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The Basicity and Catalytic Activity of Ordered Mesoporous Silicon Nitride Oxide

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The basicity and base catalytic properties of ordered mesoporous silicon nitride oxide (MSON) were investigated in our present contribution. It was found that the basic strength of MSON was stronger and comparable to the strength of MgO. In addition, MSON had a much higher base catalytic activity than not only amorphous silicon nitride oxide but also crystallized nitrogen-containing microporous molecular sieves used in the Knoevenagel condensation reaction of benzaldehyde and malononitrile. Furthermore, the catalysts were stable both in structure and in composition below 1123 K in an inert atmosphere. These stable, solid base catalysts may find their use in some important base catalyzed reactions.

Solid base catalysts have attracted a lot of attention in recent years because they have considerable potential applications in the production of fine chemicals.[1–3] Additionally, solid base catalysts have a number of practical advantages compared to liquid bases: they are easily separated from the reaction mixture, they are easily regenerated after the reaction and are non-corrosive to the reactor system. But compared to the vast number of known solid acid catalysts, reports of new solid base materials are rare.

Lednor et al. first reported amorphous silicon nitride oxide as a base catalyst and tested its basicity.[4,5] Considering the advantages of a high surface area and the ordered pore structure, crystallized microporous zeolites were treated in ammonia to obtain the "nitrogen-containing base zeolites". However, because of the high stability of zeolites crystallinity, the nitridation of them was quite difficult, resulting in the basicity of the ammonia treated zeolites being weak.[6] Recently, porous silicon nitride as a strong base catalyst was made using silicon tetrachloride and ammonia, although the pore structure was not ordered.[7,8]

The discovery of ordered mesoporous molecular sieves[9] gave us a new choice to make mesoporous silicon nitride oxide. By treating ordered mesoporous silica with ammonia or nitrogen gas, ordered mesoporous silicon nitride oxide was made.[10–12] However, it was very difficult to avoid the collapse of the framework when nitridation of mesoporous materials was performed in a flow of NH_3 or N_2 at higher temperatures for a long time, so the nitrogen content incorporated and the pore structure of the products were not ideal. Meanwhile, the base activity of the products is closely related to the nitrogen content, and the pore structures of the materials have considerable significance in catalyzed reactions, so it is very important to prepare highly ordered mesoporous materials with higher nitrogen content and base sites. In our previous letter,[13] a new mesoporous silicon nitride oxide (MSON), which was highly ordered and had a high nitrogen content, was made from a highly stable SBA-15 matrix. Considering its higher nitrogen content, MSON should exhibit excellent catalytic basicity and strong base strength, as investigated in our present contribution.

Experimental

Sample Preparation. The synthesis of SBA-15 and MSON was similar to our previous work.[13] Four grams of P123 $[(EO)_{20}(PO)_{70}(EO)_{20}]$ were dissolved into a solution of 30 mL deionized water and 120 mL HCl (2 $mol\,L^{-1}$), followed by 9.15 mL tetraethyl orthosilicate (TEOS, $>98\%$) slowly. The mixture was then maintained at 313 K for 24 h under a stirred condition. Later, the solution was loaded into an autoclave and heated at 373 K for 48 h. The solid product was recovered by filtration, washed with deionized water, dried at 353 K and defined as fresh SBA-15. The MSON1, MSON2, MSON3, and MSON4 samples were made from fresh SBA-15 through calcining in flowing ammonia at 1173, 1223, 1323, and 1423 K for 18 h, respectively. The flow rate of ammonia was 500 $mL\,min^{-1}$, the volume of the tube furnace was 4.5 L, and the heating rate was 5 $K\,min^{-1}$.

Sample Characterization. Nitrogen content was analyzed by CNH elemental analysis (Model 2400 CNH Elemental Analyzer, Perkin-Elmer, Norwalk, CT), which was performed at a temperature of 1273 K with oxygen and high temperature oxidants ($Ag_2WO_4 + MgO$) as additives.

The nitrogen sorption characterization of the SBA-15 samples before and after nitridation was conducted on a Micromeritics ASAP2010 surface area and pore size analyzer at liquid nitrogen temperature. The surface area was calculated using the BET method, and the pore size and pore volume were calculated from the desorption branches of these isotherms using BJH methods.

The powder X-ray diffraction patterns were obtained with a Cu $K\alpha$ radiation (40 kV, 60 mA) using a Rigaku D/MAX-γB instrument at a 0.002° step size over a range of $0.8^\circ < 2\theta < 5^\circ$.

The NMR spectra were recorded on a Bruker DSX-300 spectrometer using 5 kHz magic angle spinning with a 4 mm probe. The instrument operated at 300.13 MHz for ^{1}H and 59.62 MHz for ^{29}Si. The 90° pulses of ^{1}H and ^{29}Si were 4.1 µs and 4.5 µs, respectively. The high-resolution ^{29}Si spectra were obtained by CP/

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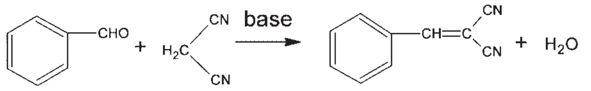
MAS/DD. The contact time of cross polarization (CP) was 3.5 ms.

TG-MS experiments were performed at a heating rate of 10 K min^{-1} in a flow of argon using a Netzsch STA 449/C instrument.

Basicity Evaluation. The amount of CO_2-adsorbed by MSON and the base strength measurement of the MSON catalysts were carried out using carbon dioxide temperature-programmed desorption (CO_2-TPD). Typically, about 100 mg of the catalyst was secured between quartz wool plugs in the micro-reactor, pre-treated in nitrogen at 823 K for 3 h and then cooled to 353 K prior to the adsorption of CO_2 at this temperature. After the adsorption of CO_2 (40 mL min^{-1}) for 60 min, the catalyst was flushed with nitrogen (40 mL min^{-1}) for 2 h to remove the physically absorbed gas from the surface of the catalyst. The desorption spectrum was recorded at a heating ramp of 10 °C min^{-1} from 353 to 873 K using a recorder connected to a gas chromatography equipped with a TCD detector.

The base catalytic activity of the catalysts was tested using the typical base catalyzed Knoevenagel condensation reaction of benzaldehyde and malononitrile. The reaction equation is illustrated in Eq. 1. The experiments were carried out in 10 mL toluene as a solvent with 0.2 g MSON as a catalyst, 16 mmol of malononitrile and 13 mmol of benzaldehyde at varied temperatures (303, 323, and 343 K). The reaction mixtures were analyzed by a Shimadzu gas chromatograph GC-8A equipped with an FID detector and a HP-5 capillary column, and the conversion (%) was calculated with the ratio of product to benzaldehyde.



(1)

Results and Discussion

The chemical and physical properties of the samples are listed in Table 1. Obviously, MSON1, MSON2, and MSON3 still had large surface areas and pore volumes, and they still kept the ordered mesoporous structure, but the mesoporous structure of MSON4 was collapsed to some degree, due to the long nitridation time at a higher temperature (1423 K). Figures 1 and 2 give the evidence for the ordered mesoporous structure existing in the MSON using the nitrogen sorption characterization, XRD and HRTEM analytical methods. Figure 1A and B show the nitrogen adsorption-desorption isotherms (A) and BJH pore size distribution (B) of SBA15 and the treated sample MSON3 as well. Figure 1C shows the low-angle XRD patterns of SBA-15 and the treated sample MSON3, where the MSON3 has good diffraction pattern with three reflections, typical in the ordered mesoporous silica. Compared with the parent SBA-15, the reduction in pore size, pore volume and pore wall thickness after nitridation arose from the contraction of lattices during the high temperature treatment. With the increase in nitridation temperature, the nitrogen content incorporated in the

Table 1. Chemical and Physical Property of the Samples before and after Nitridation

Sample	N /wt %	Composition	S_{BET} /m^2 g^{-1}	V_{BJH} /cm^2 g^{-1}	$D_{BJH}$$^{a)}$ /Å	d_{100} /Å	$a_0$$^{b)}$ /Å	$D_{Wall}$$^{c)}$ /Å
SBA-15	—	—	685	1.07	65	92.3	106.7	41.7
MSON1	3.9	$SiN_{0.16}O_{1.68}$	690	1.06	66	91.9	106.2	40.2
MSON2	9.7	$SiN_{0.39}O_{1.42}$	560	0.92	65	86.4	99.9	34.9
MSON3	20.6	$SiN_{0.78}O_{0.84}$	390	0.79	64	80.1	92.6	28.6
MSON4	27.6	$SiN_{0.99}O_{0.52}$	230	0.31	—	72.9	84.3	—

a) The pore diameter calculated from the desorption isotherm. b) The lattice parameter, from the XRD data using the formula. $a = 2d_{(100)}/\sqrt{3}$. c) Wall thickness = $a_0 - D_{BJH}$.

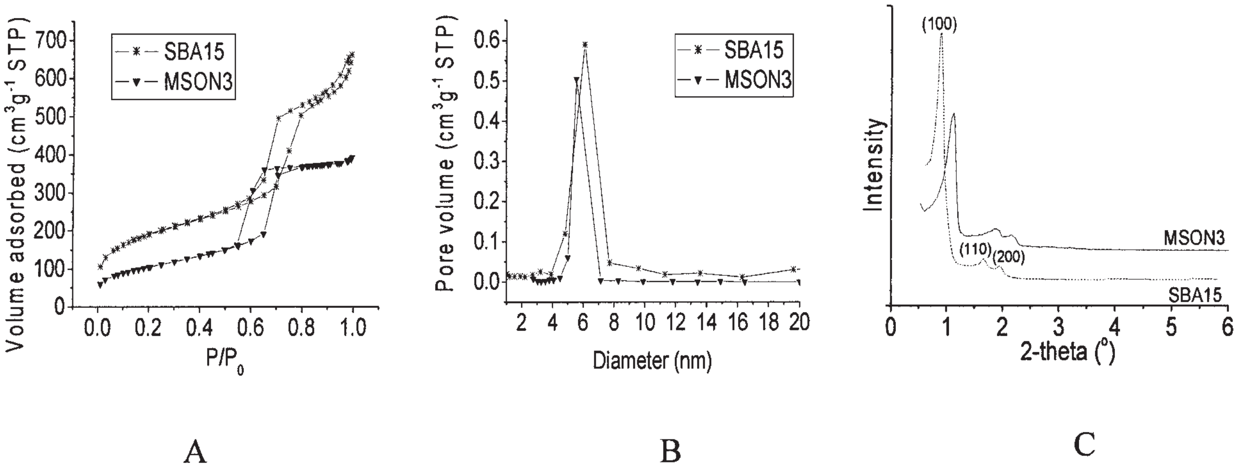


Fig. 1. A) Nitrogen adsorption–desorption isotherms. B) BJH pore size distribution of SBA-15 and treated sample MSON3. C) Low-angle XRD patterns of SBA-15 and treated sample MSON3.

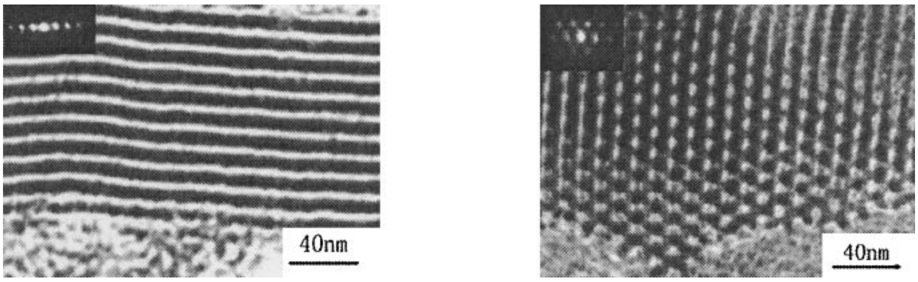


Fig. 2. HRTEM images of MSON3.

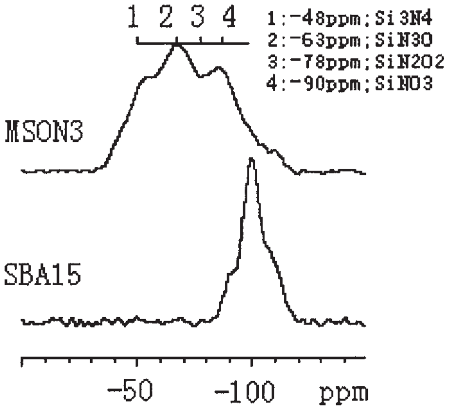


Fig. 3. ^{29}Si MAS NMR spectra of SBA-15 and MSON3.

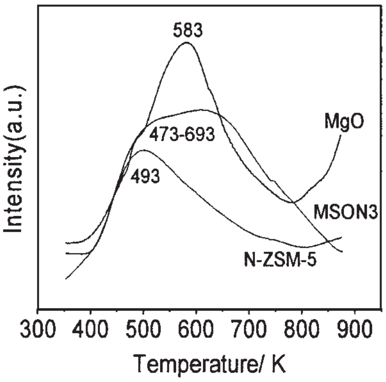


Fig. 4. CO_2-TPD plots of carbon dioxide desorbed from MSON3, N-ZSM-5, and MgO.

framework was increased accordingly, where MSON1 contained 3.9 wt % of N, MSON2 9.7 wt % of N, MSON3 20.6 wt % of N, and MSON4 27.6 wt % of N. This implied that the oxygen in the mesoporous framework was partially replaced by nitrogen, and Si–O–N or Si–N–O bonding was established. The high nitrogen displacement of oxygen has been proved from the ^{29}Si MAS NMR analysis of MSON3 shown in Fig. 3, with SBA-15 as a parallel reference, where the single peak of SBA-15 (located at about -100 ppm) was shifted left, widened, and separated into several peaks (in the range of -45 to -90 ppm) after becoming into MSON3. Generally, in this range (-45 to -90 ppm) of NMR spectrum, there are standard peaks corresponding to Si_3N_4 (-48 ppm), SiN_3O (-63 ppm), SiN_2O_2 (-78 ppm), and $SiNO_3$ (-90 ppm), respectively. The NMR spectrum analysis might imply the formation of different Si–N–O or Si–O–N bonding (SiN_xO_y) during the nitridation of SBA-15, and it is this different bonding of Si–O–N that might create different base sites. The research on the mechanism of nitridation is ongoing to determine the formation of the intermediate states of Si–O–N or Si–N–O during the process.

To explore the basicity of MSON, we measured the base strength of MSON3 using carbon dioxide temperature programmed desorption (CO_2-TPD). SBA-15, N-ZSM-5,[14] and MgO were used as parallel references, where N-ZSM-5 is the abbreviation of crystallized ZSM-5 zeolite samples nitrided with ammonia at higher temperatures by our research group. In the CO_2-TPD experiment, SBA-15 didn't adsorb CO_2. The reason was believed to be that because SiO_2 and CO_2 are both weakly acidic, they don't attract each other. It could be clearly seen that carbon dioxide desorbed from MSON3 in a wide temperature range from 473 to 693 K according to the CO_2-TPD plots (Fig. 4), which meant a wide distribution of base sites with different base strengths. This wide distribution of base strength is attributed to the different bonding of Si–O–N. The desorption temperature from 473 to 693 K means that the base strength of MSON was comparable to that of MgO. So, we could identify the basicity of MSON as stronger, as MgO is usually considered to be a strong base catalyst.[11,15] We can also clearly see from the CO_2-TPD plots that the base strength of MSON is much higher than the strength of N-ZSM-5. Additionally, the amount of the CO_2-absorbed by MSON3 calculated from the CO_2-TPD plots was about 0.21 $\mathrm{mmol\,g^{-1}}$, higher than the amount by SBA-15 (no absorption) and N-ZSM-5 (0.099 $\mathrm{mmol\,g^{-1}}$), and lower than that of MgO (0.56 $\mathrm{mmol\,g^{-1}}$). Usually, the higher the amount of CO_2 absorbed, the higher the number of base sites, so the number of base sites in MSON3 was in the middle of SBA-15, N-ZSM-5, and MgO.

Considering the stronger base strength and the number of base sites, MSON should have a higher base catalytic activity. Therefore, the Knoevenagel condensation reaction between benzaldehyde and malononitrile was designed to be the probe for the base catalytic activity of MSON. Knoevenagel condensation reactions carried out in the present research in the range of temperature from 303 to 343 K using 0.2 g MSONs as catalysts, so the effect of the reaction temperature could be explored. It can be clearly seen (Fig. 5A) that the conversions of 50%, 88%, and 100% were reached after 30, 120, and 240 min at 303 K, and also the conversions of 65%, 98%, and 99.7% were observed after 30, 120, and 150 min above 323 K, and also 95% and 99.9% observed after 30 and 60 min at 343 K just using MSON3 as a catalyst. Comparatively, the catalytic activity of MSON was much higher than not only the amorphous silicon

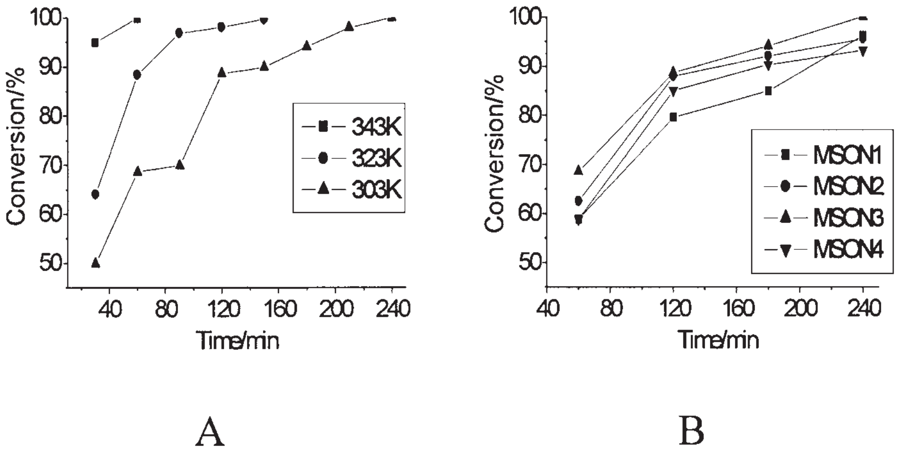


Fig. 5. Effect of (A) reaction temperature (using MSON3 as catalyst), and (B) nitrogen content and structure of four MSONs (reaction condition: $T = 303$ K) on the Knoevenagel condensation in different reaction time.

Table 2. Comparison among the Varied Base Catalysts Activity for the Same Knoevenagel Condensation Reaction

Catalyst	Reaction temperature/K	Time/min								
		30	60	90	120	150	180	210	240	1440
MSON1[a)]	303		58		78		84		96	
MSON2[a)]	303		62		87		91		95	
MSON3[a)]	303	50	68	70	88	90	94	98	100	
	323	65	89	97	98	99.7				
	343	95	99.9							
MSON4[a)] (amorphous)	303		58		85		90		93	
Si–O–N[5b)] (amorphous)	323								90	
AlPON[6c)]	353						87			
$AlPO_4$-5N[6c)]	353						50			85
ZSM-5N[6c)]	353						6			12

a) With 0.2 g MSON as catalyst, 16 mmol malononitrile and 13 mmol benzaldehyde as reactant, in toluene, with 3.9, 9.7, 20.6, and 27.6 wt % N incorporated in MSON1, MSON2, MSON3, and MSON4, respectively. b) With 0.5 g amorphous Si–O–N as catalyst, 10 mmol malononitrile and 10 mmol benzaldehyde as reactant, in toluene, with 17 wt % N incorporated.[5] c) With 0.2 g amorphous AlPON, $AlPO_4$-5N, and ZSM-5N as catalysts, 4 mmol malononitrile and 4 mmol benzaldehyde as reactant, in toluene, with several weight percent of N incorporated.[6]

nitride oxide (Si–O–N),[5] but also the crystallized and amorphous nitrogen-containing microporous molecular sieves, ZSM-5N and $AlPO_4$-5N, for the same Knoevenagel condensation of benzaldehyde and malononitrile.[6] For example, a conversion of 90% was observed for the amorphous Si–O–N after 240 min at a temperature of 323 K using 0.5 g Si–O–N as the catalyst.[5] From another example, a conversion of 85% was observed for the $AlPO_4$-5N (or crystalline nitrogen-containing microporous molecular sieves) after 1440 min at a much higher temperature of 353 K using 0.2 g $AlPO_4$-5N as the catalyst.[6] The differences among the varied base catalysts activities for the same Knoevenagel condensation reaction are summarized in Table 2. Obviously, the higher activity of MSON can be attributed to the stronger base strength and the larger amount of base sites existing in the framework of MSON, which are very important in increasing the reaction conversion rate and decreasing the reaction temperature. The high surface area and mesoporous structure of MSON might also contribute to the high activity.

In Fig. 5B, the catalytic activity of the four samples (MSON1, MSON2, MSON3, and MSON4) from various preparations and with different nitrogen content and surface areas (Table 1) was compared using the Knoevenagel condensation reaction as the probe. From MSON1 to MSON3, the catalytic activity increased with the increase in nitrogen content. The activity of MSON4 was a little lower than that of MSON2, although the MSON4 had the highest nitrogen content of 27.6 wt %. This phenomenon could arise from the disrupted pore structure and the low surface area of MSON4 (Table 1), whose surface area value was just about a third of that of MSON1, owning to the rather higher nitridation temperature (1423 K) of MSON4.

To exclude the catalytic activity of the parent SBA-15, a comparable experiment of SBA-15 was done at 353 K for

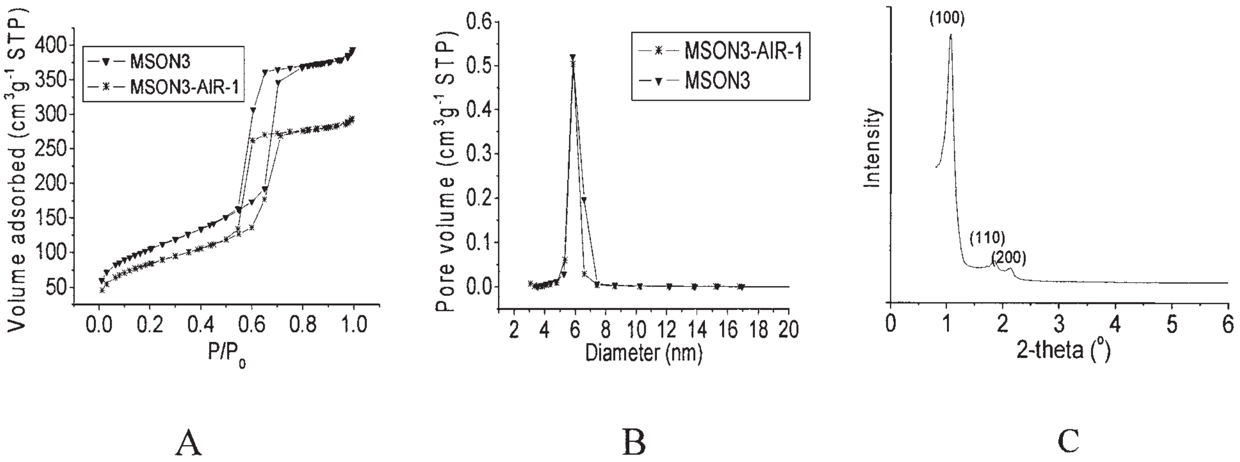


Fig. 6. A) Nitrogen adsorption–desorption isotherms. B) BJH pore size distribution of MSON3-AIR-1 and MSON3. C) Low-angle XRD pattern of MSON3-AIR-1.

4 h, and no conversion was found. Further support for the high catalytic activity of MSON was provided by finding that the second and third run of the catalytic experiments with the reused MSON3 still had a similarly high conversion, with conversions of 96% and 95% respectively (reacted at 303 K for 4 h).

Except for the catalytic activity, the thermal stability is also an important criterion in evaluating a catalyst. MSON had good stability, which was proved from the preparation of MSON at high temperatures (in the range of 1173–1423 K), but the composition stability is still unknown. So, in this article, the thermal stability of MSON3 was characterized using a TG-MS method in argon gas. The weight loss was less than 0.5% from 473 to 1473 K, and no peak was found in the TG or DSC spectrum from 473 to 1473 K, which indicated a high thermal stability for MSON. Although the amount of decomposition was below the resolution of the TG-DSC analyzer (~0.4%), O_2, N_2, and NH_3 peaks were found between 1123 and 1223 K in the MS spectrum because of the higher resolution of the MS spectrum. The MS spectrum meant some chemical decomposition in MSON happened when temperature was above 1123 K. We therefore believe that MSON catalysts are stable both in structure and in composition below 1123 K in inert atmosphere. Furthermore, in order to evaluate the thermal and structural stability of MSON in air, the MSON3-AIR-1 and MSON3-AIR-2 samples were prepared from MSON3 through calcining at 1023 K and 1123 K for 12 hours in air, respectively. Based on the nitrogen sorption characterization for MSON3-AIR-1 and MSON3-AIR-2, the mesoporous structure of MSON3-AIR-2 collapsed, while the mesoporous structure of MSON3-AIR-1 was basically stable, as seen in Fig. 6. Figure 6A and B show the nitrogen adsorption-desorption isotherms (A) and BJH pore size distributions (B) of MSON3-AIR-1 and MSON3. Figure 6C shows the low-angle XRD pattern of MSON3-AIR-1, in which MSON3-AIR-1 has good diffraction patterns with three reflections, which is typical in the ordered mesoporous silica. It can be seen that MSON3-AIR-1 had a tiny reduction in pore size and pore volume compared with MSON3. Moreover, the nitrogen content of MSON3-AIR-1 is 2.5 wt %, about 12% the amount in MSON3. Thus, it can be concluded that the mesoporous structure of MSON can be kept up to 1023 K in air, without its composition changing greatly.

In conclusion, based on the making of highly ordered mesoporous silicon nitride oxide (MSON) with a high nitrogen content, the basicity and base catalytic properties of MSON were investigated in our present contribution. It was found that the base strength of MSON was stronger and comparable to the strength of MgO. And MSON had a much higher base catalytic activity than amorphous silicon nitride oxide and also crystallized nitrogen-containing microporous molecular sieves for the same Knoevenagel probe reaction. Additionally, the ordered, adjustable mesopores and high surface area of MSON offer potential advantages for selective base catalyzed reactions. The catalysts were stable both in structure and in composition below 1123 K in inert atmospheres. These stable solid base catalysts may find their use in some important base catalyzed reactions.

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