

Nitrogen-Incorporated SAPO-11 Molecular Sieve: Synthesis, Characterization, and Properties

Jianmin Xiong,[†] Yunjie Ding,^{*,†} Hejun Zhu,[†] Li Yan,[†] Xiumei Liu,[‡] and Liwu Lin[‡]

Natural Gas Utilization and Applied Catalysis Laboratory and State Key Laboratory of Catalysis, Dalian Institute of Chemistry and Physics, The Chinese Academy of Sciences, Dalian, 116023, China

Received: March 27, 2002; In Final Form: September 23, 2002

Nitrogen-incorporated SAPO-11 molecular sieves were synthesized by a secondary synthesis technique at low nitridation temperature (400 °C) with a starting material of SAPO-11 zeolite doped with 2 wt % Ru. The obtained powder samples showed high activity in Knoevenagel condensation, which acts as a probing reaction for base catalysis. The changes in structure of the nitrogen-incorporated samples were investigated by means of ²⁷Al-MAS NMR and ³¹P-MAS NMR spectra, X-ray diffraction, and BET surface area measurements. It was found that nitrogen-containing species had incorporated into the framework of SAPO-11 zeolite, in which some N atoms directly bonded to Al and P atoms and formed AlN₄, AlN₂O₂, and PN₄ groups. These species with terminal –NH₂ groups on the surface together were responsible for the basicity of nitrogen-incorporated SAPO-11 zeolite.

Introduction

The replacement of liquid acids and bases by solids as catalysts in organic reactions is a requisite for better environmental preservation. While the research on solid acid catalysts was boomed by oil refining through the discovery of a large number of systems including zeolites, clays, mixed oxides, and sulfates, only a few solid base catalysts are yet available. Among them, nitrogen-incorporated molecular sieves are of interest due to their high surface area and shape-selectivity.

The SAPO-11 molecular sieves are composed of PO₄[x]AlO₄ and SiO₄ tetrahedron, and if the oxygen atoms of the tetrahedron were replaced to some level by certain isoelectronic groups, such as –NH– species, as a result of such substitution, it will be expected that the Lewis basicity of the framework increases due to the lower electronegativity of nitrogen with respect to oxygen. Nitrogen-incorporated compounds may thus become candidates of catalysts for a new set of base catalytic reactions.

In recent years there have been many of reports on the nitridation of amorphous AlPO₄, in which amorphous AlPO₄ precursors with high surface area were synthesized through different methods^{1,2} and then nitridized in a flow of dry ammonia at about 800 °C. The basic strength of the oxynitrides could be controlled by the conditions of nitridation due to the nitrogen content of the oxynitrides varying with the time and temperature of nitridation. The content of nitrogen could achieve up to about 20 wt %, and the BET surface area remained almost unchanged after nitridation.^{3,4} The obtained amorphous oxynitrides showed high activity in the Knoevenagel condensation between benzaldehyde and methylene compounds. In situ IR and NMR spectra exhibited that the species of Al–NH–P, Al–NH₂ and P–NH₂ on the surface were responsible for the basicity of the amorphous oxynitrides.^{5,6} However, few reports on nitrogen-incorporated molecular sieves appeared. It is very difficult to avoid the collapse of molecular sieve framework when nitridation of the molecular sieves was performed in a flow of NH₃

at a temperature of 800 °C. Therefore, it is not easy to obtain nitrogen-incorporated molecular sieves. Meanwhile, fine crystallinity and pore structures of molecular sieves, which have considerable significance in shape-selective reactions, would be maintained when nitridation was carried out at low temperature.⁷ It is well-known that on some transition metals, such as ruthenium metal, the ammonia molecule can be easily decomposed into NH_x ($x = 1\sim 2$) groups, which are very reactive species for the above substitution reaction. In this way, oxygen bridging atoms in molecular sieves could be replaced by –NH– species at low temperature.

The objective of this work is to develop an improved method for preparation of nitrogen-incorporated SAPO-11 zeolite base catalyst at low temperature and to characterize the structure changes during nitridation by means of MAS NMR, BET, and XRD methods.

Experimental Section

Sample Preparation. SAPO-11 zeolite was synthesized by a sol–gel method, which has been presented elsewhere.^{8–10} The as-synthesized SAPO-11 was first baked at about 580 °C for about 4 h to remove the template, and then soaked in RuCl₃ (purchased from Johnson Matthey company) solution to get a Ru loading of 2.0 wt %. Then it was dried at ambient temperature for several days, and dried finally in an oven at 120 °C for about 4 h (denoted as Ru–SAPO-11). Nitridation of SAPO-11 molecular sieve powder was carried out in a tubular quartz reactor at 400 °C in a flow of pure ammonia. The flow rate of ammonia was controlled at ca. 30 mL/min. At the end of the nitridation process, the sample was slowly cooled to room temperature in a nitrogen flow. The powders obtained after nitridizing for different times of 5, 25, and 50 h are denoted as SAPO-11–5N, SAPO-11–25N, and SAPO-11–50N, respectively. The Mg–Al hydrotalcite used in this paper as contrast was Mg₄Al₂(OH)₁₆CO₃. The method of its synthesis is presented in ref 11.

Basicity Evaluation: The Content of Nitrogen and the Knoevenagel Condensation Reaction. The contents of nitrogen in the nitrogen-incorporated samples were detected by alkaline

* Corresponding author. E-mail: dyj@dicp.ac.cn. Fax: 86-411-4379143.

[†] Natural Gas Utilization and Applied Catalysis Laboratory.

[‡] State Key Laboratory of Catalysis.

TABLE 1: BET Surface Area Measurements and Nitrogen Contents for Nitrated SAPO-11 Molecular Sieves

	SAPO-11	SAPO-11-5N	SAPO-11-25N	SAPO-11-50N	SAPO-11-5N-800 ^a
S_{BET} (m ² /g)	185	137	126	125	28
N (% w/w)	0	0.52	0.77	1.23	1.25

^a This is a SAPO-11 without Ru nitrated at 800 °C.

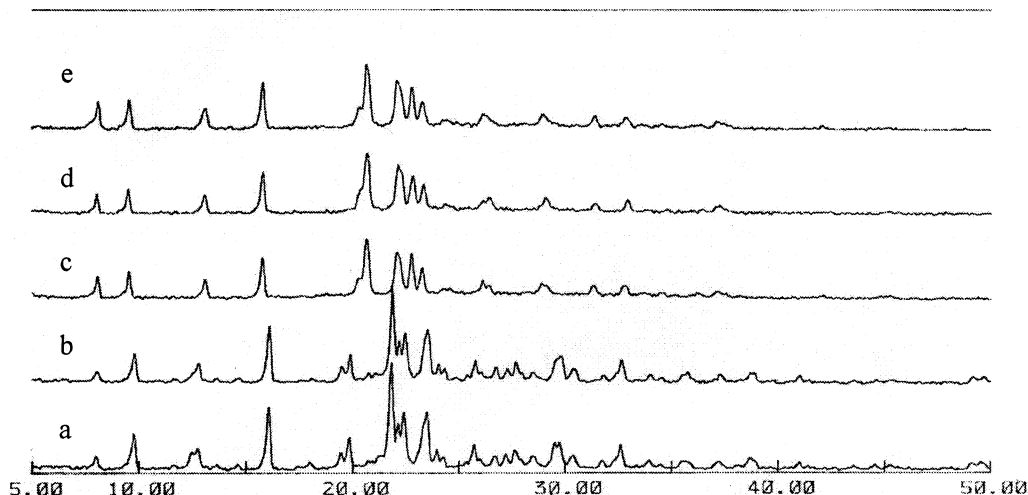


Figure 1. XRD patterns for nitrated SAPO-11 molecular sieves (a) calcined SAPO-11; (b) Ru-SAPO-11; (c) SAPO-11-5N; (d) SAPO-11-25N; (e) SAPO-11-50N.

digestion with molten NaOH at 400 °C, and the resulting NH₃ was titrated with 1 N H₂SO₄; the detailed procedure is founded in the literature.¹² All reactions were carried out under an inert atmosphere (N₂), in a round-bottom flask fitted with a reflux condenser. The flask was immersed in a thermostated water bath and the reaction mixture was magnetically stirred. A mixture of previously distilled benzaldehyde (4 mmol) and ethyl cyanoacetate (4 mmol) was introduced with toluene as a solvent (30 mL) into the flask. Once the mixture reached 50 °C, 0.2 wt % of the catalyst was added. Samples of the reaction mixture were then periodically withdrawn by a 1 μL microsyringe at time intervals of 30, 60, 120, 180, and 240 min and analyzed by Shimadzu gas chromatograph GC-8A, equipped with an FID detector and an HP-5 (cross-linked 5% PH ME siloxane) capillary column.

MAS NMR Measurement. MAS NMR experiments were performed on a Bruker DRX-400 spectrometer. Data of ³¹P were obtained by measuring the samples using a frequency of 161.97 MHz, pulse width of π/8, delay of 2.0 s, and 100 scans. For ²⁷Al-MAS NMR experiments, a frequency of 104.26 MHz and 400 scans instead were used.

XRD Analysis. XRD patterns were measured in air on Rigaku D/Max-rb diffractometer using Cu Kα radiation at 40 kV and 50 mA. The 2θ angles were scanned from 5° to 50° at a rate of 2° min⁻¹.

BET Measurement. The surface areas of the different nitrogen-incorporated SAPO-11 samples were obtained by nitrogen adsorption using an ASAP 2010 (Micromeritics) after outgassing the samples under vacuum at 250 °C.

Results and Discussion

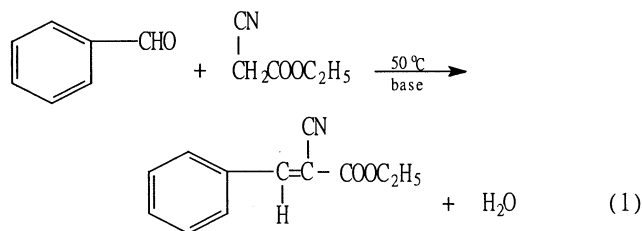
Nitrogen Content. The nitrogen contents in the nitrogen-incorporated samples are summed in Table 1. The nitrogen content increased with the time of nitridation for Ru-doped samples. It is notable that the content of nitrogen for SAPO-11-50N that was nitrated at low temperature of 400 °C was almost comparable to that of the sample without Ru that was nitrated at 800 °C.

BET Measurements. From the data shown in Table 1, it is found that the surface areas of SAPO-11-5N, SAPO-11-25N, and SAPO-11-50N samples decreased very little after nitridation, which is comparable to that of the SAPO-11 precursor, but the sample lost most surface area if nitridation is conducted at 800 °C.

XRD Analysis. The XRD patterns of samples are presented in Figure 1. From the spectra it was found that the intensity of diffraction peak at 2θ = 8.09 increased, the rest of diffraction peaks at lower-angle remained unchanged, and the peak at 2θ = 19.89 disappeared while a new peak at 2θ = 20.65 appeared after nitridation. These results show that some changes in chemical composition (this was further confirmed by the results of ²⁷Al and ³¹P MAS NMR measurements) and crystal-line structure occurred during nitridation.

Basicity Evaluation of Nitrogen-Incorporated SAPO-11 Zeolites. The Knoevenagel condensation is usually used in organic synthesis to produce alkenes from molecules containing carbonyl groups. This reaction is catalyzed by bases under mild reaction conditions. Knoevenagel condensation is often used as a probing reaction to evaluate the basicity of oxynitrides. Indeed, by reacting one mole aldehyde with one mole molecule containing activated methylene groups with different pK_a value in the presence of a base catalyst, it is possible to find the minimum pK_a value of the reactant from which the catalyst becomes active. Thus, in this way catalysts with different basicities can be conveniently compared.^{5,13}

Here the Knoevenagel condensation was reaction 1. That little



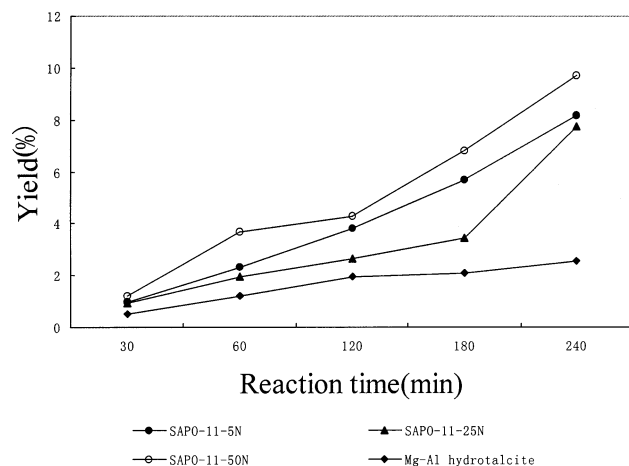


Figure 2. Conversion vs reaction time for nitrated SAPO-11 and Mg-Al hydrotalcite.

activity was found for all samples without doping Ru, even through nitridation carried out in a whole range of nitridation temperatures from 400 to 800 °C, means that there were no basic sites in these samples at all.

The same reaction was performed with the SAPO-11-5N, SAPO-11-25N, SAPO-11-50N, and Mg-Al hydrotalcite catalysts. From the results shown in Figure 2, we can see that the nitrides were much more active than Mg-Al hydrotalcite in Knoevenagel condensation. The nitrogen-incorporated SAPO-11 samples gave 8.3%, 7.9%, and 9.5% conversion, respectively, depending on the time of nitridation. The conversion of benzaldehyde for SAPO-11-5N was higher than that for SAPO-11-25N, due to a significant number of $-NH_2$ terminal groups existing in the samples at the beginning of nitridation.⁴ The selectivity of this condensation product (malononitrile benzylidene) was about 100% for all samples, no further reaction following a Michael-type addition was observed.

According to the observation from Benitez,¹² freshly prepared amorphous aluminophosphate oxynitride (AIPON) catalysts readily underwent hydration and hydrolysis under atmospheric conditions. Hydration and hydrolysis were observed for nitrogen-incorporated SAPO-11 molecular sieve catalysts, but the loss of basicity was not obvious. For the SAPO-11-50N, the conversion of benzaldehyde still remained at about 8%, which was comparable to the fresh counterpart, even though the sample was placed under atmospheric conditions for more than two months, implying that oxygen atoms in the framework of SAPO-11 zeolites could be substituted to some levels by nitrogen-containing groups. This substitution occurring during nitridation would be confirmed by the following NMR measurements.

MAS NMR Spectrum Characterization. High-resolution magic-angle spinning solid-state NMR is a powerful tool to elucidate details of molecular sieve structure. In the case of this study, the combined results of ^{27}Al (Figure 3) and ^{31}P (Figure 4) MAS NMR data provided more information about the changes that occurred after treatment of SAPO-11 with ammonia.

(1) ^{27}Al -MAS NMR Spectra. The ^{27}Al -MAS NMR spectra of the calcined SAPO-11 and the nitrogen-incorporated SAPO-11 samples are shown in Figure 3. The assignments of chemical shifts, found in the literature, are summed in Table 2. The peak at 38.83 ppm was typically the AlO_4 tetrahedron with neighboring PO_4 tetrahedron.¹⁴ There were many opinions about the assignment of 30 ppm: one ascribed it to four-coordinated Al,¹⁵⁻¹⁹ another related it with the five-coordinated Al,²⁰⁻²² and Chen and co-workers considered its assignment as either four-

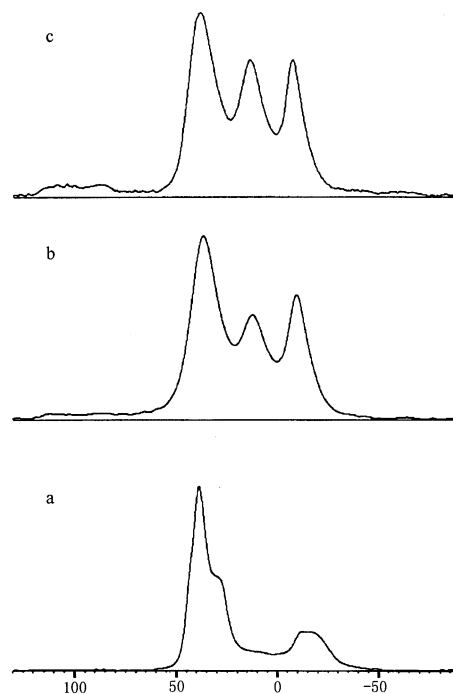


Figure 3. ^{27}Al MAS NMR (a) calcined SAPO-11; (b) SAPO-11-25N; (c) SAPO-11-50N.

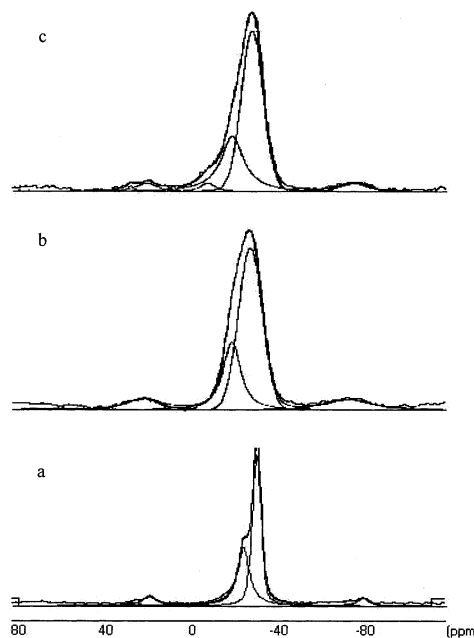


Figure 4. ^{31}P MAS NMR (a) calcined SAPO-11; (b) SAPO-11-25N; (c) SAPO-11-50N.

coordinated Al or five-coordinated Al based on the calcination temperature.²³ The peak at -14 ppm was ascribed to octahedral Al coordinated with 4 PO_4 tetrahedron and 2 H_2O molecules.¹⁴

The ^{27}Al -MAS NMR spectra of SAPO-11-25N (Figure 3b) and SAPO-11-50N (Figure 3c) samples indicated that the peak at -9 ppm is Al hexacoordinated to 4 PO_4 and 2 NH_3 , implying the H_2O of octahedron in the calcined SAPO-11 sample was substituted by NH_3 during nitridation. A new peak at 12.48 ppm occurred in the spectra of SAPO-11-25N and SAPO-11-50N and was ascribed to Al pentacoordinated with 4 PO_4 and 1 NH_3 .⁴ It is emphasized to note that the signals between 84 and 126 ppm, which belonged to the structural nitrogen $Al(N_xO_{4-x})$ ($x = 1\sim 4$), swelled up after the SAPO-11 had been nitrided for 25 h. After 50 h nitridation, two wide new signals at 108

TABLE 2: Summary of Assignment of Chemical Shifts for ^{31}P and ^{27}Al MAS NMR

	chemical shift (ppm)	assignment	ref
^{27}Al	38.83	$\text{Al}(\text{OP})_4$	14
	30	(1) four-coordinated Al	15–19
		(2) pentacoordinated Al	20–22
		(3) decided by the calcination temp.	23
	–14	$\text{Al}(\text{4OP}, 2\text{H}_2\text{O})$	14
	–9	$\text{Al}(\text{4OP}, 2\text{NH}_3)$	4
	12.48	$\text{Al}(\text{4OP}, 1\text{NH}_3)$	
	88	AlO_2N_2	24
	108	AlN_4	
	–29.6	$\text{P}(\text{OAl})_4$	25,26
^{31}P	–23.65	$\text{P}(\text{3OAl}, \text{OH})$	27
	–6.4	PN_4	4,28

and 88 ppm appeared in Figure 3c, which are ascribed to Al tetracoordinated with 4 nitrogens (AlN_4) and Al tetracoordinated with 2 nitrogens and 2 oxygens (AlO_2N_2) respectively.²⁴ This implied that the N atoms were directly bonded to the structural Al atoms.

(2) ^{31}P -MAS NMR Spectrum. The ^{31}P -MAS NMR spectra of the calcined SAPO-11 and its samples treated with NH_3 at 400 °C for 25 and 50 h are shown in Figure 4. The summed assignments of chemical shifts are listed in Table 2. In the ^{31}P -MAS NMR spectrum of calcined SAPO-11 sample (Figure 4a), a resonance at –29.60 ppm is attributed to the typical tetrahedral P site with 4 neighboring AlO_4 tetrahedrons,^{25,26} and the peak at –23.65 ppm should be assigned to tetrahedral P (3AlO_4 , OH).²⁷ In comparing the spectrum of calcined SAPO-11 with that of SAPO-11–50N (Figure 4c), it is worth noting that a new peak at –6.40 ppm appeared, which was ascribed to the tetrahedral PN_4 . This shift is consistent with the replacement of O by N in PO_4 tetrahedron.^{4,28} The results provide evidence for the incorporation of nitrogen into the SAPO-11 framework. Therefore, we can conclude that the nitrogen has directly bonded to P atoms, just as to Al atoms.⁴ Oxynitrides have the character of being liable to hydrolysis,¹⁴ but the nitrogen-incorporated SAPO-11 zeolites were exposed to the moist air for different times and found that the activity in Knoevenagel condensation was lost very little even after two months. These results further proved that the nitrogen had entered into the framework of SAPO-11, because the terminal groups of $-\text{PNH}_2$ or hydroxylamine physically adsorbed are liable to hydrolysis.

Conclusion

A new family of solid base catalysts, nitrogen-incorporated SAPO-11 molecular sieves, has been synthesized with a starting material of SAPO-11 zeolite doped with 2 wt % Ru by nitriding in an ammonia flow at a low temperature of 400 °C. The nitrogen-incorporated SAPO-11 zeolites were characterized by high specific surface areas, fine crystallinity, shape-selectivity, and being active catalysts for the Knoevenagel condensation. The changes in structure of the obtained samples were studied by means of ^{27}Al -MAS NMR and ^{31}P -MAS NMR spectra; it

can be concluded that nitrogen-containing species incorporated into the framework of SAPO-11 zeolite, in which some N atoms directly bonded to Al and P atoms and formed AlN_4 , AlN_2O_2 , and PN_4 groups. These species, together with the terminal $-\text{NH}_2$ group, are responsible for the basicity of nitrogen-incorporated SAPO-11 zeolites.

Acknowledgment. Supported financially by the National Natural Science Foundation of China (20043001).

References and Notes

- (1) Centeno, M. A.; Grange, P. *J. Phys. Chem. B* **1999**, *103*, 2431.
- (2) Benitez, J. J.; Odriozola, J. A.; Marchand, R.; Laurent, Y.; Grange, P. *J. Chem. Soc., Faraday Trans.* **1995**, *91*(24), 4477.
- (3) Centeno, M. A.; Debois, M.; Grange, P. *J. Phys. Chem. B* **1998**, *102*, 6835.
- (4) Stein, A.; Wehrle, B.; Jansen M. *Zeolites* **1993**, *13*, 291.
- (5) Grange, P.; Bastians, P.; Conanec, R.; Marchand, R.; Laurent, Y. *Appl. Catal. A* **1994**, *114*, L191.
- (6) Climent, M. J.; Corma, A.; Fornes, V.; Frau, A.; Guil-lopez, R.; Iborra, S.; Primo, J. *J. Catal.* **1996**, *163*, 392.
- (7) Ding, Y.; Xiong, J.; Lu, Y.; He, X.; Lin, L. *Chin. J. Catal.* **2001**, *22*(3), 227.
- (8) Escalante, D.; Giraldo, L.; Pinto, M.; Pfaff, C.; Sazo, V.; Matjushin, M.; Méndez, B.; López, C. M.; Machado, F. J.; Goldwasser, J.; Ramírez de Agudelo, M. M. *J. Catal.* **1997**, *169*, 176.
- (9) Machado, F. J.; López, C. M.; Goldwasser, J.; Méndez, B.; Yvan, C.; Escalante, D.; Tovar M.; Ramírez-Agudelo, M. M. *Zeolites* **1997**, *19*, 387.
- (10) Alfonso, M.; Goldwasser, J.; López, C. M.; Machado, F. J.; Matjushin, M.; Méndez, B.; Ramírez Agudelo, M. M. *J. Mol. Catal. A: Chem.* **1995**, *98*, 35.
- (11) Tichit, D.; Lhouty, M. H.; Guida, A.; Chiche, B. H.; Figueras, F.; Auroux, A.; Bartolini, D.; Garrone, E. *J. Catal.* **1995**, *151*, 50.
- (12) Benítez, J. J.; Díaz, A.; Laurent, Y.; Odriozola, J. A. *Appl. Catal. A: General* **1999**, *176*, 177.
- (13) Massion, A.; Odriozola, J. A.; Bastians, Ph.; Conanec, R.; Marchand, R.; Laurent, Y.; Grange, P. *Appl. Catal. A: General* **1996**, *137*, 9.
- (14) Jahn, E.; Muller, D.; Richter-Mendau, J. In *Synthesis of microporous materials*; Ocelli, M. L., Robson, H. E., Eds.; Van Nostrand Reinhold: New York, 1992; Vol. 1 Molecular Sieves, p 248.
- (15) Jahn, E.; Müller, D.; Becker, K. *Zeolites* **1990**, *10*, 151.
- (16) Ray, G. J.; Samoson, A. *Zeolites* **1993**, *13*, 410.
- (17) Haddix, G. W.; Narayana, M.; Gillespie, W. D.; Georgellis, M. B.; Wu, Y. *J. Am. Chem. Soc.* **1994**, *116*, 672.
- (18) Samoson, A.; Lippmaa, E.; Engelhardt, G.; Lohse, U.; Jerschewitz, H. G. *Chem. Phys. Lett.* **1987**, *134*, 589.
- (19) Kosslick, H.; Tuan, V.; Fricke, R.; Martin, A. *Studies in Surface Science and Catalysis*; Elsevier: Amsterdam, 1994, Vol. 84 Zeolites and Related Microporous Materials, State of the Art 1994, p 1013.
- (20) Alemany, L. B.; Kirker, G. W. *J. Am. Chem. Soc.* **1986**, *108*, 6158.
- (21) Gilson, J. P.; Edwards, G. C.; Peters, A. W.; Rajagopalan, K.; Wormsbecher, R. F.; Roberie, T. G.; Shatlock, M. P. *J. Chem. Soc. Chem. Commun.* **1987**, *2*, 91.
- (22) Coster, D.; Blumenfeld, A. L.; Fripiat, J. J. *J. Phys. Chem.* **1994**, *98*, 6201.
- (23) Chen, T.; Wouters, B. H.; Grobet, P. J. *Eur. J. Inorg. Chem.* **2000**, *2*, 281.
- (24) Smith, M. E. *J. Phys. Chem.* **1992**, *96*, 6(3), 1444.
- (25) Müller, D.; Jahn, E.; Ladwig, G.; and Haubenreisser, U. *Chem. Phys. Lett.* **1984**, *109*, 332.
- (26) Engelhard, G. *High-Resolution Solid-State NMR of Silicates and Zeolites*; John Wiley: Chichester, 1987; and references therein.
- (27) Jahn, E.; Müller, D.; Becker, K. *Zeolites* **1990**, *10*, 151.
- (28) Bunker, B. C.; Tallant, D. R.; Balfe, C. A.; Kirkpatrick, R. J.; Turner, G. L.; and Reidmeyer, M. R. *J. Am. Ceram. Soc.* **1987**, *70*, 675.