Nitrogen-incorporated NaY Zeolite as Promising Basic Microporous Catalytic Material

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Abstract. A promising basic microporous catalytic material is prepared by nitridation of dehydrated NaY zeolite. The base strength of zeolite framework is enhanced due to the replacement of oxygen by nitrogen with lower electronegativity. Various characterization methods, including XRD, CHN elemental analysis, SEM and FTIR spectra of CO adsorption, are employed to analyze the physico-chemical properties of the nitrogen-incorporated NaY zeolite. High crystallinity and high specific surface areas of NaY are well preserved in nitrogen-incorporated NaY. Compared to parent NaY zeolite, the nitridized materials exhibit improved basic catalytic performances in Knoevenagel condensation reaction and side-chain monomethylation reaction of phenylacetonitrile.

Introduction

Nitridation can be employed as an effective method to prepare basic microporous catalytic material. The oxygen atoms of the zeolite framework are replaced to some level by certain isoelectronic groups, such as -NH- species. The Lewis basicity can be enhanced due to the lower electronegativity of nitrogen with respect to oxygen [1]. Various types of nitrogen-incorporated zeolites, such as SAPO-11 [1], NaY [2-5], ZSM-5 [6-8], SAPO-34 [9], Beta [10] and B-SSZ-13 [11] have been successfully synthesized by post-treatment of parent zeolites in ammonia flow at elevated temperatures. The as-prepared nitrogen-incorporated zeolites are expected to be promising candidates for a new set of base-catalyzed reactions.

Compared to mesoporous molecular sieves and amorphous silicas, the nitridation of microporous molecular sieves is much more difficult and the nitrogen contents are quite low, resulting from the highly-stable framework of parent microporous molecular sieves. It represents great difficulties in the characterizations and applications of nitrogen-incorporated zeolites. Recently, Auerbach et.al [5,12] reported a reproducible and effective synthesis method of nitrogen-incorporated zeolites. They conducted dehydration of zeolites prior to the nitridation process under nitrogen flow at 400 $^{\circ}$C for 10 h. This dehydration-nitridation method remarkbaly improved the conventional direct nitridation process. The total nitrogen contents of nitridized zeolites could be enhanced to a large extent.

In this paper, we prepare nitrogen-incorporated NaY zeolite by the dehydration-nitridation processes. Various characterization methods, including XRD, CHN elemental analysis, SEM and FTIR spectra of CO adsorption, are employed to analyze the physico-chemical properties of as-prepared materials. The basic catalytic performances of nitrogen-incorporated NaY zeolite are evaluated by two typical base-catalyzed reactions, e.g. Knoevengel condensation reaction and side-chain monomethylation reaction of phenylacetonitrile. The Knoevengel condensation reaction between benzaldehyde and malononitrile is the most frequently used probe reaction for solid base catalysts. While the side-chain monomethylation reaction of phenylacetonitrile is a key step towards the synthesis of ibuprofen, a well-known anti-inflammatory drug [13]. Phenylacetonitrile is very selectively monomethylated into 2-phenylpropionitrile over NaY zeolite using dimethyl carbonate as methylating agent [14]. The nitrogen-incorporated NaY exhibits improved basic catalytic activities in these two reactions compared to parent NaY zeolite.

Experimental section

Commercial NaY zeolite (Si/Al= 2.8) from Nankai Catalysts Plant (Tianjin, PRC) was used as the starting material. Dehydration of the samples prior to the nitridation process was performed in a quartz tube furnace under high-purity N_2 flow at 400 $^{\circ}$C for 10 h. Following this dehydration step, the N_2 was immediately switched to NH_3 (99.0% purity) for the nitridation process at 850 $^{\circ}$C for different duration. The sample was cooled down to room temperature and further treated in vacuum at 120 $^{\circ}$C for 3 h to remove the adsorbed NH_3.

Powder X-ray diffraction patterns were collected on a D/Max-2500 powder diffractometer (36 kV and 20 mA) using Cu Kα (k = 1.54178 Å) radiation at a scan rate of 4°/min. The total nitrogen contents of as-prepared samples were determined by CHN elemental analysis on an Elementar Vario EL analyzer. Scanning electron microscopy (SEM) images of samples were taken on a HITACHI S-3500N electron microscope with SEI of 25 KV, 10^{-11} A. FTIR studies of CO adsorption were carried out using a Bruker Tense 27 spectrometer equipped with a heatable and evacuable IR cell with ZnSe windows, connected to a gas dosing-evacuation system. After activated at 400 $^{\circ}$C in He for 1 h, the FTIR spectra of CO adsorption was measured at room temperature using 2% CO/He mix gas.

The Knoevengel condensation reaction between benzaldehyde and malononitrile was performed into a round bottom flask equipped with a magnetic stirrer and a reflux condenser. 20 mmol benzaldehyde and 20 mmol malononitrile were added into the round bottom flask with 10 ml toluene used as solvent. Once the mixture reached 80 $^{\circ}$C, 0.15 g catalyst was added into the flask. 0.2 µl of the liquid samples was then periodically withdrawn from the reaction mixture with a syringe and analyzed in a GC 7890F equipped with a flame-ionization detector and a FFAP capillary column.

The side-chain monomethylation reaction of phenylacetonitrile (PAN) with dimethyl carbonate (DMC) was carried out on a fixed-bed microreactor at atmospheric pressure. About 0.4 g of the catalyst (20-40 mesh) was placed in the isothermal region of the reactor. The reactant mixture of dimethyl carbonate and phenylacetonitrile having a 16:1 molar ratio was pumped by a syringe pump into a vaporize device and preheater device where it was vaporized, mixed with high-purity N_2, and then pre-heated to 240 $^{\circ}$C. The reaction was performed at 260 $^{\circ}$C. The products were analyzed by gas chromatography using GC 7890F equipped with a FID detector and a FFAP capillary column.

Results and discussion

The total nitrogen contents in NaY nitridized for different duration (labeled as NaY-tN and t represents the nitridation duration in hours) are summarized in Table 1. The nitrogen contents in NaY-tN undergo obvious increase with nitridation duration prolonged to 36 h when the highest nitrogen content of 4.05% can be obtained. Excessively nitridation duration causes the decrease in nitrogen content, probably due to the elimination of nitrogen species by the H_2O originated from the nitridation process [15].

Table 1. Nitrogen contents in NaY nitridized for different duration

Samples	Nitridation temperature	Nitridation duration	Nitrogen content
NaY-12N	850 $^{\circ}$C	12 h	2.63 %
NaY-24N	850 $^{\circ}$C	24 h	3.04 %
NaY-36N	850 $^{\circ}$C	36 h	4.05 %
NaY-48N	850 $^{\circ}$C	48 h	3.21 %

Fig. 1 shows the powder X-ray diffraction patterns of calcined NaY zeolite and samples nitridized for different duration. No obvious changes in XRD diffraction peaks, both in position and intensity, can be observed, indicating that the framework of NaY is well preserved after nitridation at 850 ^{o}C.
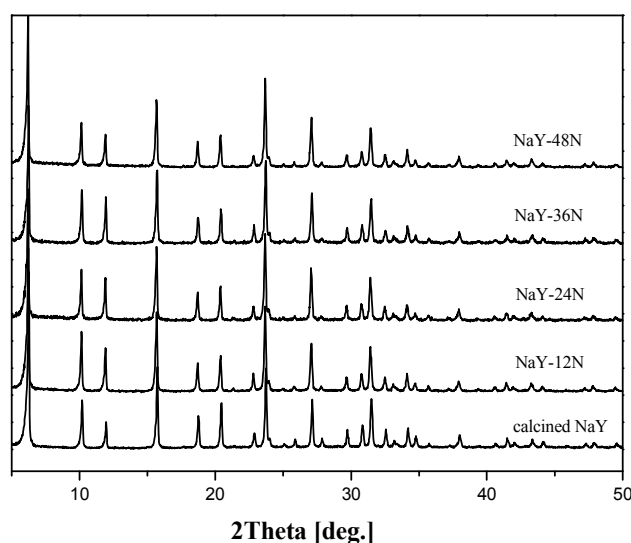

Fig. 1 XRD patterns of calcined NaY and samples nitridized for different duration.

Fig. 2 shows the SEM images of NaY zeolite before and after nitridation. The NaY zeolite presents the morphology of regular sheet with uniform crystal particle size. It is seen that the shape and size of crystallites are well preserved after dehydration and nitridation processes. That is, the high crystallinity and framework of parent NaY zeolite are well preserved, in consistence with XRD results.
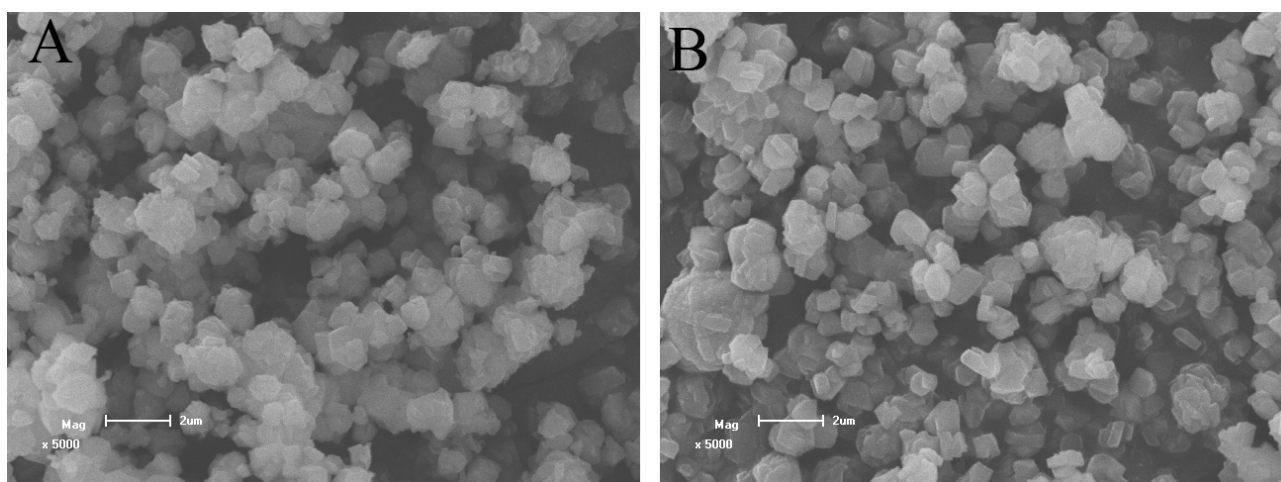

Fig. 2. SEM images of samples NaY (A) and NaY-36N (B)

Carbon monoxide is the most frequently used probe molecule for determination of surface basicity known so far [16]. Fig. 3 shows the FTIR spectra of CO adsorption on NaY and NaY-36N catalyst. For NaY-36N, bands at 2290 cm^{-1} and 2186 cm^{-1} appear upon CO adsorption, assigned to NCO species [17]. The appearance of NCO species can be ascribed to the incorporation of nitrogen into NaY framework after nitridation. The band at 2165 cm^{-1} assignable to Na^{+}-CO species is observed on NaY and NaY-36N catalysts [18,19]. For NaY-36N, two more intense bands at 1683 cm^{-1} and

1259 cm^{-1} are clearly observed due to the inhanced basicity by nitridation. The band at 1683 cm^{-1} is assigned to the stretching vibration of bridged carbonates while the band at 1259 cm^{-1} is assigned to the asymmetrical stretching vibration of bidentate carbonates [20,21].
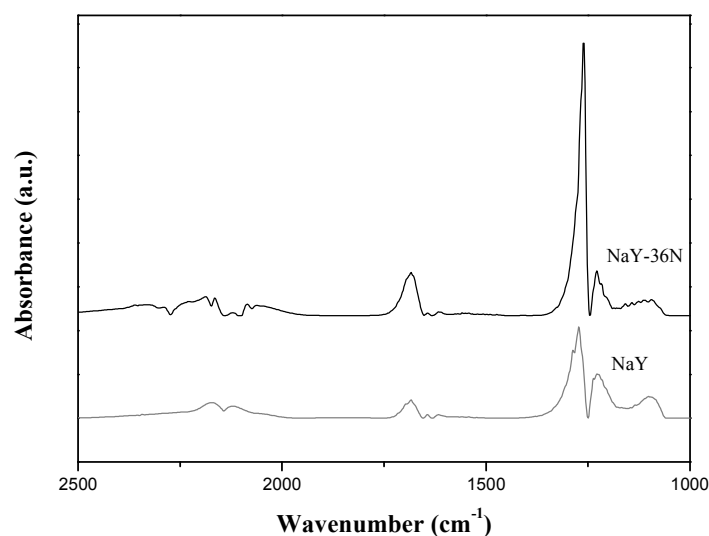

Fig. 3. FTIR spectras of CO adsorption on NaY and NaY-36N.

The Knoevenagel condensation reaction between benzaldehyde and malononitrile has been extensively used as a probe reaction for the evaluation of solid base catalysts (Scheme 1). We perform Knoevenagel condensation reaction to evaluate the basicity of as-prepared materials at 80 °C. The catalytic results are presented in Fig. 4. It is found that the parent NaY zeolite exhibits moderate benzaldehyde conversion due to its inherent basicity. Compared to parent NaY, the benzaldehyde conversion over NaY-N catalyst is much higher, suggesting that the basicity of NaY increase distinctly after proper nitridation. No Michael addition products can be detected under our reaction conditions and the selectivity to target product 1, 1-dicyanophenylethylene is approaching 100%.

Scheme 1: The Knoevenagel condensation reaction between benzaldehyde and malononitrile
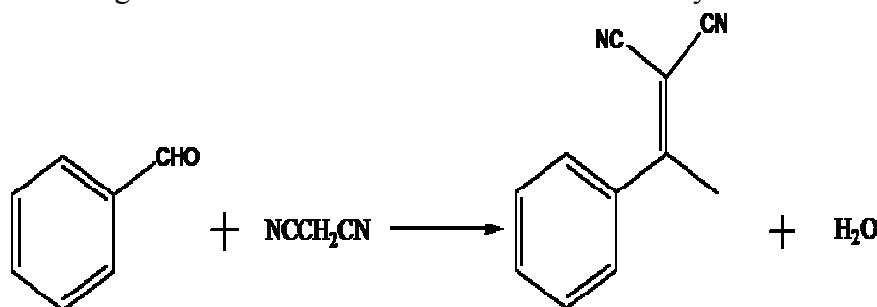
Scheme 2: The side-chain monomethylation reaction of phenylacetonitrile with dimethyl carbonate
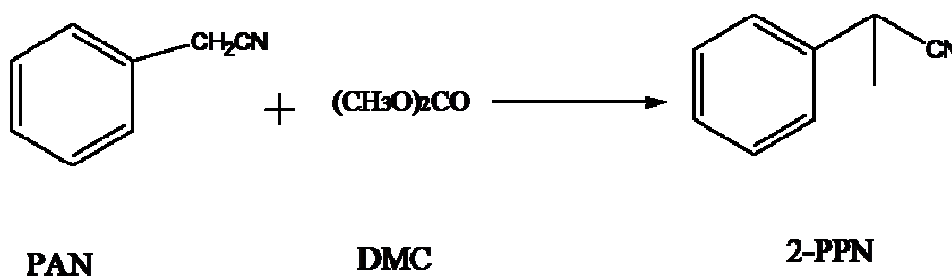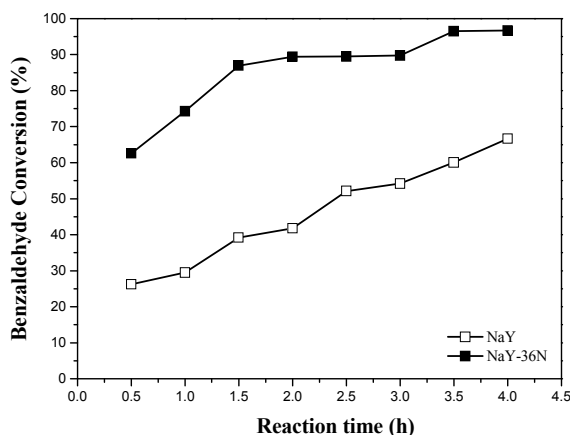
Fig. 4. Benzaldehyde conversion of Knoevenagel condensation reaction over NaY and NaY-36N.

The side-chain monomethylation reaction of phenylacetonitrile is an important step towards the synthesis of ibuprofen. Phenylacetonitrile (PAN) is very selectively monomethylated into 2-phenylpropionitrile (2-PPN) over NaY zeolite using dimethyl carbonate (DMC) as methylating agent (Scheme 2). Fig. 5 shows the results of monomethylation reaction of phenylacetonitrile with dimethyl carbonate over NaY and NaY-36N catalysts at 260 ^{o}C. The conversion of PAN decreases slightly over NaY-36N. But the selectivity of 2-PPN increased observably over NaY-36N catalyst. Thus the obvious enhancement in the yield of 2-PPN can be seen over NaY-36N catalyst compared to parent NaY. Here other products mainly include tolylacetonitrile by methylation of the aromatic. NaY-36N is a promising catalyst for the production of 2-PPN from monomethylation of PAN.
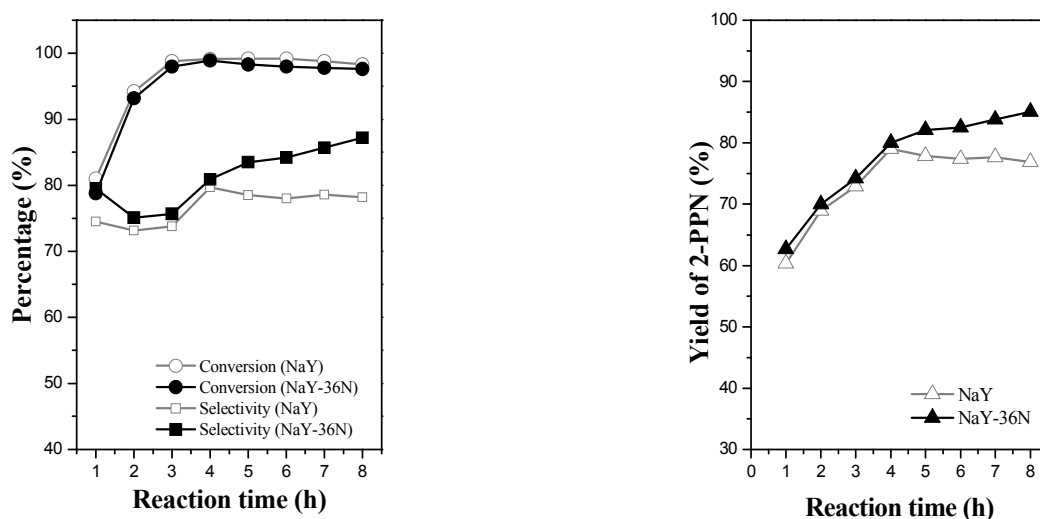

Fig. 5. The results of phenylacetonitrile monomethylation over NaY and NaY-36N catalysts.

Conclusions

The nitrogen-incorporated NaY material is prepared from parent NaY by dehydration-nitridation processes and highest nitrogen content of 4.05 % can be obtained when nitridized at 850 ^{o}C for 36 h. The high crystallinity and structure of parent NaY can be well preserved during nitridation while the base strength of NaY is enhanced to some extent. FTIR spectra of CO adsorption reveal the appearance of NCO species on NaY after nitridation, which should be originated from the CO adsorption on N atoms in the framework. Nitrogen-incorporated NaY exhibits improved catalytic performances in two typical base-catalyzed reactions, *e.g.* Knoevenagel condensation reaction and side-chain monomethylation of phenylacetonitrile.

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