



Study on the oxidation transformation of cyclohexylamine in a confined region of zeolites and their adsorption for Ni (II) from aqueous solution

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ABSTRACT

Mordenite and ZSM-5 (with MOR and MFI topology, respectively) have been synthesized using cyclohexylamine (CHA) as structure directing agent. The zeolite crystals obtained were characterized by X-ray diffraction (XRD), infrared spectra (IR), Raman spectra, thermal analysis (TG/DTA), elemental analysis (EA) and ¹³C MAS NMR spectroscopy. It was found that CHA was trapped in the two zeolites in its protonated state together with some other organic species. Furthermore, the oxidation of CHA restricted in zeolites by H₂O₂ has been studied. The oxidation products of restricted CHA were nitro compound and saturated hydrocarbons in mordenite, whereas nitro compound, cyclanes and amines in ZSM-5. 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.

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1. Introduction

Zeolites are generally synthesized from aluminosilicate hydrogels 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 the generation of environmentally gases due to the calcination of the SDA [4] and even the 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]. 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 H₂O₂ or HIO₄ trapped in different zeolites [15,16]. It was found that the oxidation properties of restricted n-butylamine and ethylene glycol molecules are different from themselves in aqueous solution. These research shows that the property of the SDA is influenced by the geometrical restrictions, Si/Al ratios and framework charges of the zeolites [17–19]. In order to insight into the properties of SDA restricted in zeolites, we need to continue to study the state and properties of SDA in a confined region.

In the present study, mordenite and ZSM-5 have been synthesized in the CHA-H₂O system. Mordenite zeolite, with the MOR topology, possesses two channels, one consists of 12-MR channels running along the c-axis, while the other one consists of 8-MR pore along the b-axis [20,21]. ZSM-5 with MFI structure contains two intersecting 10-MR channels, among which straight channels parallel to b-axis and zig-zag channels parallel to a-axis [22,23]. The state of CHA molecules in the two zeolites was characterized. In

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order to investigate the properties of CHA restricted in zeolites, the oxidation of CHA restricted in mordenite and ZSM-5 has been studied firstly by adding H_2O_2 . The pore size of mordenite is 0.65×0.70 nm and 0.26×0.57 nm, while 0.51×0.55 nm and 0.53×0.56 nm of ZSM-5. The gallery height of H_2O_2 molecule is smaller than the pore size of zeolites. Thus, H_2O_2 molecules can penetrate into the two zeolite pores. It was found that the oxidized products of CHA in the two zeolites by H_2O_2 were influenced by the confined environment of the zeolites, and differ from the bulk reaction [24,25]. The adsorption of Ni (II) by the as-synthesized zeolites and their oxidized products were also studied. This work provides the way for prospective research of zeolites as novel reactors for confined chemical reactions, and new opportunities for further research into zeolites on the inorganic hybrids and for their application in adsorption.

2. Experimental

2.1. Synthesis of mordenite and ZSM-5

The hydrothermal synthesis of ZSM-5 in the presence of cyclohexylamine was carried out as follows. The hydrogel was obtained by adding the source of silica (99.8% Silica fume, Aldrich) to a previously prepared homogeneous solution consisting of cyclohexylamine $C_6H_{13}N$ (Prolabo, 98.5%), sodium aluminate (45% Al_2O_3 , 55% Na_2O , Aldrich), sodium hydroxide (Carlo Erba, > 96%) and distilled water. The molar composition of the resultant mixture was 1 SiO_2 : 0.01 Al_2O_3 : 0.1 Na_2O : 0.4 CHA: 25 H_2O . The gel was sealed in a 50 mL stainless steel Teflon lined autoclaves and subjected to hydrothermal treatment at 170 °C for 2 d. The synthesis gel to obtain mordenite had the following molar composition: 1 SiO_2 : 0.04 Al_2O_3 : 0.042 K_2O : 0.098 Na_2O : 16 CHA: 54 H_2O . The mixture was sealed in a 50 mL stainless steel Teflon lined autoclaves, and crystallization was conducted at 140 °C for 3 d.

After crystallization, the as-synthesized samples were filtered, washed with distilled water, and dried at 100 °C overnight. The as-synthesized mordenite and ZSM-5 were assigned as CHA/mordenite and CHA/ZSM-5, respectively. After calcining at 550 °C for 6 h, the materials were shown as mordenite and ZSM-5, respectively.

2.2. Oxidation of as-synthesized mordenite and ZSM-5 by H_2O_2

0.4 g H_2O_2 (30 wt% solution in water) was added to a suspension of CHA/mordenite or CHA/ZSM-5 (0.3 g) in deionized water (50 mL). After stirring for 24 h, the product was subsequently isolated by filtration under suction and dried at 100 °C overnight. The oxidized products were denoted by CHA/mordenite+ H_2O_2 and CHA/ZSM-5+ H_2O_2 , respectively.

2.3. Characterization

The crystalline structures of solid products were determined by powder X-ray diffraction (XRD) patterns on a PANalytical X'Pert Powder diffractometer (Cu $K\alpha$). The range of scanning was 4–50° at a rate of 8° min^{-1} . The content of Na, Si, Al and Si/Al ratios were recorded by inductively coupled plasma emission spectrometer (ICP, Optima, 2000DV, PerkinElmer). IR transmission spectra were measured by a Nicolet 6700 FTIR spectrometer over the spectral region from 4000 to 300 cm^{-1} at 4 cm^{-1} resolution. The standard KBr disc method was used. Raman spectra were measured by 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 700 °C at a heating rate of 10 °C min^{-1} under nitrogen flow. The content of

carbon and nitrogen in the synthesized zeolites was determined by Elementarvario EL 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. Batch adsorption study

All the adsorption experiments were carried out by using batch technique under ambient conditions. The materials for the adsorption study included mordenite and ZSM-5, CHA/mordenite and CHA/ZSM-5, CHA/mordenite+ H_2O_2 and CHA/ZSM-5+ H_2O_2 . Metal ion solutions were prepared by dissolving analytical $NiCl_2 \cdot 6H_2O$ in deionized water. In the batch experiments, 0.03 g of the samples were added to erlenmeyer flasks which contain 50 mL 100 $mg L^{-1}$ Ni (II) solution, respectively. Erlenmeyer flasks were sealed and shaken in a vibrator at 150 rpm at ambient temperature of 25 °C for 24 h. The solution was filtered through a 0.45- μm syringe filter, and 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 was calculated by following equation [26,27]:

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

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 mordenite and ZSM-5

XRD patterns of the as-synthesized mordenite (Fig. 1a) and ZSM-5 (Fig. 1b) in the CHA- H_2O system are shown in Fig. 1. As observed, pure phase mordenite and ZSM-5 zeolites were obtained [20,28,29].

Fig. 2 shows the FT-IR spectra of CHA/mordenite and CHA/ZSM-5. In Fig. 2a, the band observed at 1230 cm^{-1} is represented to T-O

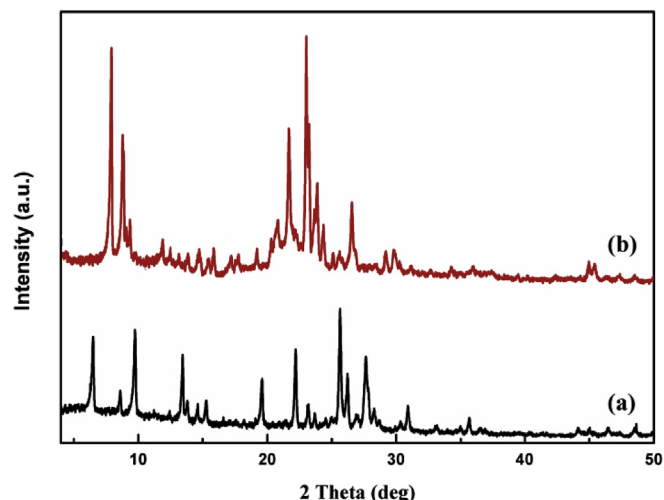


Fig. 1. XRD patterns of as-synthesized (a) mordenite and (b) ZSM-5.

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