Thermal-Degradation Process Analysis of Mesoporous Silica in Different Atmospheres

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The thermal-degradation process of the mesoporous structure in silica MCM-41 was investigated in the present research via a series of thermal-stability experiments in different atmospheres with varied technique analysis (N_2-sorption, XRD, IR, and NMR spectra). The research showed that the atmosphere was also a very important factor to affect the thermal stability of mesoporous silica as well as the temperature and time; the oxygen atmosphere obviously accelerated the degradation process of the ordered pore structure in mesoporous silica. We considered that the thermal vibration of atom groups, silanol condensation, and the reconstruction of bridge oxygen bonds between SiO_4 tetrahedra in the mesopore wall can be the main causes resulting in the contraction of the inorganic networks and the degradation of the pore structure in mesoporous silica. The oxygen molecule could play an important role during the heat treatment. The oxygen can not only promote silanol condensation, but also make some original bridge oxygen bonds rupture more easily, and then the ruptured units immediately reconstruct more stable bonds with other ruptured units, SiO_4, which results in the contraction of inorganic networks and degradation of the mesoporous structure.

Ordered mesoporous silica materials open up the possibilities for shape-selective conversions of bulky molecules, such as those encountered in the manufacture of fine chemicals and pharmaceuticals.[1] For practical applications, a catalyst needs not only a high initial catalytic activity, but also needs good stability under the process conditions. Therefore, the stability of mesoporous materials is a crucial factor in their potential applications. After studies for about 10 years, the stability of mesoporous silica materials was greatly improved.[2–5] So far, however, the stability of these materials still limits their broader application. Improving the stability of these materials is being kept a very important job in the field. Some authors have reported that the structural instability of mesoporous silica materials was due to the hydrolysis of the bare Si–O–Si bonds in the presence of adsorbed water.[6–8] Again, the structure of mesoporous silica could also be destroyed under mechanical compression due to the mechano-chemical hydrolysis of Si–O–Si bonds.[5,6]

At the present time, all of the reported studies concerning the thermal stability of mesoporous silica materials were performed in air, but ignored effects of the atmosphere. No systematic analysis was performed to study the thermal-degradation process of mesoporous silica. In the present work, we deeply investigated the effect of the atmosphere on the thermal stability of mesoporous silica by a variety of techniques (N_2-sorption, low-angle XRD, IR, and NMR spectra), analyzed the thermal-degradation process of the materials, and presented available mechanisms.

Experimental

Sample Preparation. The MCM-41 samples used were synthesized by a sol–gel method. In a typical preparation route, 1.20 g of NaOH was added into 200 mL of deionized water, followed by the addition of 4.85 g of cetyltrimethylammonium bromide (CTAB). After the mixture was stirred for about 1 h at 35 °C, 24.8 mL of tetraethylorthosilicate (TEOS) was added into the colloidal product by slowly dropping with vigorous stirring. Finally, the slurry was stirred for 2 h to obtain a homogeneous mixture at 35 °C. The final gel was then loaded into autoclaves and heated at 110 °C under autogenous pressure for 48 h. The resulting gel mixture had a chemical composition of $1.00SiO_2$–0.12CTAB–$0.12Na_2O$–$100.0H_2O$. The solid products were obtained by filtrating, washing with deionized water, and drying at 80 °C for 24 h in a vacuum dryer. Templates were removed at 550 °C for 12 h.

Heat Treatment of MCM-41. Thermal-stability experiments were accomplished by heating MCM-41 powder in various atmospheres in an alumina boat, which was inserted into a flow-through quartz-tube furnace at desired temperatures. The flow rate of gas was 400 mL/min. The quartz tube was evacuated several times and flushed with various gases (air, oxygen, and nitrogen accordingly) before the run was started. The powders obtained after the treatment were denoted as G–*T*–*t*, where G is the gas; *T*, the treatment temperature (°C); and *t*, the treatment time (h), as used in the following sections; for example, N_2–1000–12 means a sample treated at 1000 °C for 12 h in N_2 gas.

Characterization. Low-angle XRD was carried out on a D/max2550V diffractometer (40 kV, 100 mA) with a 0.02° step size over a range of $1.8° < 2\theta < 10°$ to determine the structure stability. The nitrogen sorption characterization was conducted on a Micromeritics ASAP2010 surface area and a pore size analyzer at −196 °C using accompanying software from Micromeritics. The surface areas were calculated by using the conventional BET method. The pore parameters were calculated from the desorption branches of these isotherms using the BJH method. The *t*-plot was

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used to show the pore size change. A Perkin-Elmer 1600 FT-IR spectrometer was used to record infrared spectra of the MCM-41 samples before and after a heat-treatment, in the range of 400–2000 and 3100–4000 cm^{-1} to provide useful information about the sample surface. The MAS ^{29}Si NMR Spectra (Bruker DSX-300) without a cross-polarization (CP) technique were obtained at a frequency of 59.62 MHz and a spinning rate of 4 kHz with 90° pulses of 5 µs and a relaxation delay of 600 s.

Results and Discussion

Reduction in Surface Area and Pore Size. The textural properties of MCM-41 materials are listed in Table 1, before and after a heat treatment in different atmospheres. These data show that the thermal stability of the mesoporous silica is severely affected by the atmosphere. Although the surface area and the pore volume of the samples treated in air were higher than in oxygen, their differences were smaller. However, the samples treated in nitrogen had the highest surface area, and also the highest pore volume at a same temperature and time level. The results indicated that the oxygen-containing atmosphere should be an important reason for decreasing the stability of mesoporous silica. In addition, the pore size reduced after the heat treatment and the pore volume reduced more considerable than the surface area for all situations. This phenomenon can indicate that the reduction in pore size is a major process during the thermal degradation of MCM-41 materials at the present heating temperature.

The pore structure of some contrast samples before and after the treatment was evaluated by N_2 sorption isotherms; the pore-size distribution is also shown in Fig. 1. For the N_2 effects, the sample N_2–1000–12 exhibited a type-IV isotherm with a typical capillary condensation step into uniform pores, but without the hysteresis, seen in Fig. 1A. With temperature or holding time's increasing, the pore structure of mesoporous silica might degrade slowly, as the situation in N_2–1030–12 (at higher temperature) and N_2–950–100 (after a long time even at a relatively mild treatment condition). However, in an O_2 atmosphere, the mesoporous structure seriously collapsed under higher temperature conditions, as sample O_2–950–12, which exhibits a type-I isotherm showed in Fig. 1B. Otherwise, from the pore-diameter figures at the upper left hand corner in Figs. 1A and 1B, the pore size for all samples was obviously reduced after undergoing the heat treatment.

Further details about the structural characteristic of three typical samples (O_2–950–12, N_2–950–100, and N_2–1030–12) with a degraded mesoporous structure are presented in *t*-plots (Fig. 2). Generally, the *t*-plots are considered to be graphs of the N_2 volume adsorbed (v) vs thickness of adsorbed (*t*) on the mesopores surface (inner and outside) when conducting the nitrogen sorption characterization, which can distinguish

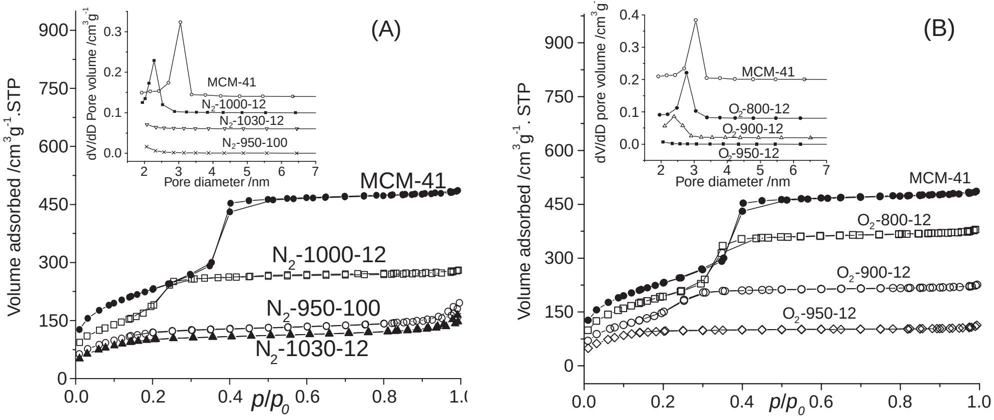

Fig. 1. N_2 sorption isotherms and pore size distribution of samples treated in different atmosphere (A) in nitrogen; (B) in oxygen.

Table 1. Structural Parameters of MCM-41 before and after Heat Treatment in Different Atmosphere

Sample	A (BET)/$\mathrm{m^2\,g^{-1}}$	V (BJH)/$\mathrm{cm^2\,g^{-1}}$	D (BJH)/Å
MCM-41	882	0.82	30.4
Air–800–12	790	0.61	28.2
Air–900–12	680	0.48	26.1
Air–950–12	435	0.12	—
O_2–800–12	745	0.60	28.2
O_2–900–12	600	0.42	25.3
O_2–950–12	382	0.05	—
N_2–950–12	838	0.69	29.3
N_2–950–100	440	0.19	—
N_2–1000–12	741	0.58	28.5
N_2–1030–12	362	0.09	—

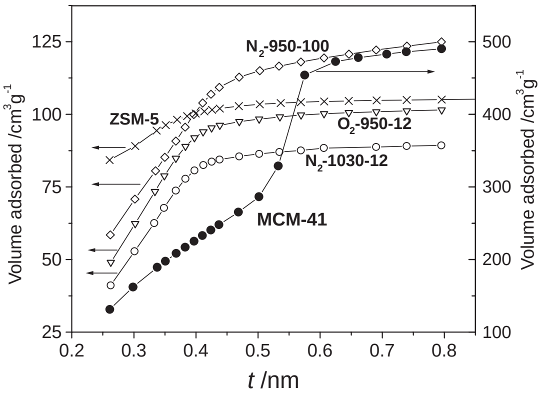

Fig. 2. *t*-Plots of samples O_2–950–12, N_2–950–100, and N_2–1030–12, with contrast samples: micropore ZSM-5 and mesopore MCM-41.

any difference in the pore structure. In Fig. 2, the horizontal departures from a straight line segment indicate the presence of micropores, using a typical curve of micropore ZSM-5 as a reference. Further, the vertical departures reveal the presence of mesopores in the *t*-plot figure, with a typical curve of mesopore MCM-41 as a reference in Fig. 2 either. The *t*-plots in Fig. 2 show that all samples after heat-treatment had the structural characteristic of microporous materials, and had similar shapes in *t*-plots with zeolite ZSM-5. This information also clearly shows that a large number of mesopores (MCM-41-like) had transferred into micropores (ZSM-5-like) after long-time thermal degradation.

The structural ordering among the samples (MCM-41, O_2–900–12, N_2–950–12, and N_2–1000–12) was assessed by the XRD method. As shown in Fig. 3, the intensity of all the diffraction peaks for the treated samples obviously decreased, which implies that the structural ordering of MCM-41 degraded after the heat treatment. It is also found that all diffraction peaks shift to higher 2θ angles, which indicates contraction of the MCM-41 lattice after the thermal process. A closer examination of these X-ray patterns reveals that the intensity of diffraction (100) of sample O_2–900–12 was the lowest, and the contraction of lattice was also the most severe among the four samples.

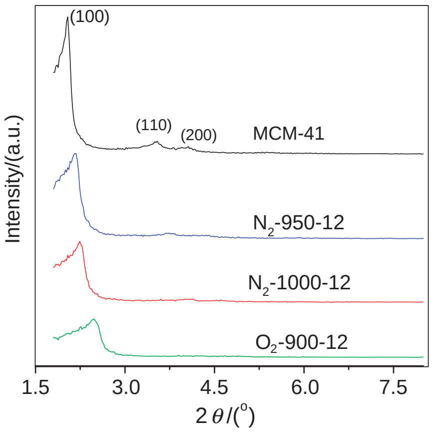

Fig. 3. Low-angle XRD patterns of contrast samples: MCM-41, O_2–900–12, N_2–950–12, and N_2–1000–12.

Change of Symmetry and Aggregation in Inorganic Network. The nature of the framework in mesoporous silica can be effectively assessed from infrared (IR) spectroscopy studies.[9] Figure 4 shows the infrared spectra of some contrast samples (MCM-41, O_2–950–12, and N_2–950–12). The three well-known vibration modes of amorphous SiO_2-like are clearly visible in Fig. 4A. The absorption band near 1100 cm^{-1} corresponds to the asymmetric stretching mode of Si–O–Si from SiO_4 tetrahedra groups, the absorption band near 475 cm^{-1} corresponds to the symmetric bending mode of O–Si–O, and the absorption band near 800 cm^{-1} corresponds to a symmetric bending mode of Si–O–Si. As shown in Fig. 4A the intensity of the absorption bands near 475 cm^{-1} and 800 cm^{-1} in the sample O_2–950–12 are much higher than the values of MCM-41 and N_2–950–12. The major absorption band at ~1100 cm^{-1} becomes obviously wider in the sample O_2–950–12. The above information implies that the symmetry and aggregation degree of inorganic networks SiO_4 of sample O_2–950–12 were obviously improved after a heat treatment in oxygen environment. The absorption band at ~960 cm^{-1} corresponds to the vibration mode of the silanol groups (SiOH) in mesoporous silica MCM-41. However, this absorption band has disappeared in the spectra of the sample O_2–950–12. In addition, the IR spectra of the SiOH groups in the higher wave number range of 3100–4000 cm^{-1} generally possess three kinds of characteristics: single SiOH groups with an IR absorption band at 3738 cm^{-1}; hydrogen-bonded SiOH groups with a band at 3200–3600 cm^{-1}; and geminal SiOH groups also with a band at 3738 cm^{-1}. Figure 4B clearly shows that the intensity of absorption at 3200–3800 cm^{-1} in the sample O_2–950–12 is much lower than the values of MCM-41 and N_2–950–12, which gives evidence that the number of free or hydrogen-bonded or geminal SiOH groups greatly decreases after a heat treatment in an oxygen environment. The above information shows that the silanol groups may be more prone to condensation after a heat treatment in oxygen than in a nitrogen atmosphere.

In order to further investigate the effect of different atmosphere conditions on the structure in a mesoporous framework after a heat treatment, ^{29}Si MAS NMR spectra of the three contrast samples (MCM-41, O_2–950–12, and N_2–950–12) were examined, as shown in Fig. 5. Based on the literature,[9,10] it is

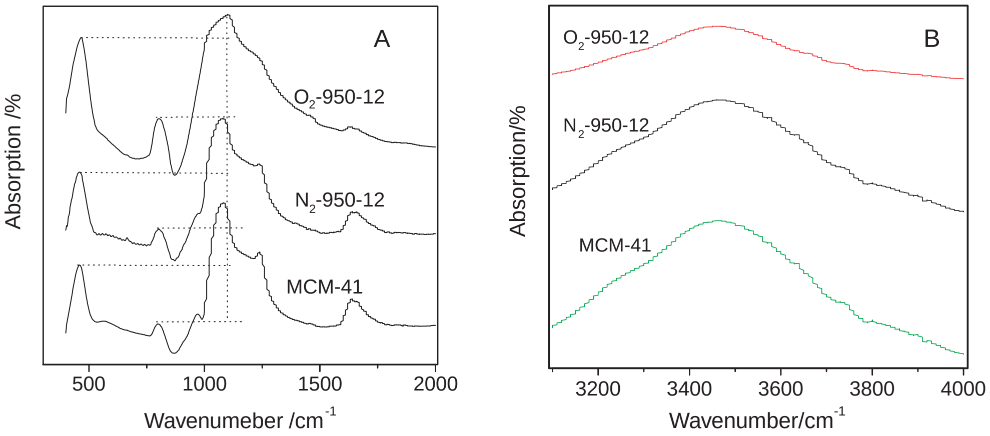

Fig. 4. IR spectra of contrast samples: A) 400–2000 cm^{-1}; B) 3100–4000 cm^{-1}.

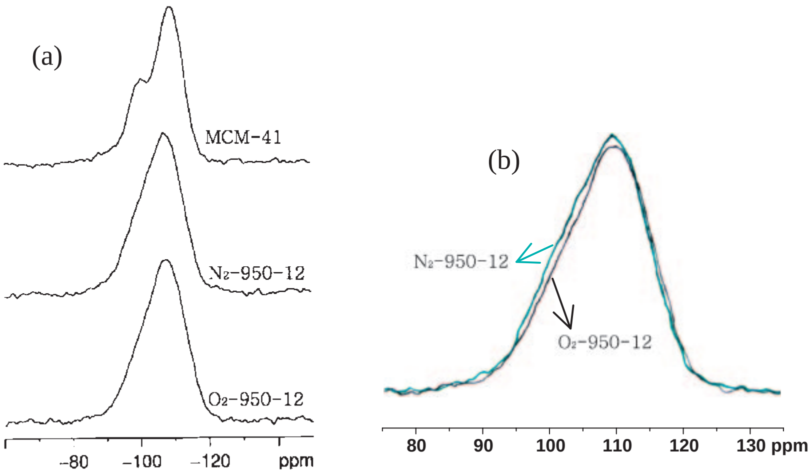

Fig. 5. ^{29}Si MAS NMR spectra of contrast samples: MCM-41, O_2–950–12, and N_2–950–12.

known that the chemical shifts for silica $(SiO)_4{*}Si$ (Q^4) (right), $(SiO)_3{*}SiOH$ (Q^3) (middle), and $(SiO)_2{*}Si(OH)_2$ (Q^2) (left) are approximately −110 ppm, −101 ppm, and −92 ppm in the ^{29}Si MAS NMR spectra, respectively. Obviously, the spectra shape of the samples N_2–950–12 and O_2–950–12 are different from the one of the original sample, MCM-41 (seen in Fig. 5a), which indicates that the SiOH or $Si(OH)_2$ groups decrease after a heat treatment at higher temperatures and for a long time. In fact, the difference in the spectra between samples N_2–950–12 and O_2–950–12 can be more important for our understanding the effects of an oxygen-containing or an un-oxygen-containing atmosphere; then, an accurate comparison for the two NMR spectra (N_2–950–12 and O_2–950–12) was made (Fig. 5b). It was found that the downfield of the signal for sample N_2–950–12 was slightly convex, but for sample O_2–950–12 the downfield of the signal was slightly concave. This information indicates that the numbers of SiOH and $Si(OH)_2$ groups were much lower after the heat treatment in oxygen than in nitrogen, which corresponds to the results of the IR spectra. Otherwise, according to the fit results by mixed Lorentzian and Gaussian, the areas of Q^3 and Q^4 were calculated and the ratios of Q^3 to Q^4 for samples N_2–950–12 and O_2–950–12 were 0.56 and 0.46, respectively. The result supports the idea that an oxygen atmosphere plays an obvious role for substitution of the terminal OH group by a heat treatment at higher temperatures, and for a long time. The heat-treatment process in oxygen can more easily make SiO_4 networks distort and contract, make more SiOH groups close to each other, and finally result in the dehydroxylation of SiOH groups.

Thermal-Degradation Mechanisms Analysis. According to the above experimental results, the thermal-degradation process of the pore structure for MCM-41 materials after heat treatment in gas can be described according to the following scheme: the reduction of mesopores occurs first, and then the aggregation of inorganic networks. The contraction of inorganic networks is not only related to temperature and time, but also closely related to atmosphere (Chart 1).

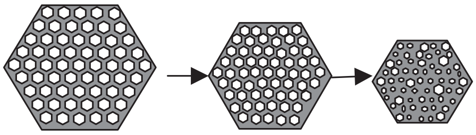

Chart 1.

Except for the contraction of inorganic networks, the distortion and contraction of inorganic networks SiO_4 is one of the important reasons. The thermal vibration of atoms or groups caused by heat activation makes the bond length of some original bridge oxygen bonds between SiO_4 gradually lessen, and also makes the bond angle of the same bridge bonds to be gradually regulated. In addition, the silanol condensation is also an important factor, resulting in the contraction of inorganic networks. Since a large number of silanol groups lie in the inorganic networks of mesoporous silica, the contraction of inorganic networks that results from silanol condensation is also considerable, which results in improving the symmetry and aggregation degree of inorganic networks. The silanol condensation may be related to the oxygen-containing atmosphere; furthermore, oxygen could be helpful to silanol condensation, which is coincident with the IR spectra (Fig. 4) and the NMR spectra (Fig. 5) analysis above.

The reconstruction of the new bridge oxygen bonds can be another more important reason for the structure degradation of mesoporous silica. Since the structural stability of SiO_4 in MCM-41 is between those in fused SiO_2 and crystallized SiO_2, the local variations in the Si–O–Si bond angles and the lengths in MCM-41 are to be expected. Thus some of the original bridge oxygen bonds between SiO_4 with a lower bond energy first rupture due to the thermal vibration at higher temperatures, and disturbing the oxygen environment. The ruptured units then reconstruct into some more stable bridge bonds with other ruptured atom groups around, which leads to improvements of the symmetry and aggregation of the inorganic networks SiO_4. Here, we must mention the effect of oxygen on the process described above. The oxygen molecules (O_2) in the environment disturb the thermal vibration of the SiO_4 atom groups, while make some weaker bridge oxygen atom bonds more easily broken away from the bondage with the original Si atoms when all atom groups SiO_4 are vibrating; then, reconstruction of more stable bonds occurs. Thus, the structure of mesoporous silica is much easier to degenerate during a heat treatment in an oxygen atmosphere.

Conclusion

In the present work, the thermal stability of mesoporous silica in different atmosphere was systematically investigated by a large number of experiments. The results showed that the atmosphere is also a very important factor that affects the thermal stability of mesoporous silica as well as the temperature and time; oxygen-containing gas can accelerate the degradation of the ordered pore structure in mesoporous silica. The contraction of inorganic networks results in a degradation of the pore structure in mesoporous silica.

We consider that the thermal vibration of atom groups SiO_4, silanol (SiOH and $Si(OH)_2$) condensation and the reconstruction of bridge oxygen bonds between SiO_4 can arouse the contraction of inorganic networks. Furthermore, an oxygen-containing atmosphere could play an important role in silanol condensation and the reconstruction of bridge oxygen bonds, which would accelerate the contraction of inorganic networks and degradation of the pore structure.

The thermal degradation of mesoporous silica is completely different from hydrothermal degradation, in essence. Hydrothermal degradation greatly decreases the aggregation of inorganic networks by the hydrolysis of Si–O–Si bonds. However, the thermal degradation of mesoporous silica accompanies improving the symmetry and aggregation of inorganic networks. According to this mechanism analysis, improving aggregation of inorganic networks is an effective way to improve the thermal stability of mesoporous silica. Mesoporous silica as a high-temperature catalyst is more suitable to use in non-oxygen environments.

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