

Effect of copper cation on the adsorption of nitrosamines in zeolite

Fang Na Gu, Ting Ting Zhuang, Yi Cao, Chun Fang Zhou, Jian Hua Zhu*

*Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering,
Nanjing University, 22 Hankou Road, Nanjing 210093, China*

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Abstract

Removal of carcinogens such as nitrosamines in environment is one of the potential applications of zeolites in life science, which involves the molecular reorganization and selective adsorption. To explore how copper species promote the adsorption of volatile nitrosamines in zeolite, NaY was chosen as the host to be modified with copper cation through ion exchange and impregnation. The instantaneous adsorption of *N*-nitrosopyrrolidine (NPYR) was used to assess the actual capture of nitrosamines by the modified zeolite in order to reveal the relation between the location of the copper cation and its promotion on the adsorption of nitrosamines. As the results revealed, incorporation of copper species in zeolite strengthened the electrostatic interaction between the nitrosamines and the adsorbent but occupies the space inside the channel to cause hindrance. According to the study, the promotion of the copper species overcame their negative effect and desorption of volatile nitrosamines from zeolite at 453 K was thus suppressed. Rather, the copper species dispersed in the channel of zeolite played the main role to improve adsorption of volatile nitrosamines.

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1. Introduction

Removal of carcinogenic pollutants in the environment is one of the potential applications of zeolites and molecular sieves. Among many extensive efforts one of the new developing areas of study is to reduce nitrosamine in the environment [1–4]. Many volatile nitrosamines species such as *N*-nitrosodimethylamine (NDMA), *N*-nitrosopyrrolidine (NPYR) and *N*-nitrosohexamethyleneimine (NHMI) are carcinogenic [5], and they are difficult to be removed in tobacco smoke owing to their volatility. Although zeolite has the unique function of selective adsorption and catalysis, it is still difficult for the porous material to lock and capture nitrosamines among the thousands of compounds in the gas stream. In addition, nitrosamines are widespread in environment, from industrial workplace like rubber factory to tobacco smoke, so that controlling nitrosamines' pollution is of growing interest; and any progress

obtained in the investigation of removing nitrosamines will deepen the understanding of the selectivity of zeolite.

Among the common zeolites tested in laboratory, NaY showed the largest capacity to adsorb volatile nitrosamines than NaZSM-5 and NaA [2,3], due to its larger pore size and pore volume, but novel materials are sought to eliminate the volatile nitrosamines in complex environment systems such as tobacco smoke where the competitive adsorption of other constituents lowers the ability of NaY zeolite in trapping nitrosamines [4]. Monocyclic nitrosamines such as NPYR are known to take planar structure because of their large rotational barriers of the N–NO bond [6]. They are usually adsorbed on zeolite through insertion of the N–NO groups into the zeolite channels [7], similar to adsorption of NO_x in zeolite. Therefore, copper was selected to modify zeolite because Cu was an essential element to enhance the zeolite properties of chemisorption towards NO [8]. As expected, the copper modified zeolite prepared through impregnation exhibited an enhanced capability to adsorb volatile nitrosamines, and they could trap more nitrosamines in side-stream smoke than the parent zeolite [7,9]. However, many questions still exist in the

* Corresponding author. Tel.: +86 25 83595848; fax: +86 25 83317761.

E-mail address: jhzhu@netra.nju.edu.cn (J.H. Zhu).

modification of zeolite with copper species concerning the distribution of the modifier and their actual function in attracting nitrosamines. The ion exchange between the original sodium ion of the zeolite and the new introduced copper ion was unavoidable during the impregnation process that was performed in aqueous solution of copper nitrate, but it was unclear which exerted the primary promotion on the adsorption of nitrosamines, the exchanged copper cation or the copper species coated in zeolite through impregnation? Besides, incorporation of copper species into zeolite brought an ambivalent effect on the adsorption. These new-coming species strengthened the electrostatic interaction between the nitrosamines and the adsorbent, but they also occupied the space inside the channel of zeolite to cause hindrance for the entering and diffusion of the adsorbate. It is necessary to know how the two factors affect the adsorptive behavior of the modified zeolite and how to control the impact through adjusting the amount of modifier in the zeolite along with the loading manner. Answering these questions is not only helpful to understand the surface modification of zeolite but also beneficial to develop new strategy and materials for environment protection. Thus, zeolite NaY was chosen to be modified with copper species through impregnation and ion-exchange methods. And the instantaneous adsorption of volatile nitrosamines by zeolite was selected as the probe to assess the adsorption of nitrosamines in zeolite, because in this test the contact time between the adsorbate and the adsorbent was less than 0.1 s so that the promotion of copper on the adsorption by the zeolite could be obviously observed.

2. Experimental

NPYR, NDMA and NHMI were purchased from Sigma and dissolved in CH_2Cl_2 (1:19, v/v). Zeolite NaY, a commercially available powder with a Si/Al ratio of 2.86 and surface area of $766 \text{ m}^2 \text{ g}^{-1}$, was stirred in 1 M NaCl solution for six times, then washed with distilled water to Cl^- free and finally calcinated in air prior to usage. Zeolite NaA was also the commercially available powder [4]. Copper oxide modified zeolites were prepared by ‘drying impregnation’ [9]: 0.091 g Cu $(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 5 ml H_2O and 1.94 g NaY added, the mixture was stirred strongly at 303 K and heated at 353 K up to half dryness, then dried at 373 K overnight, finally the product was ground to 100 mesh and calcined at 773 K for 6 h in order to convert $\text{Cu}(\text{NO}_3)_2$ to copper oxide. The resulting sample contained 3% (w/w) CuO and was denoted as 3CuY-i. Other samples were prepared in the same way with various concentrations of aqueous solution to get different loading of copper cations, and the obtained sample was denoted as $n\text{CuY-i}$ where n presented the weight percent of copper oxide.

To study the influence of preparation on the function of copper modified zeolite, some samples denoted as CuY-ex n were prepared by ion-exchange method, where n represents the exchange times (1, 2, 3, etc.). Briefly, 0.288 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 94.5 ml H_2O then 1.94 g NaY was added into the solution at 303 K. The mixture was stirred for 24 h and

filtered, washed thoroughly at 353 K, then dried at 373 K overnight before calcination at 773 K in air for 6 h. The copper contents were determined by inductively coupled plasma (ICP) to reflect the exchange degree of the zeolite, and the percentage of copper on CuY-ex1, CuY-ex2 and CuY-ex3 samples was 2.51%, 6.49% and 7.17%, respectively.

Powder XRD patterns were recorded with D/MAX-RA X-ray Diffractometer with Cu $K\alpha$ radiation in which the X-ray tube was operated at 40 kV and 100 mA, over the $2-\theta$ range from 5° to 70° . Diffuse reflectance spectra were taken on a Lambda 900 UV–vis–NIR spectrophotometer at room temperature. The powder sample was mounted onto a round disk with the thickness larger than 3 mm, and the spectra were recorded in 400–2500 nm wavelength range using BaSO_4 as a reference. The reduction behaviors of Cu modified NaY sample were examined by H_2 -TPR. About 100 mg of sample (20–40 mesh) was heated in nitrogen flow at 773 K for 2 h. After the sample was cooled to 303 K and purged by reducing gas ($\text{H}_2/\text{Ar} = 1/9$, v/v) with a rate of 30 ml min^{-1} for 1 h, the temperature was raised to 1273 K at a rate of 10 K min^{-1} meanwhile the hydrogen consumption caused by reduction was measured by an ‘on line’ Varian 3380 gas chromatograph (GC). Before the gas reached thermal conductivity detector (TCD), it was led via a CaA zeolite trap to remove the product water.

Instantaneous adsorption of NPYR by zeolite was performed in a stainless steel micro-reactor with 3 mm diameter and 150 mm length. A sample of 5 mg (20–40 mesh) was filled in the one end of the reactor and sealed by glass wool to fix the position. And this part was inserted into the injector port of Varian 3380 GC and another end connects with the separation column in the GC [3]. The sample was directly heated to 338 K in He (99.999%) flow with a rate of 30 ml min^{-1} , and the NPYR solution was pulse injected with amounts of $2 \mu\text{l}$ each time. The TCD of GC analyzed the gaseous effluent, and the decrement in the ratio of solute to solvent was utilized to calculate the adsorbed amount [3,9].

3. Results

3.1. Characterization of copper modified zeolite

Fig. 1 delineates the XRD patterns of zeolite NaY modified with copper by different methods. The diffraction peaks of 1CuY-i, 3CuY-i and 5CuY-i samples were identical to that of NaY but the intensity slightly decreased as the loading amount of copper oxide was increased. It appeared that copper oxide could be adequately dispersed on zeolite NaY provided the loading amount was around 5 wt.%, coincided with the report of Xie and Tang [10] in which the threshold was 5.7 wt.%. As the loading amount of copper oxide exceeded 5 wt.%, two peaks of copper oxide appeared with $2-\theta$ values of 35.4° and 38.9° on the XRD patterns of the sample prepared by impregnation (Fig. 1A). Changing the loading method from impregnation to ion exchange made the characteristic of CuO absent on the sample CuY-ex because there was no extra-fine particles of CuO remained on the composites once the

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