Synthesis of Mesoporous Silicon Oxynitrides via Direct Nitridation with Nitrogen

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An entirely new route for the synthesis of thermally stable ordered mesoporous silicon oxynitride (MSON) by direct nitridation with nitrogen of periodic ethane-bridged mesoporous silica material is reported.

The substitution of bridging oxygen atoms by N or NH species are of considerable interest and can offer a great potential as an alternative basic catalyst for variety of applications, molecular sieving and adsorption.[1] The common method of creating the crystalline silicon oxynitrides is the direct thermal nitridation of silica materials with ammonia.[2–4] Several mesoporous materials are reported where the silica aliquots have been replaced by diversity of cations in the framework,[5,6] while a little attention is paid concerning anionic substitution in the ordered mesoporous silica. Nitridation of mesoporous silica with ammonia was reported for the synthesis of ordered mesoporous oxynitrides.[7]

In the present work, we report an alternative route to produce mesoporous silicon oxynitrides by direct nitridation with nitrogen of periodic ethane-bridged mesoporous silica materials. The ethane-bridged silicas with two and three dimensional hexagonal and cubic (*Pm3n*) symmetries were synthesized using a bridged organosilane $(CH_3O)_3Si–CH_2–CH_2–Si(OCH_3)_3$ as a precursor.[8–10] The details on synthesis, adsorption and thermogravimetric characterization of ethane-bridged silica materials are described elsewhere.[8,11,12] The thermogravimetrical curve of mesoporous ethane-silica under nitrogen atmosphere (Figure 1A) exhibits the weight gain above 700 °C is likely to be assigned to the reaction with nitrogen.[11–13] Therefore, we have systematically investigated this interesting phenomenon and established the novel route for the synthesis of mesoporous silicon oxynitrides (MSON).

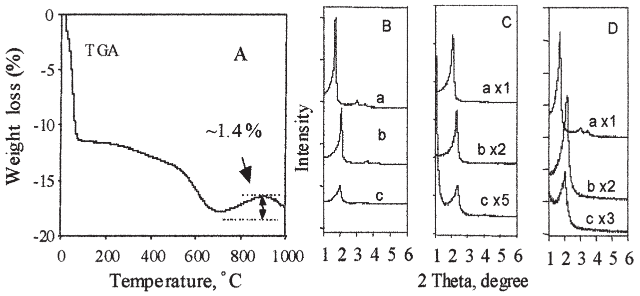

Figure 1. A) Thermogravimetrical curve of surfactant free ethane-bridged silica under nitrogen atmosphere. PXRD patterns of MSON materials; B) **a**- surfactant free ethane-bridged silica, **b**- MSON-900-6 h; **c**- MSON-1050-6 h; C) MSON-900 calcined in air for 4 h at **a**- 650 °C; **b**- 1000 °C; **c**- 1050 °C; D) hydrothermal stability measured as per ref. 14. **a**- ethane-bridged silica; **b**- MSON-900; **c**- MSON-1050.

Nitridations were performed using ethane-bridged mesoporous silica with two-dimensional hexagonal symmetry at different temperatures of 900 and 1050 °C (Figure 1B). The ceramic crucible containing ethane-bridged mesoporous silica was heated in a quartz tube furnace under continuous nitrogen flow (purity 99.999%) and kept for aimed reaction time and then cooled down to ambient temperature. The mesoporous silicon oxynitrides prepared at 900 and 1050 °C are denoted MSON-900 and MSON-1050 symbols, respectively. In addition, the surfactant containing ethane-bridged mesostructured organosilica did not produce MSON materials under similar reaction conditions.

Powder X-ray diffraction (PXRD) of MSON-900 showed an intense low angle peak ($d_{100} = 42.4$ Å) along with additional weak reflections ($d_{110} = 24.5$ Å and $d_{200} = 21.1$ Å) with a hexagonal cell, indicating almost perfect preservation of mesoscopically ordered structure, while the MSON-1050 material showed weaker reflections although some ordering was present. The MSON materials were subsequently calcined in air to remove the carbon deposited during the nitridation process and evaluate thermal stability. The black color of MSON materials changed to white after calcination in air, indicating the decrease in considerable amount of carbon deposited. The intense low angle reflection of MSON-900 could be retained up to the temperature of 1000 °C. Moreover, the low angle reflection was still observed at 1050 °C, indicating exceptionally high thermal stability (Figure 1C). These MSON materials were also hydrothermally stable in hot water (Figure 1D).

In the porosity measurement (Table 1) all MSON materials exhibited clear capillary condensation step with type IV characteristic, similar to parent ethane-bridged organosilica.[8] Transmission electron microscopy (TEM) image also supports the PXRD and porosity measurement observations, indicating the presence of well-defined hexagonal arrangement of uniform channels (Figure 2A).

Table 1. Textural properties of MSON materials

Materials	D_{BJH} /Å	S_{BET} /m^2g^{-1}	V_P /cm^3g^{-1}	a_o /Å
Ethane-bridged silica	35.0	817	0.82	58.9
MSON-900	24.5	745	0.44	49.0
MSON-1050	21.4	563	0.35	49.2
Ethane-bridged-1000	17.6	437	0.23	46.1
MSON-900-1000	15.2	416	0.22	43.9
MSON-1050-1000	15.1	305	0.17	42.8

D_{BJH} = pore diameter; S_{BET} = surface area; V_P = pore volume; a_o = lattice constant ($= 2d_{100}/\sqrt{3}$).

The evolution of the nitrogen content in resultant MSON materials depends on the procedural variables (i.e. temperature and reaction time). The effective nitridation was achieved at 1050 °C with intact mesoporous network. Compared to the

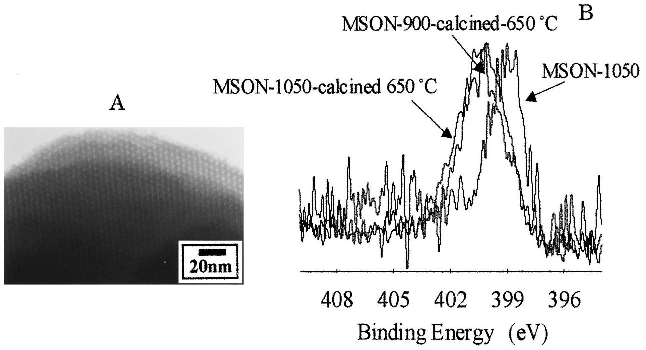

Figure 2. A) Transmission electron microscopy image of MSON-900 and B) XPS spectra of N1s line of MSON materials.

MSON-900 ([N] $=$ 0.021; [C] $=$ 13.5 wt%), the nitrogen content (by elemental analysis) was 8 fold higher for MSON-1050 ([N] $=$ 0.16; [C] $=$ 12.8 wt%) after 6 h of nitridation. However, the nitrogen content that incorporates the MSON silica network is largely differs from those reported for the nitridation with ammonia[7] (from 0.5 to 2.5 wt%, depending on procedural variables as well as structural and textural characteristics of the parent silica precursors).

The chemical composition determined by X-ray photo spectroscopy (XPS) also confirmed the formation of silicon oxynitrides. Binding energies obtained for Si2p (103.8 eV), O1s (533.5 eV), C1s (284.9) and N1s (399.0) photoelectrons were somewhat different from those reported earlier for amorphous silicon oxynitrides.[1,15] After 6 h of nitridation, the nitrogen contents (by XPS) were $<$0.1 at% (0.08 wt%) and 0.3 at% (0.22 wt%) for the MSON-900 and MSON-1050, respectively. After removing the carbon upon calcinations at 650 °C in air, the nitrogen contents determined were 0.6 at% (0.43 wt%) and 0.7 at% (0.50 wt%) for MSON-900 and MSON-1050 material, respectively (Table 2).

Table 2. Chemical composition (at%) of MSON materials determined by X-ray photo spectroscopy

Materials	Si2p	O1s	N1s	C1s
MSON-900	27.9	55.2	<0.1	17.0
MSON-1050	28.3	54.8	0.3	16.6
MSON-900-Calcined	30.7	64.4	0.6	4.3
MSON-1050-Calcined	30.9	65.2	0.7	3.1

The excess carbon that covered the surface hinders the exact measurement of nitrogen content. The larger estimation of nitrogen contents for XPS analysis than chemical analysis suggested that nitridation is preferentially occurred on the particle surface. N1*s* binding energy increased (400.1 eV) after calcination of the MSON materials (the charge referencing was performed using Si2p line) suggesting that the excess of carbon strongly interacted with nitrogen species of the MSON before calcination (Figure 2B). The plausible mechanism for the mesoporous oxynitrides formation is believed to proceed in the following steps: First, the release of ethane fragment from the silica network creates active sites of defective silica species that in turn rapidly react to N_2 (g) species and yield silicon oxynitrides.

In summary, the results demonstrated that the thermally stable ordered mesoporous silicon oxynitrides (MSON) can also be synthesized from mesoporous ethane-bridged organosilica via direct nitridation with nitrogen.

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References and Notes

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