Ultrasound as a tool to synthesize nano-sized silica–alumina catalysts with controlled mesoporous distribution by a novel sol–gel process

Nan Yao [a], Guoxing Xiong [a,*], Shishan Sheng [a], Mingyuan He [b], Weishen Yang [a], and Xinhe Bao [a]

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, PO Box 110,*
Dalian 116023, PR China
[b] *Research Institute of Petroleum Processing SINOPEC, Beijing 100083, PR China*

Received 18 May 2001; accepted 17 September 2001

A novel sol–gel process is used to synthesize mesoporous silica–alumina catalysts with controlled pore size distribution without using templates or pore-regulating agents. The nitrogen sorption analysis shows that the synthesized materials have high specific surface area in the range 587–692 m^2/g and similar mesoporous distribution within 2–11 nm. Ultrasound is applied to prepare precursor silica–alumina sol with narrow particle diameter distribution. By calculation, it is found that ultrasonic treatment is able to provide 22.94 kJ/mol energy, which is just in accordance with the weak bond's bonding energy. Based on the calculation result, it is proposed that the role of ultrasonic treatment followed by acid peptization is to provide energy to break down the weak bonds. After gelation, the regular and close packing of similar-sized sol particles is capable of formation of controlled-sized interstices which are the precursors of mesopores. Solid-state ^{27}Al MAS NMR and TEM are used to characterize the samples' structure and particle morphology. They show that most of the aluminum is located in the tetrahedral position in the present materials. According to TEM results, it is shown that the synthesized materials have spherical particles with size of about 15 nm.

KEY WORDS: ultrasonic treatment; mesoporous distribution; silica–alumina; catalysts; sol–gel

1. Introduction

As is well known, amorphous silica–alumina materials had been used extensively as catalysts and supports before the introduction of zeolites. Since the mid-1960s, due to the inferior performance of amorphous silica–alumina when compared with zeolites, the interest in amorphous silica–alumina as catalysts decreased, until the recent discovery of silica–alumina with controlled porosity in the mesopore region [1]. It has been found that the amorphous MSA (mesoporous silica–alumina) materials possess catalytic properties similar to those of the zeolites but without the restrictions due to the micropores. For example, Perego and Bellussi *et al.* reported that MSA could be used as catalysts for the alkylation of aromatic hydrocarbons with olefins to produce some important chemical intermediates [2]. The work of Corma, Calemma and Peratello showed that MSA materials are very suitable acidic components for preparing supported metal bi-functional catalysts, which are applied in the olefins oligomerization, hydroisomerization and hydrocracking of long chain *n*-alkane, respectively, due to their controlled mesoporosity and suitable Brønsted acid [3–5].

After the first synthesis of MSA, many attempts were made to prepare this type of material *via* different processes [6–8]. However, all of the preparation pathways mentioned in the literature used various templates and pore-regulating agents such as tetraalkylammonium cations (TMA (methyl) or TBA (butyl)) and tetraalkylammonium hydroxide (TPA-OH) [9–11]. These tetraalkylammonium cations were used with the objective of constructing the mesoporosity structure and regulating most of the aluminum to be located in the tetrahedral position, while at the same time controlling the pore size distribution, the hydrothermal stability and the density of acid sites. As far as we know, no one has described methods of synthesizing silica–alumina materials with controlled mesoporous distribution other than by using templates and pore-regulating agents [12]. In addition, alkoxides were often used as raw materials in the preparation of MSA materials [13–15]. It is clear that the disadvantages of using of alkoxides include the high cost of the raw materials, health hazards of organic solution, pollution, and so on [16].

In this work, we report that a novel sol–gel process, which leads to the formation of controlled mesoporosity, is successfully explored by the utilization of ultrasound. For the first time, this novel preparation method has allowed us to synthesize amorphous SA (silica–alumina) materials with controlled mesoporous distribution, and what is more important, without using any templates or pore-regulating agents. And it can also be noted that cheaper inorganic salts such as aluminum nitrate and water glass solution have been used as raw materials in order to decrease the synthesis cost and diminish pollution.

---

[*] To whom correspondence should be addressed. E-mail: gxxiong@ms.dicp.ac.cn

1011-372X/02/0300-0037/0 © 2002 Plenum Publishing Corporation

Table 1
Specific surface area and pore texture of MSA materials as a function of Si/Al molar ratio

Sample No.	Si/Al molar ratio	pH value[a]	ν_{BJH}[b] (ml/g)	ν_{t}[c] (ml/g)	Specific surface area (m^2/g)	Pore size distribution (nm)
UMSA1	3	2.01	0.305	0.01	587.24	3.20–11.70
UMSA2	7	2.48	0.355	0.01	648.59	3.24–11.23
UMSA3	10	2.55	0.291	0.01	692.54	2.04–10.20

[a] pH value of the precursor sol.
[b] Pore volume calculated by the BJH method.
[c] Pore volume calculated by the *t*-plot method.

2. Experimental

2.1. Synthesis of catalysts

All the chemicals used were AR grade, and the water was deionized and twice distilled. Sufficient ammonium hydroxide (2.5%) was added dropwise to 25 ml of 0.96 M aluminum nitrate solution under vigorous stirring, which brought the pH to about 9.20. The precipitate was collected by centrifugation and then washed by putting it into 50 ml water, and stirred for about 15 min. Washing was continued until the pH of the final suspension was near 7.0. A 0.94 M nitric acid was then added to this aluminum hydroxide suspension until the $[H^+]/[Al^{3+}]$ molar ratio was 0.27. As soon as the addition of the nitric acid was completed, the beaker that contained the suspension was transferred to the cleaning tank of an ultrasonic cleaner. Having been treated by ultrasound for 10 min, a stable alumina sol was obtained. The alumina sol was used as a precursor to prepare MSA.

A necessary amount of nitric acid (0.94 M) was added to 50 ml of a water glass solution (SiO_2 0.78 mol/l, Na_2O 0.25 mol/l) with vigorous mechanical agitation to adjust the pH value to about 10.0. A certain quantity of prepared alumina sol was then added to the water glass solution until the desired Si/Al molar ratio was attained, and the silica–alumina precipitate was formed immediately. Subsequently, a certain amount of a 0.94 M nitric acid, depending on the Si/Al molar ratio, was added to the precipitate to peptize. The beaker that contained the suspension was then transferred to the ultrasonic cleaner for ultrasonic treatment of about 1 min to obtain a stable SA sol. The pH values of SA sols with different Si/Al molar ratios are presented in table 1. During the whole preparation process, the temperature was strictly controlled at room temperature. The temperature of the sol system would not exceed 40 °C even after ultrasonic treatment for 20 min.

When the SA sol formed a homogeneous and lightly opalescent gel at room temperature without agitation, 70 ml of a NH_4NO_3 solution (1.2 M) was added to the SA gel to remove the sodium ions. At the end of 24 h, the solution was drained off by centrifugation, and this procedure was repeated three times. Finally, the gel samples were calcined at 550 °C in air for 10 h to obtain the solid samples. The preparation process is shown schematically in figure 1.

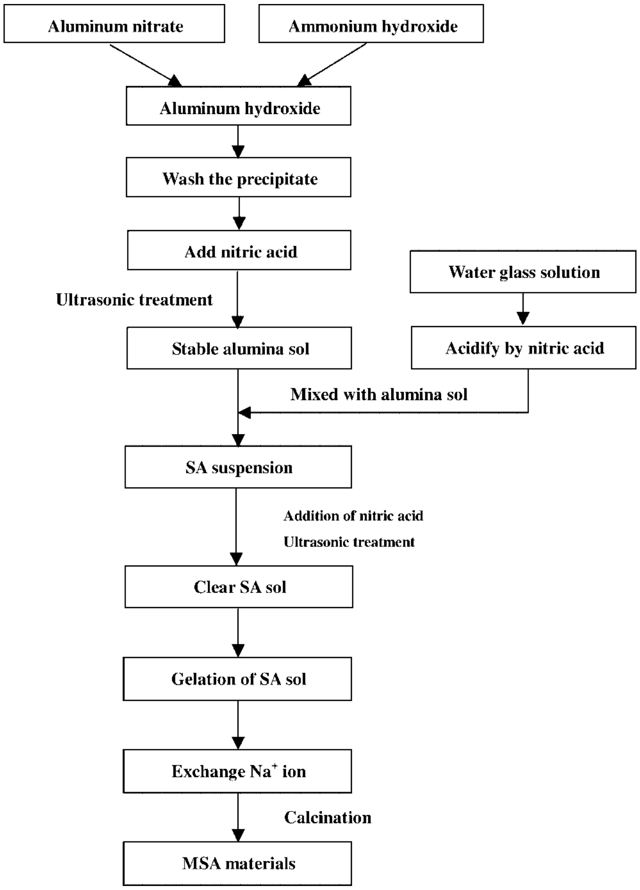

Figure 1. Scheme for preparing MSA materials by utilization of ultrasound.

2.2. Characterization of catalysts

The pH values of the sol samples were monitored using a Cole–Parmer 5986-50 pH meter. An M4 density meter was used to measure the density of the liquid medium. The crystalline phases of solid samples were analyzed by powder X-ray diffraction with a Rigaku D/MAX-RB using a copper target at 40 kV and 100 mA. An SB2200 commercial ultrasonic cleaner from Branson was used as the ultrasound source. The operating frequency of this ultrasonic cleaner is 50 kHz.

N_2 adsorption–desorption isotherms of these MSA materials at 77 K were obtained by a static volumetric method with an Omnisorp-100CX apparatus from Coulter. The solid samples were first degassed at 350 °C under vacuum (10^{-6} Torr) for at least 3 h before recording their isotherms. From the adsorption isotherm, the Barrett, Joyner and Halenda theory (BJH) was used to calculate the mesopore volume and the mesoporous distribution, and the t-plot method was applied to calculate the micropore volume.

Solid-state ^{27}Al MAS NMR spectra of solid samples were run at 104.3 MHz at a spinning rate of 8 kHz on a DRX400 NMR spectrometer (Bruker). A 0.75 μs pulse width was used, along with 2.0 s delay time, 600 acquisition times and a 23.58 kHz spectral width. Chemical shifts were referenced to 1 M $Al_2(SO_4)_3$ solution.

TEM was performed on a JEM1200EX transmission electron microscope with a 100 kV accelerating voltage. The solid specimen was crushed into powder, embedded in copper metal and polished on both sides of the specimen until the powder was exposed. Then ion etching was performed to make the specimen transparent to electrons. In order to keep the original structure of the powder, neither high temperature treatment nor chemicals including acid and base were used during the specimen preparation for TEM [17].

3. Results and discussion

In all cases, the crystalline phases of synthesized solid samples were amorphous (the XRD profiles are not shown in this paper). The main pore textures and specific surface areas of samples are listed in table 1, where $v_{\rm BJH}$ and $v_{\rm t}$ are the pore volumes calculated by the BJH and t-plot method, respectively. It is seen that the synthesized solids have high specific surface areas, and the values diminish as the Si/Al molar ratio decreases. In table 1, a noticeable feature is the pore size distribution. It is clear that these MSA materials have similar and narrow pore size distribution, though they have different Si/Al molar ratios. This property is different from the results reported in the literature [6]. Usually, the BJH method can only be used to calculate a material's mesoporous distribution. For checking the existence of micropores, the t-plot method is applied. The result suggests that very few micropores were detected in the samples.

In this work, in order to obtain a clear elucidation, the UMSA3 solid sample is selected as representative example to exhibit some physico-chemical characteristics of the synthesized materials. Figure 2(A) shows UMSA3 solid sample's N_2 adsorption–desorption isotherms. The sample shows a broad, but well-defined, step in the adsorption isotherm curve for P/P_0 partial pressures ranging from 0.4 to 0.75, which is indicative of the filling of the framework-confined mesopores. A plateau with a slight inclination appears at high relative pressures between P/P_0 0.75–0.98 in the adsorption isotherm. This plateau is associated with multilayer adsorption on the external surface of the materials. There is no sharp rise in N_2 uptake as the pressure reaches saturation (P/P_0 reaches 1), which indicates that no macropores exist in the material [18].

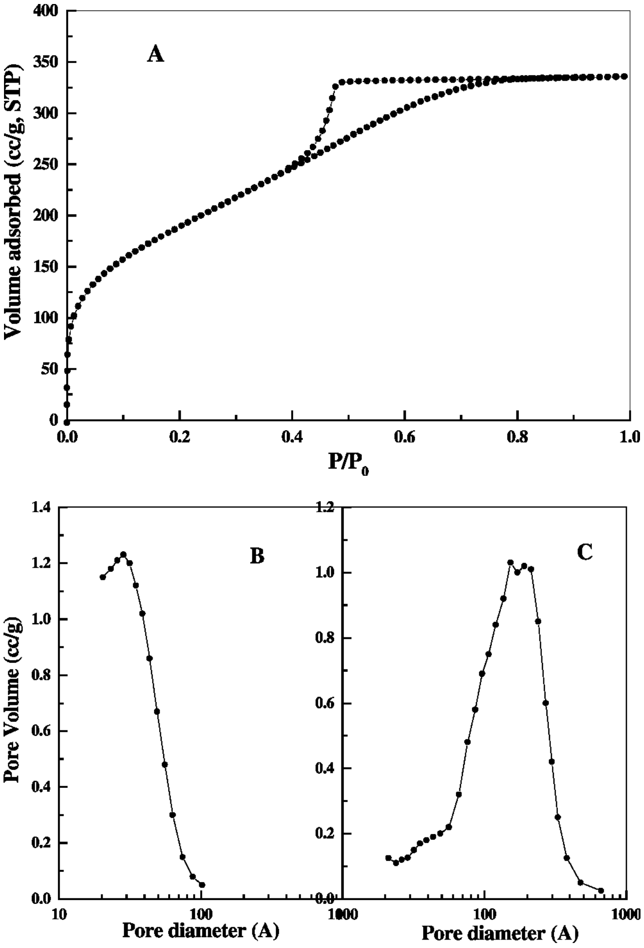

Figure 2. (A) N_2 adsorption–desorption isotherm of the UMSA3 solid sample. (B) Pore size distribution of the UMSA3 solid sample. (C) Pore size distribution of a solid sample prepared by conventional co-gel method.

On the other hand, a hysteresis loop is also observed in this case, thus indicating the existence of a well-developed mesoporous texture. And the shape of the hysteresis loop agrees with type H2 of IUPAC classification. Generally, the desorption branch is often chosen to calculate the material's pore size distribution. However, by taking into account the recent study [19], the calculation of pore size distribution of samples presenting H2-type hysteresis loops has to be done using the adsorption branch and not the desorption branch. The location of the latter is largely controlled by network-percolation effects and is thus unsuitable for the pore size distribution calculation. For this reason, in our case the calculation was performed starting from the data obtained in the adsorption branch. Figure 2(B) shows the UMSA3 sample's pore size distribution. In contrast, figure 2(C) shows the pore size distribution of silica–alumina sample prepared by the conventional co-gel method. It is obvious that the present method can synthesize silica–alumina materials with narrow mesoporous distribution. Hence, the results shown in table 1 and figure 2 imply that, without using any organic templates or pore-regulating agents, the mesoporous materials with controlled pore size distribution and high specific surface area can be successfully obtained with the developed method.

Figure 3 displays the ^{27}Al MAS NMR spectrum of the solid sample. Only a large peak centering near 50 ppm can

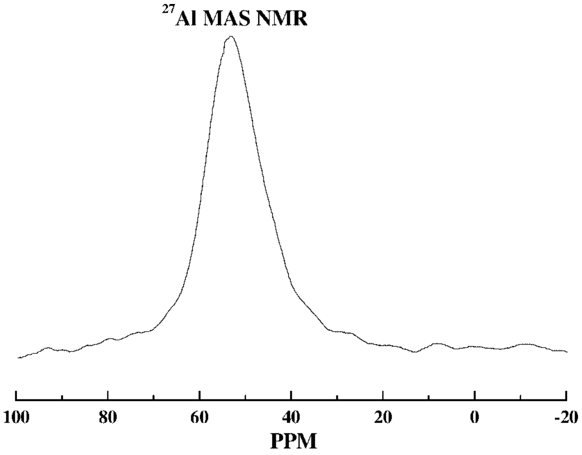

Figure 3. ^{27}Al MAS NMR spectrum of the UMSA3 solid sample.

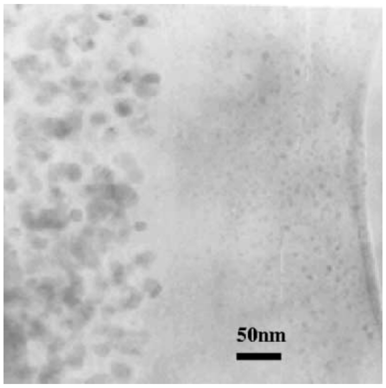

Figure 4. TEM micrograph of UMSA3 solid sample.

be observed, which is assigned as tetrahedrally coordinated aluminum. It is very interesting to note that most of the aluminum is located in the tetrahedral position. As mentioned above, the effect is being exerted to synthesize amorphous MSA with a high content of tetrahedral aluminum in order to obtain stronger Brønsted acid sites in the materials. And this is one of the reasons why many researchers choose tetraalkylammonium cations as pore-regulating agents during the preparation of MSA materials. In this study, the noted result of ^{27}Al MAS NMR characterization reveals that, according to our novel method, the silica–alumina materials with high content of tetrahedrally coordinated aluminum can be synthesized without using any type of tetraalkylammonium cations.

Figure 4 shows the morphology of particles in the solid sample, as observed by TEM. Two features of the micrograph deserve special comment. First, it is shown that there is neither apparent order nor shape in the pore arrangement, which is different from the shapes of the pores existing in the M41S mesoporous molecular sieves. In fact, such ordered mesostructure existing in the M41S materials are formed from the electrostatic assembly process between inorganic precursor and organic template [20]. Second, it is clear that there are pure nanoparticles with similar size of 15 nm in the solid sample; and this feature may be used to interpret the results reported in table 1, which show that the MSA materials have high specific surface area and controlled mesoporous distribution. Moreover, it can be noticed that this is one of the important advantages of the present method. It is thus concluded that the developed method is able to synthesize nanomaterials.

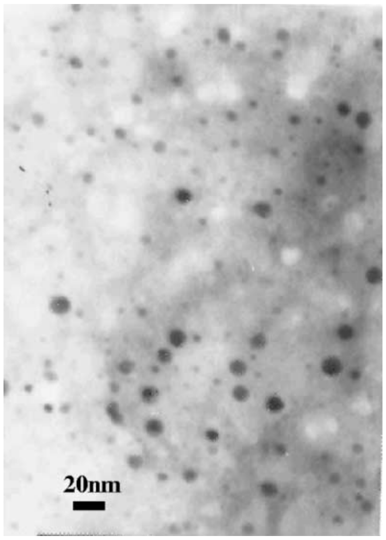

Figure 5. TEM micrograph of UMSA3 precursor sol sample.

The reported synthetic approach is based on a very simple idea that the regular packing of sol particles with similar size should essentially give rise to the controlled mesoporosity in the final solid. Therefore, the first problem to be resolved is how to prepare a stable sol with narrow particle diameter distribution. But as a matter of fact, it has been found that no matter how long a time and how vigorous mechanical stirring were used after the addition of the nitric acid, a stable silica–alumina sol could not be formed at room temperature.

Recently, ultrasound has found many new applications in chemistry, because it provides a form of energy that can modify the chemical reactivities in different ways [21]. Hence, our attention is drawn to the possibility of utilizing ultrasound as a tool to obtain stable sols, together with the use of an acid. Figure 5 shows the particle morphology of the UMSA3 sol sample. It is clear that spherical particles with a size of 10 nm disperse well in the sol system. The result indicates that stable sols with narrow particle diameter distribution can be obtained by treatment with ultrasound.

In this study, the sol system's temperature was measured during the ultrasonic treatment. It showed that the temperature was not higher than 40 °C even after ultrasonic treatment for 20 min. So the heat effect is not a main factor. A possible explanation for the effect of ultrasonic treatment is described below. It is known that, when a solid–liquid mixture is treated ultrasonically, the cavitation bubbles formed in the rarefaction cycle undergo unsymmetrical collapse near the solid surface, which causes "in-rush" of the liquid into the solid. This effect is called "microjet formation" or "microstreaming", wherein the velocity of the in-rushing liquid is as high as 100 m/s [22,23]. Therefore, according to equation (1), the ultrasonic treatment can provide 22.94 kJ/mol energy, which is in agreement with the bond energy of weak bonds such as the hydrogen bond or van der Waals force. It is thus reasonable to suggest that the ultrasonic treatment is able to provide enough energy to break down weak bonds which lead to particle aggregation.

$$\begin{aligned} &\rho = 1180\ \mathrm{kg/m^3}, \quad V = 70\ \mathrm{ml}, \\ &M = 18\ \mathrm{g/mol}, \quad v = 100\ \mathrm{m/s}, \\ &w = \frac{1}{2}\frac{m}{M}v^2 = \frac{1}{2}\frac{V\rho}{M}v^2 = 22.94\ \mathrm{kJ/mol}, \end{aligned} \tag{1}$$

where W – molar energy, m – mass, ρ – density of the bulk liquid medium, V – volume of liquid medium, v – velocity, M – molar mass of water.

Based upon the above calculation, we would like to suggest that ultrasonic treatment and acid peptization have a co-operative effect to produce a stable sol. During the preparation, after the addition of the acid, the precipitate was peptized to small sized particles. But at room temperature, these small particles aggregate together due to the fact that the system has hardly enough energy to break down the weak bonds that cause this aggregation. Therefore, a sol system cannot be formed. Since enough energy can be provided by the ultrasonic treatment, the ultrasound applied immediately after the addition of the acid can smash these weak bonds to form a stable sol. After gelation, these similar-sized sol particles will regularly and closely pack together; the fluid-filled interstices are the precursors of the mesopores in the final materials. In summary, ultrasonic treatment is the vital factor for a successful preparation under our experimental condition. More detailed study on the effect of ultrasonic treatment will be reported in our succeeding research.

4. Conclusions

The present work provides a novel synthesis method for preparing nano-sized silica–alumina catalysts with controlled mesoporous distribution, large specific surface area and high content of tetrahedrally coordinated aluminum, which are attained by regular packing of similar-sized sol particles. The application of ultrasonic treatment, which provides energy to smash the weak bonds to obtain a stable precursor sol at room temperature, is the indispensable step during the whole preparation process. Thus, besides the electrostatic assembly process which is often used to design various types of mesostructure in the materials, this novel preparation process provides another method to synthesize nanomaterials with controlled mesoporous distribution without using organic templates and pore-regulating agents.

Acknowledgment

We are grateful to Ms. Xiumei Liu for acquiring the NMR spectra with DRX 400. The financial support from the Chinese Academy of Sciences (No. KJ951-Al-508), the Research Institute of Petroleum Processing SINOPEC (No. X599007) and the National Sciences Foundation of China (No. 20073043) is also acknowledged.

References

[1] A. Corma, J. Perez-Pariente, V. Fornes, F. Rey and D. Rawlence, Appl. Catal. 63 (1990) 145.
[2] C. Perego, S. Amarilli, A. Carati, C. Flego, G. Pazzuconi, C. Rizzo and G. Bellussi, Micropor. Mesopor. Mater. 27 (1999) 345.
[3] A. Corma, A. Martinez, S. Pergher, S. Peratello, C. Perego and G. Bellusi, Appl. Catal. A 152 (1997) 107.
[4] S. Peratello, M. Molinari, G. Bellussi and C. Perego, Catal. Today 52 (1999) 271.
[5] V. Calemma, S. Peratello and C. Perego, Appl. Catal. A 190 (2000) 207.
[6] B.M. De Witte and J.B. Uytterhoeven, J. Colloid Interface Sci. 181 (1996) 200.
[7] R. Snel, Appl. Catal. 11 (1984) 271.
[8] J.P. Reymond, G. Dessalces and F. Kolenda, Stud. Surf. Sci. Catal. 91 (1995) 453.
[9] G. Bellussi, C. Perego, A. Carati, S. Peratello, E.P. Massara and G. Perego, Stud. Surf. Sci. Catal. 84 (1994) 85.
[10] G. Perego, R. Millini, C. Perego, A. Carati, G. Pazzuconi and G. Bellussi, Stud. Surf. Sci. Catal. 105 (1997) 205.
[11] G. Bellussi, M.G. Clerici, A. Carati and F. Cavani, US Patent 5 049 536 (1991).
[12] S. Biz and M.L. Occelli, Catal. Rev. Sci. Eng. 40 (1998) 330.
[13] R.D. Gonzalez, T. Lopez and R. Gomez, Catal. Today 35 (1997) 293.
[14] G.A. Pozarnsky and A.V. McCormick, J. Non-Cryst. Solids 190 (1995) 212.
[15] C. Hernandez and A.C. Pierre, Langmuir 16 (2000) 530.
[16] C.J. Brinker and G.W. Scherer, *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing* (Academic Press, Harcourt Brace Jovanovich, 1990) p. 840.
[17] X.F. Zhang and Z. Zhang, *Progress in Transmission Electron Microscopy, I. Concepts and Techniques* (Tsinghua University Press, Springer, 1999) p. 353.
[18] S.J. Gregg and K.S.W. Sing, *Adsorption, Surface Area and Porosity*, 2nd Ed. (Academic Press, New York, 1982).
[19] F. Rouquerol, J. Roquerol and K.S.W. Sing, *Adsorption by Powders and Porous Solids* (Academy Press, London, 1999).
[20] S.A. Bagshaw and T.J. Pinnavaia, Angew. Chem. Int. Ed. Engl. 35 (1996) 1102.
[21] S.S. Kenneth, H.A. David and C.E. Raymond, Jr., J. Am. Chem. Soc. 108 (1986) 5641.
[22] T.J. Mason, Chem. Soc. Rec. 26 (1997) 443.
[23] L.H. Thompson and L.K. Doraiswamy, Ind. Eng. Chem. Res. 38 (1999) 1215.