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Study on the oxidation transformation of hexamethyleneimine in a confined region of zeolites

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ABSTRACT

Two kinds of zeolites (mordenite and $AlPO_4$-5, with MOR and AFI topology, respectively) have been synthesized using hexamethyleneimine (HMI) as structure directing agent. It is found that HMI is incorporated intact in its protonated form in MOR and AFI. Furthermore, the oxidation of HMI restricted in the two zeolites by H_2O_2 has been studied. Analysis of FT-IR, Raman spectra, TG/DTA, EA and ^{13}C MAS NMR show that the restricted HMI molecules are changed into saturated hydrocarbons and some other amines in AFI, whereas unchanged in MOR. The adsorption tests illustrated that the as-synthesized samples and their oxidized products have high adsorption capacity for Ni(II). This work opens new opportunities for further research of molecular reactions on the inorganic hybrids, and provides a new idea for the application of SDAs present in molecular sieves.

1. Introduction

Zeolites are generally synthesized in the presence of inorganic and/or organic structure-directing agent (SDA) [1,2]. Typically, organic molecules employed as SDAs usually control zeolite crystal morphology and stabilize the zeolite framework. SDAs are also trapped in zeolite void space during synthesis process and should be eliminated by combustion in order to open zeolite porosity [3]. However, the removal of organic SDAs has certain drawbacks such as generation of environmentally gases due to the combustion of the SDA [4] and even decomposition of zeolite during SDA elimination [5]. Therefore, it is significant to study the use of the SDAs trapped in zeolites.

In recent years, considerable attention has been paid to explore the multifarious functions of layered double hydroxides especially the interlayer chemical reaction of the restricted organic and potential applications [6–10]. However, although widely applications (adsorption, catalysis, and ion-exchange) of zeolites and zeolite-like materials due to their desirable properties (such as having a unique framework structure, solid acidity, molecular sieving and ion-exchange abilities) [11–14], there are few reports on the investigation of the properties and applications of organic molecules in a restricted region of zeolite. Recently, we have investigated the oxidation of n-butylamine and ethylene glycol molecules by H_2O_2 or HIO_4 trapped in different zeolites [15,16]. It was found that due to the host-guest interactions occurring within zeolites, the oxidation properties of n-butylamine and ethylene glycol molecules are different from the organic molecules in aqueous solution.

In the present work, hexamethyleneimine (HMI) restricted in mordenite and $AlPO_4$-5 are served as the research subject to study the properties and applications of SDAs occluded in zeolites. Mordenite zeolite (framework type MOR), possesses two channels, one consists 12-MR pores running along the c-axis, while the other one called side pocket consists of 8-MR pore along the b-axis [17,18]. $AlPO_4$-5, with the AFI topology, possesses uniform one-dimensional hexagonal-packed channels with 12-MR windows paralleling to the c-axis of the crystal [19,20]. Due to the different structure types of MOR and AFI, the conformation of the HMI molecules and the relative mobilities of the different atoms in the organic cations are different [21]. Hence, the molecular property of the HMI should be different as a result. In this paper, the oxidation of HMI occluded in the two zeolites has been studied by adding H2O2. The adsorption of Ni(II) by the as-synthesized zeolites and their oxidized products were also studied. The study of the oxidation transformation of HMI in confined regions of zeolites opens new opportunities for further

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research of zeolites on the inorganic hybrids, and provides a new idea for the application study of SDAs present in zeolites.

2. Experimental

2.1. Synthesis of mordenite and $AlPO_4$-5

The synthesis gel to obtain MOR has the following molar composition: 7.5 SiO_2: 1 Al_2O_3: 1.5 Na_2O: 2.6 HMI: 82.5 H_2O. The hydrogel was obtained by adding the source of silica (99.8% Silica fume) to a previously prepared homogeneous solution consisting of $NaAlO_2$ (45% Al_2O_3), HMI ($C_6H_{13}N$, 99.0%), NaOH and distilled water. The gel was charged into 30 mL stainless steel Teflon lined autoclaves and kept at 170 °C for 3 d in a static system oven [22].

The molar compositions of the reactant gel to obtain AFI is: 1 Al_2O_3: 1.8 P_2O_5: 4.5 HMI: 45 EG. $Al(OH)_3$ was dissolved in ethylene glycol (99.7%), and then H_3PO_4 (85%) was added into the above solution. The mixture was stirred for 2 h at room temperature. After stirring, HMI was added and the final mixture was kept at 200 °C for 15 d [23].

The as-synthesized samples (assigned as HMI/MOR and HMI/AFI, respectively) were filtered, washed with distilled water, and dried at 100 °C overnight. The organic species were removed by calcining the as-synthesized samples in air at 550 °C for 6 h and the products were respectively shown as MOR and AFI.

2.2. Oxidation of as-synthesized MOR and AFI by H_2O_2

0.8 g H_2O_2 (30 wt% solution in water) was added to a suspension of as-synthesized samples in deionized water (100 mL). Due to the different weight ratio of organic in the two zeolites (2.20% in HMI/MOR and 19.47% in HMI/AFI, see Table 1 below), the weight of HMI/MOR added was 1.2 g while HMI/AFI was 0.13 g. After stirring for 24 h, the oxidized products (denoted by HMI/MOR + H_2O_2 and HMI/AFI + H_2O_2, respectively) were subsequently isolated by suction filtration and dried at 100 °C overnight.

2.3. Characterization

The crystalline structures of solid products were determined by powder X-ray diffraction patterns on a Panalytical X'Pert Powder diffractometer (Cu Kα). The range of scanning was 3–50° at a rate of 8° min^{-1}. IR transmission spectra were measured by a Nicolet 6700 FTIR spectrometer over the spectral region from 4000 to 400 cm^{-1} with of 4 cm^{-1} resolution. The standard KBr disc method was used. Raman spectra were recorded with a Thermo Scientific Raman spectrometer, with a 532 nm excitation line. The thermogravimetric analysis was performed on a TA Instrument, Q50. The measurement was conducted from 25 to 800 °C at a heating rate of 10 °C min^{-1} under nitrogen flow. The content of Si, Al, P, Na and Si/Al, P/Al ratios were recorded by inductively coupled plasma emission spectrometer (ICP, Optima2000DV, PerkinElmer). The content of carbon, nitrogen and hydrogen in the samples was determined by ElementarvarioEL III elemental analyzer. The ^{13}C MAS NMR spectra were recorded on a Bruker AVANCE III 600 spectrometer at a resonance frequency of 150.9 MHz. Magicangle spin rates of 8 kHz and a 4 mm MAS probe was used for the ^{13}C MAS measurement. The chemical shifts of ^{13}C were externally referenced to TMS.

2.4. Adsorption study

The adsorption study was carried out by using MOR, HMI/MOR and HMI/MOR + H_2O_2, AFI, HMI/AFI and HMI/AFI + H_2O_2 as original materials. Analytical $NiCl_2 \cdot 6H_2O$ was used to prepare Ni(II) solutions. In the batch experiments, 0.05 g of the samples were added to erlenmeyer flasks equipped with 50 mL 100 mg L^{-1} Ni(II) solution, respectively. After shaking 24 h in a vibrator at 150 rpm at ambient temperature of 25 °C, the solution was filtered through a 0.45-μm syringe filter. Then the Ni(II) content was determined by Atomic Absorption Spectroscopy (AAS). The data of these experiments were the averages of duplicate determinations.

The adsorption capacity of the adsorbent can be calculated by the following equation [24,25]:

$$q_e = \frac{(C_0 - C_e)}{M} \times V \tag{1}$$

where q_e is the equilibrium adsorption capacity of the adsorbent (mg g^{-1}), C_0 and C_e are the initial and equilibrium concentration of nickel ion (mg L^{-1}), M and V are amount of sorbent (g) and volume of solution (L), respectively.

3. Results and discussion

3.1. Characterization of as-synthesized MOR and AFI

XRD patterns of HMI/MOR and HMI/AFI are shown in Fig. 1. As observed in Fig. 1a, the characteristics XRD lines of the synthetic MOR have good agreement with the XRD data of MOR-type zeolite reported in the literature [26–28]. Similarly, no peaks of any impurities are detected in Fig. 1b corresponding to AFI [29]. Thus, pure MOR and AFI were synthesized in the presence of HMI.

Fig. 2 shows the FT-IR spectra of HMI/MOR and HMI/AFI. The infrared spectrum of Fig. 2a shows the main bands of mordenite zeolite: 1224 cm^{-1} (T-O symmetric stretch) [30], 1048 and 781 cm^{-1} (T-O-T asymmetric and symmetric stretching vibrations), 628 and 581 cm^{-1} (double five member rings), 449 cm^{-1} (T-O-T bending vibrations) [31]. In Fig. 2b, the weak bands at 462, 629, 734 and 1219 cm^{-1} are related to the symmetric and asymmetric stretching vibrations of the Al-O-P units, and the band appearing at 548 cm^{-1} arises from the P-O or Al-O bending modes [32,33]. The

Table 1
Chemical analysis and organic content of HMI/MOR, HMI/AFI, HMI/MOR + H_2O_2 and HMI/AFI + H_2O_2.

Samples	Content (%)							Si/Al or P/Al Ratio[c]
	C[a]	N[a]	H[a]	C/N[a]	Organic[b]	Si or P[c]	Al[c]	
HMI/MOR	1.89	0.36	1.36	6.12	2.20	23.55	7.54	3.01
HMI/AFI	14.47	2.00	2.36	8.43	19.47	14.96[d]	15.97	0.82[d]
HMI/MOR + H_2O_2	2.07	0.40	1.51	6.05	2.47	22.44	7.07	3.06
HMI/AFI + H_2O_2	9.81	1.58	1.87	7.25	11.29	18.34[d]	19.61	0.82[d]

[a] Measured by CHN analysis.
[b] Measured by TG analysis.
[c] Measured by ICP analysis.
[d] Content of P or P/Al ratio.