

# Synthesis and characterization of a basic molecular sieve: Nitrogen-incorporated SAPO-34

Xinxin Guan, Fuxiang Zhang\*, Guangjun Wu, Naijia Guan

*Institute of New Catalytic Materials Science, College of Chemistry, Nankai University, Weijin Road 94, Tianjin 300071, P.R. China*

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## Abstract

Microporous nitrogen-incorporated SAPO-34 molecular sieves were synthesized by thermal post-treatment of SAPO-34 in flowing dry ammonia at elevated temperatures. The results of property characterized by DRIFTS of CO<sub>2</sub> adsorption and CO<sub>2</sub>-TPD showed that basic sites existed on the surface of nitridized samples probably due to the presence of nitrogen-containing species incorporating into the framework of SAPO-34 molecular sieves. The changes in structure of nitrogen-incorporated samples were investigated by <sup>27</sup>Al MAS NMR, <sup>31</sup>P MAS NMR spectra X-ray diffraction and BET surface area measurements. It was found that nitrogen-incorporated SAPO-34 still kept good crystallinity and high specific surface area of precursors. And N-containing species had incorporated into the framework of samples during nitridation, in which N atom presumably bounded to Al and P atoms formed N-containing groups, but unfortunately some of them were not ascribed.

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## 1. Introduction

In the past decade, much attention has been focused on the development of solid basic catalysts as substitute of liquid base catalysts [1-3], considering their advantages in separation, regeneration, noncorrosive and environmental friendly properties. Especially, basic molecular sieves are of great interest due to their high specific surface area as well as excellent shape selectivity.

Silicoaluminophosphate molecular sieves having good thermal and hydrothermal stability are commonly composed of AlO<sub>4</sub>, PO<sub>4</sub> and SiO<sub>4</sub> tetrahedron. If the oxygen atoms are substituted by isoelectronic group, such as -NH- species, the Lewis basicity of the framework will increase due to the lower electronegativity of N with respect to O. Accordingly, the nitrogen-incorporated molecular sieves can be anticipated to be desirable potential solid basic catalysts for selectivity catalysis [4]. Compared with amorphous aluminophosphate reported [5-9], the nitridization of crystalline microporous molecular sieves was too difficult to have high nitrogen content

because of their much higher crystallinity and stability of framework [10-12]. Modifying molecular sieves with doping noble metal was therefore adopted to reduce nitridation temperature and prevent the collapse of framework [12]. However, such doping will challenge new problems such as blocking pore channel to decrease catalytic stability and selectivity.

In this work, nitridation of microporous molecular sieve SAPO-34 was firstly reported at elevated temperatures without doping any metals. High nitrogen contents of samples were

Table 1  
BET surface area and nitrogen contents for nitridized SAPO-34 molecular sieves at different temperatures

Sample	Nitridation temperature (°C)	Specific surface (m <sup>2</sup> g <sup>-1</sup> )	Nitrogen content (wt.%)
SAPO-34	–	456	–
SAPO-34-700N <sup>a</sup>	700	439	0.85
SAPO-34-800N <sup>a</sup>	800	425	1.24
SAPO-34-900N <sup>a</sup>	900	364	0.82

<sup>a</sup> 700N, 800N, and 900N denote temperature of nitridation as 700°C, 800°C and 900°C respectively.

\* Corresponding author. Tel./fax: +86 22 2350 0341.

E-mail address: [zhangfx@nankai.edu.cn](mailto:zhangfx@nankai.edu.cn) (F. Zhang).

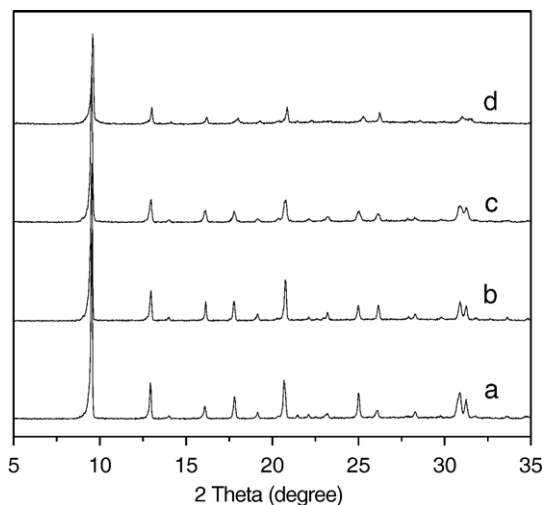


Fig. 1. XRD patterns for pure SAPO-34 (a) and nitridized SAPO-34 molecular sieves at: (b) 700°C, (c) 800°C, (d) 900°C.

obtained with high surface areas of precursors maintained. The changes of Al and P environment were demonstrated by their corresponding NMR spectra. DRIFTS spectrum of CO<sub>2</sub>

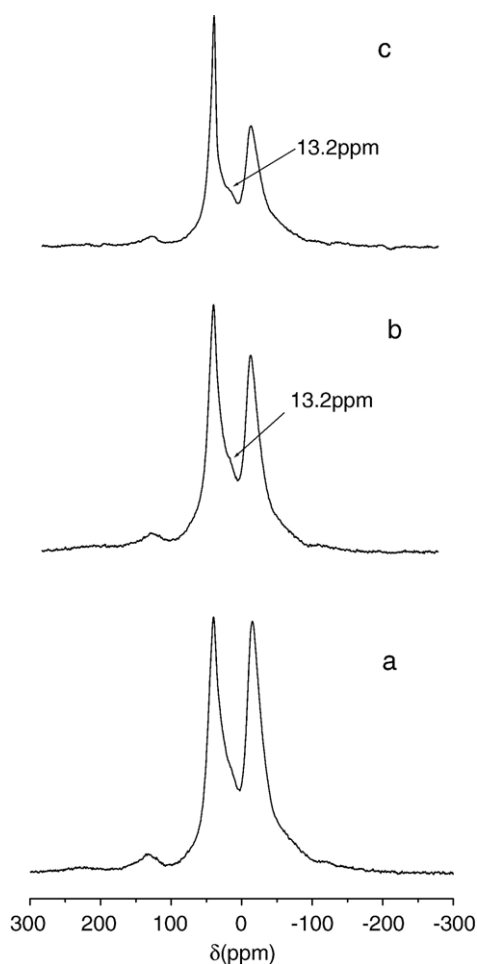


Fig. 2. <sup>27</sup>Al MAS NMR spectra of samples: (a) pure SAPO-34; (b) SAPO-34-N (0.82 wt.% N); (c) SAPO-34-N (1.24 wt.% N).

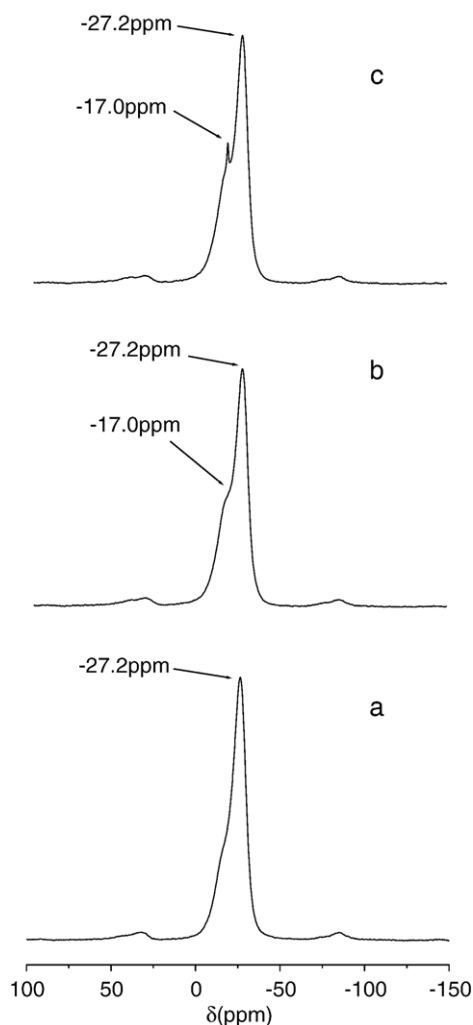


Fig. 3. <sup>31</sup>P MAS NMR spectra of samples: (a) pure SAPO-34; (b) SAPO-34-N (1.24 wt.% N); (c) SAPO-34-N (1.62 wt.% N).

adsorption as well as CO<sub>2</sub>-TPD indicates the existence of basic sites on the nitrogen-incorporated samples (SAPO-34-N).

## 2. Experimental

SAPO-34 molecular sieve was synthesized by hydrothermal method as reported in Ref. [13]. The as-synthesized SAPO-34 was dried overnight and calcined at 550°C for 6 h to remove template prior to the nitridization in the isothermal region of a tubular furnace in flowing dry ammonia at different temperatures. Nitrogen content was detected by alkaline digestion with molten KOH at 400°C, and NH<sub>3</sub> produced was adsorbed by excess H<sub>2</sub>SO<sub>4</sub> solution, which was titrated by standard NaOH solution. XRD patterns were collected in air on a D/Max-2500 commercial instrument; the surface areas of samples were obtained by nitrogen adsorption using a NOVA 1000e after degassing the samples for 1 h under vacuum at 300°C; MAS NMR spectra were performed on a VARIAN INOVA 300M spectrometer; CO<sub>2</sub> adsorption DRIFTS spectra were collected in an FT Bruker Vector 22 infrared spectrometer equipped with a DTGS detector at 4 cm<sup>-1</sup> resolution; the TPD–

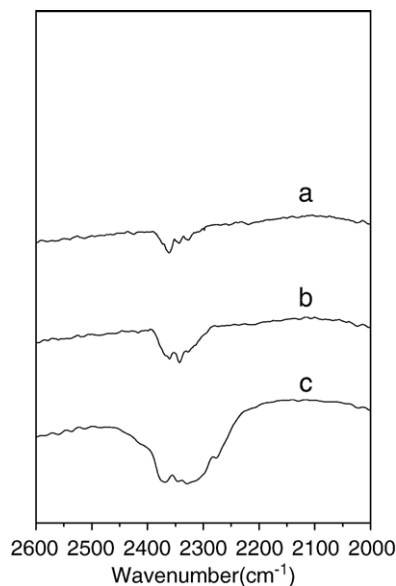
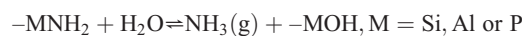


Fig. 4. DRIFTS spectra of CO<sub>2</sub> adsorption for samples: (a) pure SAPO-34; (b) SAPO-34-N (0.82 wt.% N); (c) SAPO-34-N (1.24 wt.% N).

CO<sub>2</sub> experiments were carried out using a TG-DSC thermal analyzer assembly.

### 3. Results and discussion

The nitrogen contents and the surface areas of nitrogen-incorporated samples were summarized in Table 1. Different from the nitridation of amorphous aluminophosphate whose nitrogen content was increased with the enhancement of nitridation temperature [2], the nitrogen content undergoes first an increase and subsequently a decrease as a function of nitridation temperature in this study. Excessively high temperature will lead to a decrease of nitrogen content and surface areas of nitrogen-incorporated samples. The decreased nitrogen content at high temperature may be ascribed to partial destruction of the framework and elimination of some nitrogen species caused by the H<sub>2</sub>O originated from the substitution of O atom by N atom during nitridation (see the following reaction) [14].



The destruction of the framework can be well demonstrated by the XRD patterns (Fig. 1), from which no obvious changes in crystalline were observed for nitrogen-incorporated SAPO-34 sieves treated at below 800 °C, while a certain decline of those happened to the samples treated at 900 °C. This indicates that the thermal stability of nitrogen-incorporated SAPO-34 with respect to pure SAPO-34 was decreased, as may also be ascribed to the formation of water during nitridation.

Such surface species of Al-NH-P, P-NH<sub>2</sub> and Al-NH<sub>2</sub>, which are responsible for the basicity of aluminophosphate oxynitrides (AlPONs) [5], have been studied by in situ IR, XPS and NMR [6–8], but a uniform agreement has not been reached so far on the nature of nitrogen species in nitrogen-incorporated molecular sieves. In this study, high-resolution magic angle spinning solid state NMR and DRIFTS of CO<sub>2</sub> adsorption were mainly employed to detect the nitrogen incorporation and surface basicity on SAPO-34 respectively.

Figs. 2 and 3 showed the <sup>27</sup>Al and <sup>31</sup>P MAS NMR spectra of two representative nitrogen-incorporated SAPO-34 samples with nitrogen content of 0.82 wt.% and 1.24 wt.% respectively (pure SAPO-34 sample as a reference). Compared to pure sample, different Al and P

environment could be observed for both nitrogen-incorporated samples. In Fig. 2, the intensity of the resonance at –15.4 ppm was gradually decreased with the increase of nitrogen content, indicating that parts of hexa-coordinated Al atoms were translated into tetra-coordinated Al. An unobvious shoulder peak which was ascribed to penta-coordinated Al (4 OP, 1 NH<sub>3</sub>) [10], appeared at ca. 13.2 ppm of Fig. 2b and c, indicating that the H<sub>2</sub>O coordinated Al was substituted by NH<sub>3</sub> during nitridation. As for a very weak shoulder peak at about 13.2 ppm in Fig. 2a, it should be ascribed to penta-coordinated Al (4 OP, 1 OH) created during synthesis of molecular sieves. In <sup>31</sup>P MAS NMR spectra (Fig. 3), the peak at –27.2 ppm could be attributed to the typical tetrahedral P site (AlO<sub>4</sub>) [15]. It was interesting that a shoulder peak at ca. –17.0 ppm was observed to be promoted by the enhanced nitrogen content in Fig. 3b and c. This signal indirectly illustrated that NH<sub>3</sub> was incorporated into the molecular sieve [8]. In Fig. 3a, it also seemed to be a very weak shoulder peak at about –20 ppm, which can be assigned to tetra-coordinated P (3 AlO<sub>4</sub>, 1 OH) according to literature [12].

The DRIFTS results of CO<sub>2</sub> adsorption on three typical samples were given in Fig. 4, from which a significant adsorption peak at 2343 cm<sup>–1</sup> assignable to linearly adsorbed bands can be observed clearly. The amount of those sites increased with the nitrogen content as deduced from the evolution of the peak intensity of IR bond at 2343 cm<sup>–1</sup>. These linearly adsorbed CO<sub>2</sub> bands were suggested to be in the asymmetric stretching mode in CO<sub>2</sub> (2349 cm<sup>–1</sup>) and were associated to electron donating centers [16]. Hydroxyl groups in the nitrogen-incorporated samples surface were then acting as weak Lewis basic sites [9]. Since no band shift was observed as the nitrogen content changed, the modification in their strength cannot be expected in this study.

The surface basicity on SAPO-34-N can be further testified by the CO<sub>2</sub>-TPD measurement shown in Fig. 5. Compared to pure SAPO-34 sample, one more desorption curve was discovered at ca. 435 °C for SAPO-34-N (1.24 wt.% N) sample, which can be thought to result from the strong interaction between CO<sub>2</sub> and basic sites. Based on this losing weight data, the nitrogen content was computed and found to be well related to that calculated by the titration method.

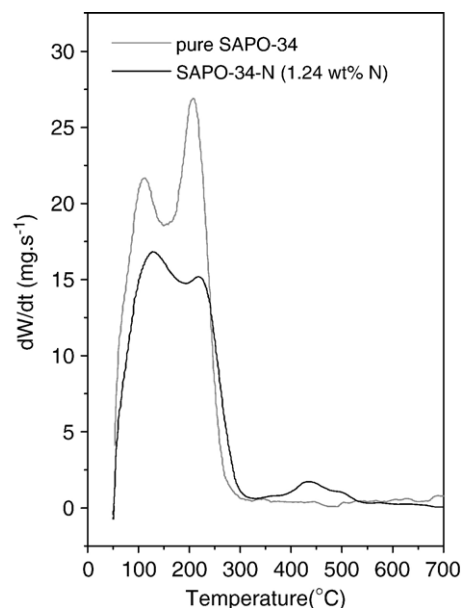


Fig. 5. The CO<sub>2</sub>-TPD plots of pure SAPO-34 and representative SAPO-34-N (1.24 wt.% N).

#### 4. Conclusions

In summary, high specific surface area nitrogen-incorporated SAPO-34 possessing basic site was obtained by nitridation of microporous molecular sieve SAPO-34 in ammonia at elevated temperature without doping any metal. MAS NMR spectra revealed the changes in structure of nitridized samples. DRIFTS results of CO<sub>2</sub> adsorption and CO<sub>2</sub>-TPD confirmed the existence of basic sites which related to the nitrogen content in nitrogen-incorporated samples. Consequently, the nitrogen-incorporated SAPO-34 molecular sieves would be of great interest for potential application in catalytic reactions due to their high surface area, good shape selectivity and basicity described above.

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