Rapid and Deep Nitridation of Silica MCM-41 without Loss of Hexagonal Pore Structure

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The nitridation of mesoporous silica MCM-41 with ammonia was carried out by using a plug flow-type reactor. The degree of nitridation was dependent on the amount of NH_3 supplied. Mesoporous silicon oxynitride containing 34 wt % of nitrogen could be prepared at 1273 K for 8 h, and the hexagonal mesoporous structure was maintained.

Silicon nitride and oxynitride are recently reported to be applicable to solid-base catalysts[1,2] and catalyst supports[3] as well as well-known high-temperature ceramics.[4] Mesoporous analogues would become more valuable as functional materials; therefore, mesoporous silicon nitride (MSN) and oxynitride (MSON) were indeed tried to be prepared by decomposition of silicon diimide or nitridation of silica. The former gave porous Si_3N_4, but the pore structure was irregular.[1] The nitridation of ordered mesoporous silica was attempted by NH_3 treatment on MCM-41 (M41),[5] -48,[2] and SBA-15[6] at 1173–1423 K. The maximum nitrogen contents, however, were 25.1 wt %[5] or lower, which are far from 40 wt % of Si_3N_4. In addition, all previous works required long operation time of ca. 20 h at 1423 K.[5] The increment in the nitrogen content and the short nitridation time are now the objectives of the studies in this field. We applied here a plug flow reactor for nitridation of the mesoporous silica M41 with ammonia and could prepare MSON with high nitrogen contents in relatively short reaction time at 1273 K.

The M41 sample was prepared by using colloidal silica and dodecyltrimethylammonium bromide as the starting materials.[7] The M41 obtained was washed with deionized water, kept in a hydrochloric acid solution at pH 6.5 and 353 K for 20 h, and finally calcined at 873 K for 6 h in air to remove organic component. Silica gel was prepared under the vigorous stirring of the same starting materials as those used for the preparation of M41. The KJS pore diameter (see the later section) of the parent M41 obtained was 3.1 nm. The nitridation of mesoporous silica was carried out in a plug flow reactor of quartz (id. 10 mm). After M41 sample was mounted into the reactor, 50 mL/min of N_2 was flowed and the reactor was heated at a desired temperature at a rate of 5 K/min. Pure NH_3 gas was introduced into the reactor at the temperature, and the flow rate of NH_3 was set at 300 mL/min unless otherwise stated. The resulting samples were characterized by XRD and FT-IR measurements, N_2 adsorption/desorption isotherms at 77 K, and elemental analyses. The nitrogen contents were determined by FT-IR measurements or ion chromatography.[8]

At first two types of reactors were compared from the viewpoint of the nitridation efficiency. When M41 was nitrided on a conventional alumina boat mounted in a tube furnace, the nitridation efficiency was low. In a plug flow-type fixed-bed reactor, the efficiency increased about twice under the same reaction conditions. This would be due to the low partial pressures of H_2O produced and the high degrees of NH_3 dissociation at the

Table 1. Nitridation conditions and properties of parent silicas and MSONs obtained

Parent	Sample Wt. /g	Temp /K	Time /h	NH_3 flow rate /mL·min^{-1}	Total NH_3 /L·g^{-1}	N content /wt %	d_{100}[a] /nm	S_{BET}[b] /m^2·g^{-1}	W_{KJS}[c] /nm
				Nitridation condition					
M41	—	—	—	—	—	0	3.40[d]	981[d]	3.09[d]
	0.2	1273	4	0	0	0	3.18[e]	812[e]	2.72[e]
	0.2	973	4	300	360	4.2	3.39	—[f]	—[f]
	0.2	1073	4	300	360	10.6	3.09	—[f]	—[f]
	0.2	1173	4	300	360	19.1	2.98	—[f]	—[f]
	0.2	1273	4	300	360	25.0	2.73	584	2.04
	0.2	1323	4	300	360	26.5	2.69	251	2.09
	0.2	1273	1	300	90	15.8	2.80	593	2.05
	0.2	1273	8	300	720	33.0	2.71	542	1.97
	0.05	1273	8	300	2880	33.8	2.74	472	2.02
Silica gel	—	—	—	—	—	0	—	224[d]	6.9[d,g]
	0.2	1273	4	300	360	22.3	—	121	6.4[g]
	0.1	1273	8	600	2880	20.8	—	—[f]	—[f]

[a]Obtained from XRD data. [b]Surface area calculated by the BET method. [c]KJS pore diameter (see the text). [d]Data of parent M41 or silica. [e]M41 was heated in N_2. [f]Not determined. [g]Pore size distributions were broad and then most frequent values were listed.

surface of M41 particles loaded in the flow-type reactor because these factors were reported to affect the degree of nitridation.[9,10] The flow-type reactor was thus employed here.

The correlation between the nitridation temperature and the nitrogen contents is summarized in Table 1. The nitridation rates increased with increasing the reaction temperature in the range 973–1273 K, while the reaction at 1323 K resulted in destruction of the pore structure. The appropriate nitridation temperature was 1273 K.

The effects of nitridation conditions such as the reaction time, the flow rate of NH_3, and the sample weight on the nitrogen contents were studied at 1273 K. Although the degrees of nitridation were strongly dependent on these factors, the most important factor was found to be the amount of NH_3 supplied per weight of sample. The correlation is depicted in Figure 1. The nitrogen content increased monotonously at 0–700 L of NH_3/g, while it remained unchanged above 700. The linear correlation means that we need to increase the flow rate of NH_3 per sample weight or the reaction time to obtain highly nitrided MSONs. The highest content in Figure 1 was as high as 34 wt %, which corresponds to 85% of the theoretical value of nitrogen in Si_3N_4. The value was much greater than those of MSON samples prepared on a boat[2,5,6,11] or in a fluidized-bed reactor.[10] Three more important findings should be pointed out. Above 700 L of NH_3/g, the nitridation did not proceed any more, though the reason is not clear yet. Secondly, the present preparation time for deep nitridation, 8 h, is much shorter than those reported in the literature.[5] Thirdly, as listed in Table 1, the maximum nitrogen content of silica gel treated by the same procedure was much smaller than that of mesoporous silica. This is
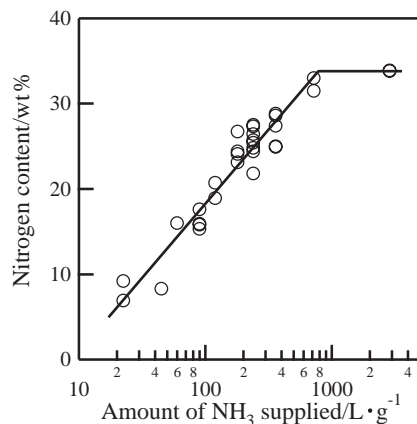
Figure 1. Dependence of the nitrogen content of MSON on the amount of NH_3 supplied at 1273 K.

well consistent with the findings that only high-temperature treatment can achieve the nitridation of silica gel.[10–12]

The structure of MSON obtained was then studied. Although the XRD intensities from the present MSON samples were lower than those of the parent M41, the typical three peaks corresponding to (100), (110), (200) diffractions of 2-D hexagonal structure were clearly confirmed without any diffraction peaks in the range 10–60 degrees. All diffraction peaks were shifted to the respective higher angles indicating the shrinkage of lattice, which is similar to the phenomena observed in various oxynitride samples.[2,5,6]

The porosities of the samples were evaluated by N_2 adsorption/desorption experiments. The BJH method is frequently employed for analyzing the adsorption/desorption data, but this is reported to underestimate the pore size especially in the range 1.5–7.5 nm.[13] Therefore, the Kruk–Jaroniec–Sayari (KJS) method[8,13] was used to determine the present primary pore sizes (W_{KJS}).

$$W_{KJS} = 1.213d(\rho V_{meso}/(1 + \rho V_{meso}))^{1/2} \qquad (1)$$

where d, ρ, and V_{meso} were the (100) XRD spacing, the wall density, and the primary mesopore volume calculated by using α_s-plot,[14] respectively. To apply the equation to the present MSONs we have to know the density ρ of the wall constructing the pores. When the densities of β-cristobalite,[15] Si_2N_2O,[16] α, β-Si_3N_4,[4] and amorphous oxynitride of several reports[10,17] were plotted against the nitrogen content, we found good correlation shown in Figure 2. We, therefore, estimated the wall densities of the present samples on the basis of the correlation. The results obtained are summarized in Table 1. The pore diameters were drastically reduced upon the nitridation treatment and were at around 2.0–2.1 nm. The values were also smaller than that of M41 heated in N_2 at 1273 K for 4 h (2.7 nm). The findings indicate that the heating treatment at 1273 K really induced the shrinkage of pores and that the nitridation treatment further reduced them. The decrement in the surface areas upon the nitridation is mostly due to the increase in the wall density.

In summary, we could successfully prepare highly ordered MSON with high nitrogen contents in a short time by using a plug flow-type reactor. The nitrogen content reached at 34 wt %, corresponding to 85% of that of Si_3N_4. The nitrogen content was dependent on the amount of NH_3 per sample weight.
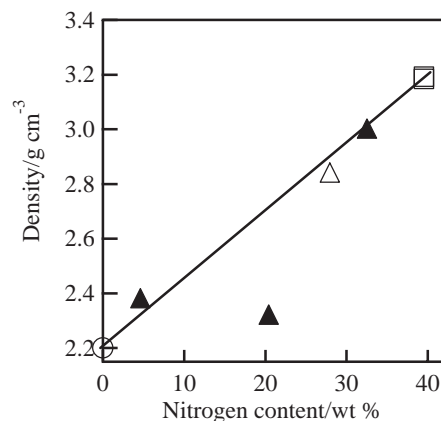

Figure 2. Correlation between the nitrogen content and the density of silica, silicon oxynitride, and silicon nitride. Samples: β-cristobalite[15] (open circle), Si_2N_2O[16] (open triangle), α,β-Si_3N_4[4] (open squares), and amorphous oxynitride[10,17] (closed triangles).

It would be worthy to add that when we treated 1.5 g of sample in a bigger reactor of id. 18 mm almost the same MSON could be obtained, suggesting the easy scale-up of the present method.

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