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Selective adsorption of zeolite towards nitrosamine in organic solution

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ABSTRACT

Experiments were carried out to study the adsorption of four nitrosamines (*N*-nitrosohexamethyleneimine (NHMI), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosonornicotine (NNN) and *N*-nirosodiphenylamine (NDPA)) by zeolites in organic solvents. It was found that zeolites of different pore structures and hierarchy exhibited different selectivity towards the nitrosamines. The behavior was generally governed by geometric matching between the adsorbate and adsorbent: zeolites with smaller pores favored the trap of smaller nitrosamines whereas mesoporous zeolites captured more bulky nitrosamines. Nevertheless the adsorption of bulky NDPA and NNN was found to take place on type A zeolite, which has a smaller pore size than the molecular diameter of the two nitrosamines. Meanwhile, the presence of other compounds with nitro group in the system appeared to interfere with the adsorption. Among the zeolites studied, CsA and KA could distinguish the bulky nitrosamines such as *N*-nitrosodiphenylamine (NDPA) and nitro compounds (nitrobenzene). The influence of the solvent on the adsorption was also studied.

1. Introduction

Reducing environmental carcinogens is one of the applications for zeolites in life science. Among many harmful constituents present in our environment, nitrosamines are a class of well-known carcinogens. They can be found in tobacco smoke, alcoholic beverages and fried meat products. Among the different forms of tobacco uses, the exposure level for tobacco-specific nitrosamines (TSNAs) are reported to be 48 (heavy smokers), 223 (tobacco chewers) and 733 (snuff users) μg per person per day and TSNAs can contribute to the induction of lung cancer, esophagus, nasal and oral mucosa [1,2]. Some of the volatile nitrosamines are also carcinogenic. The largest contributors to dietary volatile nitrosamines are alcoholic beverages, salted fish and cured meat containing nitrite. Some drugs with amines or N-substituted amides can be nitrosated in human body to generate nitrosamines [3]. Selective removal of nitrosamines from our environment is therefore beneficial. In previous studies, we have attempted to use zeolites and other molecular sieves to adsorb different forms of nitrosamines [4–6]. In principle, this relies on pore size selection and optimization of electrostatic interaction between the cations of zeolite and the oxygen atom in the N–NO group of nitrosamines, with mass transport playing a secondary role [7–9]. In this work we investigated the selective adsorption of nitrosamines by zeolites in organic solvent systems.

To improve the adsorption for nitrosamines of various structures and sizes in a mixed system (i.e., a few nitrosamines and/or with an interference agent), an adsorbent with hierarchical rather than ordered pore structure is preferred. ZSM-5 is a medium pore (0.51–0.56 nm) zeolite of MFI structure, and consists of straight along [0 1 0] and zig-zag channels along [1 0 0] defined by 10-membered rings [10]. Due to its unique shape selectivity, solid acidity, ion exchangeability, pore size, thermal stability and structural network, ZSM-5 zeolite has been widely used as catalysts and sorbents [11,12]. Recently, ZSM-5 was often preferred to create the mesopores but could maintain most of the microstructure and formed the hierarchical MFI zeolites [13]. In this respect, we tested "desilicated" HZSM-5, which was previously used to adsorb volatile nitrosamines in an artificial gastric solution [14]. Desilication introduces mesopores in HZSM-5. The effect of the modified HZSM-5 on the adsorption of different nitrosamines (volatile and tobacco-specific) in solvents was further investigated here.

Zeolite A is selected as another adsorbent because it has the smallest pore diameter among commercial zeolites. Moreover, the pore diameter of zeolite A can be adjusted through exchange with different alkali metal cations or alkaline-earth metal cations [15]. Besides, the highest cation exchange capacity [15] enables zeolite A to be utilized for the adsorption of radioactive elements such as cesium and iodine [16]. Thus, it is valuable to explore the different adsorption capabilities of CsA, KA, NaA and CaA (pore size ranging from 0.2–0.5 nm) towards the bulky nitrosamines in solution. Also, we added nitrobenzene to the system together with targeted nitrosamines. The purpose was to investigate any competitive effects of the oxygen atom in nitrobenzene on the

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adsorption of nitrosamines, i.e., can zeolites of different porous structure distinguish the two adsorbates in the solution? In addition, we also studied the influence of the solvents on the adsorption.

2. Experimental

N-Nitrosohexamethyleneimine (NHMI), *N*-nitrosopyrrolidine (NPYR) and *N*-nitrosonornicotine (NNN) were purchased from Sigma and dissolved in dichloromethane. *N*-nirosodiphenylamine (NDPA) was synthesized by reacting $NaNO_2$ and diphenylamine (DPA) in an acid solution [9,17]. Nanjing Chemistry Factory (China) provided CsA, KA, NaA and CaA (Si/Al = 1). NaY (Si/Al = 2.86) was commercially available as powders from Wenzhou Catalysts Factory. NaZSM-5 (Si/Al = 26) zeolite was bought from Nankai University. The alkaline-treated materials, denoted as Mx (x = 1, 2, 3 and 4) samples, were prepared as follows: 2 g NaZSM-5 (Si/Al = 26) was stirred in sodium hydroxide solution with different volumes and concentrations as listed in Table 1, at 358 K for 5 h, respectively. The mixture was cooled, filtered and washed with distilled water to neutral pH. The white solids thus obtained were dried at 373 K overnight. The protonated forms of ZSM-5 and Mx samples were obtained by exchanging twice with an aqueous solution of NH_4Cl (ZSM-5 or Mx: NH_4Cl: H_2O = 1:1:10, weight ratios) under stirring at 353 K for 2 h. And then they were filtrated, fully washed, dried at 383 K overnight, followed by calcination for 4 h under airflow at 813 K [5,18]. The element (Si and Al) contents of the samples were measured by use of an ARL-9800XP+ X-ray fluorescence (XRF) spectrometer.

Mesoporous silica SBA-15 was also prepared in our laboratory [19]. To assess the effects of moisture on the adsorption, three samples of SBA-15, 20 mg each, were calcined at 773 K for 2 h and then cooled down to 423 K. One sample was placed immediately in a desiccator and labeled as S1. The second sample (S2) was kept in atmosphere for 24 h and the third sample (S3) was placed in an air-tight container above saturated ammonium chloride solution for 24 h. Samples of NaA were also treated similarly and labeled as NA1, NA2 and NA3.

X-Ray diffraction studies on the alkaline-treated zeolites were carried out on an ARL XTRA diffractometer (Cu-Kα, 2-theta range from 5 to 70°) [20]. Nitrogen adsorption and desorption isotherms were measured at 77 K by a Micromeritics ASAP 2000 volumetric adsorption analyzer. The samples were evacuated at 573 K for 2 h prior to adsorption. The BET-specific surface area was calculated using adsorption data acquired at a relative pressure (P/P_0) range of 0.05–0.22 and the total pore volume V_{total} and the mesopore volume V_{meso} were determined from the amount adsorbed at a relative pressure of about 0.99. The micropore area, S_{mic}, and micropore volume, V_{micro}, were calculated by the t-plot method, according to statistical film thickness (t) in the range of 0.35–0.50 nm. The pore size distribution (PSD) curves were calculated from the analysis of the adsorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) algorithm.

Table 1
Relevant parameters of desilicated ZSM-5 samples.

Sample	M1	M2	M3	M4	HZSM-5
Concentration of NaOH solution (M)	0.2	0.1	0.05	0.1	0
Volume of NaOH solution (ml g^{-1})	100	100	100	50	0
V_{total} ($cm^3 g^{-1}$)	0.42	0.39	0.30	0.27	0.17
V_{micro} ($cm^3 g^{-1}$)	0.04	0.08	0.08	0.09	0.10
V_{meso} ($cm^3 g^{-1}$)	0.38	0.30	0.22	0.18	0.06
S_{BET} ($m^2 g^{-1}$)	225	335	331	329	325
D_{BJH} (nm)	3.8	3.8	3.8	3.9	–

For the adsorption experiments, the adsorbents were first activated at 773 K for 2 h, except for S1-3 and NA1-3 samples. For each test, 20 mg of zeolite was added into a colored bottle containing either 1 mL dichloromethane or benzene with known amount of nitrosamines. The solvent mixture was left static for 24 h at 277 K. The residual amount of nitrosamines in the solvent was determined by a spectrophotometric method [21].

Optimized calculation of nitrobenzene and NDPA molecules was completed using Gaussian 98 W. The input files were compiled and the out put files viewed by Gauss View 3.0. Theory method/basis group was B3LYP/6-31G(d) [22,23].

3. Results and discussions

3.1. Properties of alkaline-treated materials

Fig. 1 illustrates the XRD patterns of the alkaline-treated (Table 1) and the parent HZSM-5 zeolites [24,25]. The treated samples kept most of the original features but the peak intensities dropped slightly from M4 to M1. The structure of the sample M1 appeared to be altered significantly, as only the main peaks from HZSM-5 were visible. To check the influence of desilication on the composition of ZSM-5 zeolite, the content of Si and Al remained in ZSM-5 after alkali-treatment was measured. After treated with 0.1 mol L^{-1} NaOH solution, the resulting sample M2 exhibited a decreased Si/Al ratio of 14.3, significantly lower than that of parent zeolite (Si/Al of 26). This result confirmed the selective removal of silicon from the framework of ZSM-5 zeolite by alkali-treatment though it did not completely destruct the lattice.

Fig. S1 shows the N_2-adsorption isotherms from HZSM-5 zeolite before and after alkaline-treatment. HZSM-5 exhibited the characteristic type-I isotherm, mirroring its structure. The alkaline-treatment created a pronounced hysteresis loop on the isotherms of Mx samples. The large disposition of the adsorption and desorption branches of the hysteresis loop suggests the presence of slit-shaped mesopores. Fig. S1B shows the pore size distribution of HZSM-5 before and after the alkaline treatment. Table 1 lists the treatment parameters and the effects of the concentration and the volume of alkaline solution on the pore structure of Mx samples. Apart from the inherent micropores, it seems that only a small fraction of mesopores were generated by the treatment. After the ZSM-5 was treated with the 0.1 M NaOH solution, a narrow BJH distribution peaked near 3.8 nm for the sample M4. As the solution was diluted to 0.05 M and the volume of the solution was doubted,

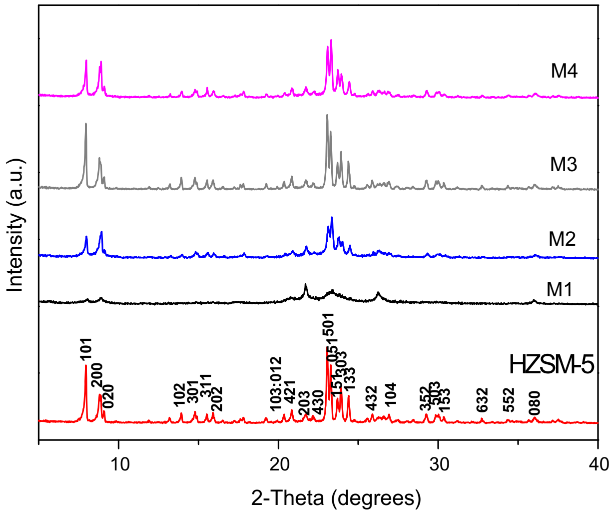

Fig. 1. XRD patterns of the alkaline-treated and the parent ZSM-5 zeolites.