005 diffractometer by using $Cu_{K\alpha}$ radiation. SEM experiments were performed on a JSM-6700F electron microscope (JEOL, Japan). TEM experiments were performed on a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. The nitrogen adsorption and desorption isotherms at liquid-nitrogen temperature were measured on a Micromeritics ASAP 2020M system. The samples were degassed for 10 h at 300 °C before measurements. The Si/Al and Si/Ti ratios of the samples were measured on a Perkin-Elmer 3300DV ICP and by chemical analysis.

Received: October 2, 2004
Revised: December 18, 2004
Published online: March 22, 2005

Keywords: hydrothermal synthesis · nanocrystals · nanotechnology · polymers · zeolites

---

[1] K. Rajagopalan, A. W. Peters, G. C. Edwards, *Appl. Catal.* **1986**, *23*, 69–80.

[2] M. A. Camblor, A. Corma, A. Martínez, F. A. Mocholí, J. P. Pariente, *Appl. Catal.* **1989**, *55*, 65–74.

[3] M. A. Camblor, A. Corma, A. Martínez, V. Martínez-Soria, S. Valencia, *J. Catal.* **1998**, *179*, 537–547.

[4] B. Notari, *Innovation in Zeolite Materials Science*, *Vol. 37* (Ed.: P. J. Grobet), Elsevier Science Publishers, Amsterdam, **1987**, pp. 413.

[5] O. Mitsui, K. Yohei (Asahi Kasei Comp), DE 3441072, May 23, **1985**; [*Chem. Abstr.* **1985**, *104*, 50589].

[6] A. J. H. P. van der Pol, A. J. Verduyn, J. H. C. van Hoff, *Appl. Catal.* **1992**, *92*, 113–130.

[7] L. C. Boudreau, J. A. Kuck, M. Tsapatsis, *J. Membr. Sci.* **1999**, *152*, 41–59.

[8] a) L. Huang, Z. Wang, J. Sun, L. Miao, Q. Li, Y. Yan, D. Zhao, *J. Am. Chem. Soc.* **2000**, *122*, 3530–3531; b) L. Huang, Z. Wang, H. Wang, J. Sun, Q. Li, D. Zhao, Y. Yan, *Microporous Mesoporous Mater.* **2001**, *48*, 73–78.

[9] A. G. Dong, Y. J. Wang, Y. Tang, N. Ren, Y. H. Zhang, J. H. Yue, Z. Gao, *Adv. Mater.* **2002**, *14*, 926–929.

[10] T. Wakihara, S. Yamakita, K. Lezumi, T. Okubo, *J. Am. Chem. Soc.* **2003**, *125*, 12388–12389.

[11] B. J. Zhang, S. A. Davis, N. H. Mendelson, S. Mann, *Chem. Commun.* **2000**, *9*, 781–782.

[12] M. H. Valkenberg, W. F. Holderich, *Catal. Rev. Sci. Eng.* **2002**, *44*, 321–374.

[13] a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710–712; b) T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kate, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988–992.

[14] C. E. A. Kirschhock, V. Buschmann, S. Kremer, R. Ravishankar, C. J. Y. Houssin, B. L. Mojet, R. A. van Santen, P. J. Grobet, P. A. Jacobs, J. A. Martens, *Angew. Chem.* **2001**, *113*, 2707–2710; *Angew. Chem. Int. Ed.* **2001**, *40*, 2637–2640.

[15] a) S. Mintova, N. H. Olson, J. Senker, T. Bein, *Angew. Chem.* **2002**, *114*, 2670–2673; *Angew. Chem. Int. Ed.* **2002**, *41*, 2558–2561; b) S. Mintova, N. H. Olson, V. Valtchev, T. Bein, *Science* **1999**, *283*, 958–960.

[16] B. J. Schoeman, J. Sterte, J. E. Otterstedt, *Zeolites* **1994**, *14*, 110–116.

[17] S. I. Zones, M. E. Davis, *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 107–117.

[18] N. K. Raman, M. T. Anderson, C. J. Brinker, *Chem. Mater.* **1996**, *8*, 1682–1701.

[19] D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548–552.

[20] J. Y. Ying, C. P. Mehnert, M. S. Wong, *Angew. Chem.* **1999**, *111*, 58–82; *Angew. Chem. Int. Ed.* **1999**, *38*, 56–77.

[21] a) A. E. Persson, B. J. Schoeman, J. Sterte, J. E. Otterstedt, *Zeolites* **1994**, *14*, 557–567; b) E. F. S. Aguiar, A. Liebsch, B. C. Chaves, A. F. Costa, *Microporous Mesoporous Mater.* **1998**, *25*, 185–192; c) R. W. Corkery, B. W. Ninham, *Zeolites* **1997**, *18*, 379–386; d) M. Yamamura, K. Chaki, T. Wakatsuki, H. Okado, K. Fujimoto, *Zeolites* **1994**, *14*, 643–649.

[22] a) B. J. Schoeman, J. Sterte, J. E. Otterstedt, *J. Chem. Soc. Chem. Commun.* **1993**, 994–995; b) B. J. Schoeman, J. Sterte, J. E. Otterstedt, *Zeolites* **1994**, *14*, 208–216.

[23] P. A. Jacobs, E. G. Derouane, J. Weitkamp, *J. Chem. Soc. Chem. Commun.* **1981**, 591–593.

[24] M. A. Camblor, A. Corma, A. Mifsud, J. Pérez-Pariente, S. Valencia, *Stud. Surf. Sci. Catal.* **1997**, *105*, 341.

[25] Z. Gabelica, J. B. Nagy, G. Debras, E. G. Derouane, *Acta Chim. Hung.* **1985**, *119*, 275–284.

[26] M. E. Davis, *Nature* **2002**, *417*, 813–821.

[27] H. T. Wang, Z. B. Wang, Y. S. Yan, *Chem. Commun.* **2000**, 2333–2334.

[28] H. T. Wang, L. M. Huang, B. A. Holmberg, Y. S. Yan, *Chem. Commun.* **2002**, 1708–1709.

[29] H. T. Wang, B. A. Holmberg, Y. S. Yan, *J. Mater. Chem.* **2002**, *12*, 3640–3643.

[30] D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry, and Use*, Wiley, New York, **1974**.

[31] C. Madsen, C. J. H. Jacobsen, *Chem. Commun.* **1999**, 673–674.

[32] H. Wang, B. A. Holmberg, Y. Yan, *J. Am. Chem. Soc.* **2003**, *125*, 9928–9929.

[33] a) B. T. Holland, C. F. Blanford, A. Stein, *Science* **1998**, *281*, 538–540; b) X. Chen, Z. Cui, Z. Chen, K. Zhang, G. Lu, G. Zhang, B. Yang, *Polymer* **2002**, *43*, 4147–4152.

[34] G. Zhang, Y. Yu, X. Chen, Y. Han, Y. Di, B. Yang, F.-S. Xiao, J.-C. Shen, *J. Colloid Interface Sci.* **2003**, *263*, 461–466.

[35] a) T. K. Bronich, A. V. Kabanov, V. A. Kabanov, K. Yu, A. Eisenberg, *Macromolecules* **1997**, *30*, 3519–3525; b) A. V. Kabanov, T. K. Bronich, V. A. Kabanov, K. Yu, A. Eisenberg, *J. Am. Chem. Soc.* **1998**, *120*, 9941–9942; c) S. V. Solomatin, T. K. Bronich, T. W. Bargar, A. Eisenberg, V. A. Kabanov, A. V. Kabanov, *Langmuir* **2003**, *19*, 8069–8076.

[36] In a typical process, the composite of polymer spheres and zeolite nanocrystals was treated with ethyl acetate to give a mixture of polymer chains and solid zeolite nanocrystals. After centrifugation of the mixture, pure polymer chains dissolved in ethyl acetate were obtained. Then, the polymer solution was slowly dripped into poly(vinyl alcohol) solution (0.5–2 wt%) or sodium dodecyl sulfate (SDS) solution (0.1–0.5 wt%) with stirring at room temperature to form an emulsion. After heating the emulsion at 40 °C for 24 h with stirring, highly dispersed polymer spheres formed, with release of the ethyl acetate in the emulsion.

[37] According to the model (Figure 5), the effective occupational space of each polymer sphere V_s can be calculated from the total volume of solution

$$V_T{:}V_s = k\,V_T/N \tag{2}$$

in which k is the density of a hexagonal close-packed structure (0.7405)[38] and N the number of polymer spheres. N can be calculated from the total weight of the polymer spheres M_T and the weight of a single polymer sphere

$$M_p{:}N = M_T/M_p \tag{3}$$

M_p can be calculated from the density of a single polymer sphere ρ_p and the volume of a single polymer sphere V_p, in which ρ_p is approximately equal to the density of polymer monomer, which could be measured.

$$M_p = \rho_p V_p \tag{4}$$

V_p can be calculated from the radius of a single polymer sphere R_p:

$$V_p = 4\pi R_p^3/3 \tag{5}$$

Combining Equations (2)–(5) gives the following expression for V_s:

$$V_s = k\,V_T \rho_p 4\pi R_p^3/3\,M_T \tag{6}$$

According to the mathematical model (see the Supporting Information), the radius of the confined voids R_v can be calculated from the radius of the effectively occupied space of a single polymer sphere R_s and R_p:

$$(R_v + R_p)/R_s = 2/3^{1/2} \tag{7}$$

$$R_s = (3\,V_s/4\pi)^{1/3} \tag{8}$$

Combining Equations (6)–(8) gives the following equation:

$$R_v = [(2/3^{1/2})\,(k\,V_T \rho_p/\mathrm{M}_T)^{1/3} - 1]\,R_p \qquad (9)$$

in which $k = 0.7405$, $V_T = 10$ mL, and $\rho_p = 1.046\ \mathrm{mL\,g^{-1}}$. Therefore, the relationship between R_v, R_p, and M_T is:

$$R_v \approx [2.29\,M_T^{-1/3} - 1] \times R_p \qquad (10)$$

[38] L. Pauling, *The Nature of Chemical Bond and the Structure of Molecules and Crystals*, Cornell University Press, **1960**.