

Decomposition of *N*-Nitrosamines over Zeolites

Bin Shen, Li Li Ma, Jian Hua Zhu*, and Qin-hua Xu

Department of Chemistry, Nanjing University, Nanjing 210093, P. R. China

(Received December 8, 1999; CL-991038)

The strong adsorption of zeolite Y and ZSM-5 for *N*-nitrosamine such as *N*-nitrosodimethylamine and *N*-nitrosopyrrolidine was firstly revealed by use of adsorption, temperature programmed surface reaction and TG-DTA techniques. Zeolite can adsorb *N*-nitrosamines without interference of organic solvent, which will be helpful for removal of the *N*-nitrosamines pollution in environmental protection.

Protecting the environment where human live is one of the challenges faced chemists in 21st century, since the pollution brought by the mordent industry became more and more serious. Among environmental pollutants *N*-nitrosamines are considered to be important contributors to the total burden of carcinogens, and tobacco, especially the tobacco smoke, along with industrial workplace are believed to be the largest known exposure to *N*-nitrosamines.¹ While much work concentrating minimization of high human exposure to *N*-nitrosamines had been successfully done in beer, baby nipples and pacifiers, and occupational exposure in the rubber industry,² less progress was obtained in tobacco and tobacco smoke. Recently zeolite was tried to be enclosed in the cigarette filter and rod to decrease the emission of toxic chemicals including *N*-nitrosamines during a cigarette burning,³ but the result was not clear. While the content of *N*-nitrosoanabasine and *N*-nitrosoanatabine as well as *N*-nitrosornicotine seemed to be decreased in the smoke, *N*-nitrosodimethylamine increased indeed. Moreover, although zeolites had been widely used as selective adsorbents, it is unknown whether zeolite can selectively adsorb *N*-nitrosamines or not and how strong the adsorption of *N*-nitrosamine will be on zeolite, which hinders the application of zeolite in controlling pollution of *N*-nitrosamine in environment. In this letter we report the adsorption of *N*-nitrosamines on zeolites at high temperature, and characterize the strong adsorption by use of TG-DTA and temperature-programmed surface reaction (TPSR).

N-Nitrosodimethylamine (NDMA) and *N*-nitrosopyrrolidine (NPYR) were purchased from Sigma, and the *N*-nitrosamines standard solutions were prepared by dissolving 5 mL *N*-nitrosamines in 100 mL methylene chloride. Zeolite NaY and NaZSM-5 used in the studies were commercially available powder, and HZSM-5 obtained by an ion exchange method from the parent zeolite as described previously.⁴ SiMCM-41 mesoporous molecular sieve was synthesized in our laboratory.⁵ The purity of carrier gases N₂ and H₂ were 99.99%, and that of He was 99.999%.

Adsorption of *N*-nitrosamines was performed in a fixed-bed microreactor filled with 5 mg zeolite catalysts, and the sample was directly heated to the given temperature without activation. The flow rate of H₂ or He carrier gases was 30 mL/min, and the *N*-nitrosamine standard solution was pulse injected on the sample with an amounts of 2 μL each time. Gaseous effluent was analyzed by an on-line Varian 3700 gas

chromatograph, and the decrement in the ratio of NPYR or NDMA to the solvent was utilized to calculate the amount of *N*-nitrosamine adsorbed on zeolite. Temperature programmed surface reaction (TPSR) of adsorbed *N*-nitrosamine was carried out in a flow reactor. A zeolite sample of 40 mg, in 20-40 meshes, was activated at 773 K in N₂ for 2 h, then cooled to 313 K prior to pulse injection of *N*-nitrosamine solution at 25 mL/g. After the sample was purged with N₂ at 313 K for 20 minutes, the temperature rose to 773 K at a rate of 10 K/min. The NO_x liberated in the TPSR process was converted to NO₂ by passing through a CrO₃ tube, and then absorbed in a solution of sulfanilamide and *N*-(1-naphthyl)ethylenediamine dihydrochloride. The amount of NO₂ was detected by colorimetric method⁶ and represented the amount of *N*-nitrosamine decomposed. TG-DTA was performed on a STD-2960 thermogravimetric-differential thermal analyzer. Zeolites sample, adsorbed *N*-nitrosamine in the same procedure as that for TPSR, was heated in N₂ to 1073 K at a rate of 20 K/min.

NPYR is of five-membered ring compounds while NDMA is of chained compounds. Both of them are strong carcinogenic compounds existing widely in foods and beverages such as beer and bacon along with tobacco and tobacco smokes. As Figure 1 reveals, NPYR or NDMA in methylene chloride solution

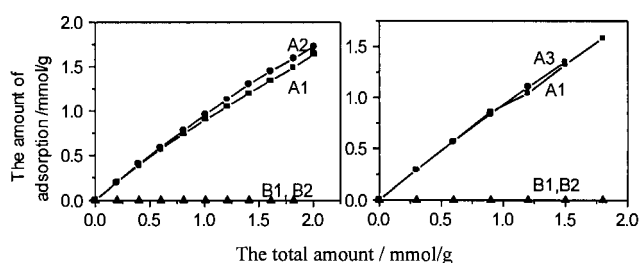


Figure 1. Adsorption of NPYR (left) and NDMA (right) on NaY (A) and MCM-41 (B) at different temperature. A1 and B1: 453 K, A2: 523 K, B2 and A3: 593K

could be adsorbed by zeolite NaY at 453 K, and 85 percent NPYR or 80 percent NDMA was thus adsorbed when the total amount of injection reached 2.01 mmol/g. Moreover, NPYR has been decomposed apparently over zeolite NaY as temperature increased to 593 K. In the range of 453-593 K, variation of temperature did not cause any obvious influence on the adsorption amount of NDMA or NPYR over zeolite NaY. Under the same conditions, however, no any change on the ratio of *N*-nitrosamine to solvent was found in the solution passed through SiMCM-41, indicating the mesoporous molecular sieve did not have the function of selective adsorption on NPYR and NDMA.

As shown in Figure 2, zeolite ZSM-5 could also adsorb NPYR and NDMA, but the amounts of adsorption were lower than that on NaY. For example, at the NPYR injection of 1.01 mmol/g, NaY adsorbed 95% of it (0.96 mmol/g) but NaZSM-5

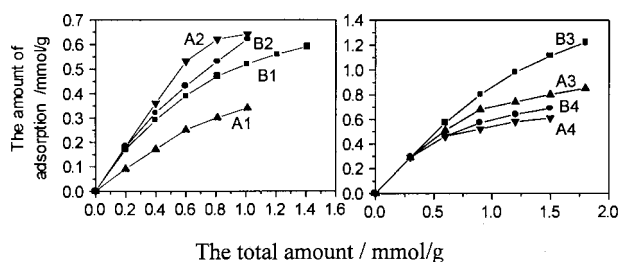


Figure 2. Adsorption of NPYR (left) and NDMA (right) on HZSM-5 (A) and NaZSM-5 (B) at different temperature. 1 and 3: 453 K, 2 and 4: 593 K

adsorbed 51% (0.52 mmol/g). Such difference can be tentatively attributed to the different pore size of two kinds of zeolite. The diameter of NPYR is 0.56 nm, smaller than the pore size of NaY (0.74 nm) but close match to that of ZSM-5 (0.54-0.56 nm), resulting in the different adsorption-diffusion of NPYR in the channel of NaY and ZSM-5 owing to the space effect. For NDMA with a molecular diameter of 0.45 nm, the difference in adsorption amount on zeolite NaY and NaZSM-5 became small in comparison of NPYR. At the NDMA injection of 1.20 mmol/g, NaY adsorbed 87% of it (1.04 mmol/g) and NaZSM-5 adsorbed 82% (0.98 mmol/g). Increasing the temperature from 453 K to 593 K increased the adsorption of NPYR but decreased that of NDMA on zeolite ZSM-5, and the reason is unclear up to now.

There were two peaks on the TG-DTA spectrum of zeolite NaY adsorbed NPYR shown in Figure 3(A). An endothermic

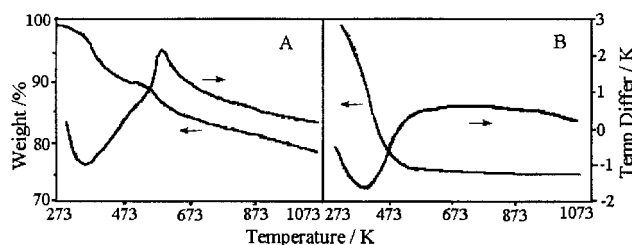


Figure 3. TG-DTA profiles of zeolite NaY contacted with (A) 5 % (v/v) NPYR- CH_2Cl_2 solution and (B) CH_2Cl_2 .

dehydration peak appeared at 363 K was followed by an exothermic peak emerging at 583 K and keeping to even 973 K resulting from the decomposition of NPYR. As a comparison, neither the obvious adsorption nor the exothermic peak was observed on the NaY sample adsorbed only methylene chloride under the same conditions, as demonstrated in Figure 3(B), providing a further proof on the adsorption of zeolite NaY for *N*-nitrosamines without interference of organic solvent. Zeolite HZSM-5 could also adsorb NPYR and such exothermic peak was kept to above 873 K on the corresponding TG-DTA spectrum. Contrarily, there is no any exothermic peak detected on the TG-DTA spectrum of SiMCM-41, mirroring its weak ability, if any, of adsorption of *N*-nitrosamines.

TPSR results over zeolite NaY, ZSM-5 and MCM-41 were shown in Figure 4. Since the N-N bond in *N*-nitrosamines is

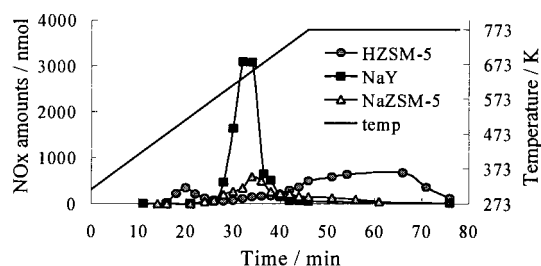


Figure 4. The NO_x desorption in the TPSR profiles of NDMA over zeolite Y and ZSM-5.

the weakest one, decomposition of *N*-nitrosamines is usually accompanied with the liberation of NO_x. Hence detection of NO_x was the key step to reveal *N*-nitrosamines degradation in the TPSR process. Pore size of zeolites seems to influence the decomposition of *N*-nitrosamines. In the TPSR of NDMA around 653 K, gaseous effluent NO_x amount over zeolite NaY was 0.08 mmol/g while 0.02 mmol/g was found over NaZSM-5. For SiMCM-41 molecular sieve sample the NO_x liberated from *N*-nitrosamines decomposition was below 0.01 mmol/g at all time. It should be pointed out that the NO_x could be detected even at 773 K during the TPSR process of NDMA and NPYR over zeolites, as demonstrated in Figure 4. However, there was no any open literature on the adsorption of NO or NO₂ on zeolite such as HZSM-5 over 473 K.⁷ Consequently it is reasonable to infer that the lots of NO_x liberation at 773 K is liberated from the in situ degradation of the adsorbed *N*-nitrosamines instead of the desorption of the NO_x adsorbed on zeolites, which indicates the strong adsorption of NDMA and NPYR on zeolite Y and ZSM-5.

From above experiment facts it is clear that zeolite can adsorb *N*-nitrosamine and such adsorption seems quite strong so that high temperature is thus needed for decomposing the *N*-nitrosamines. This feature of zeolite will be very useful to eliminate the *N*-nitrosamines pollution in environmental protection.

Financial supports from National Advanced Materials Committee of China is gratefully acknowledged.

References and notes

- 1 D. H. Fine and D. P. Rounbehler, in "*N*-Nitroso Compounds," ACS Symposium Series 174, ed by R. A. Scanlan and S. R. Tannenbaum, American Chemical Society, Washington, D. C. (1981), p. 207.
- 2 R. Preussmann, B. Spiegelhalder and G. Eisenbrand, in "*N*-Nitroso Compounds," ACS Symposium Series 174, ed by R. A. Scanlan and S. R. Tannenbaum, American Chemical Society, Washington, D. C. (1981), p. 217.
- 3 W. M. Meier, J. Wild, and F. Scanlan, EP 0740907A1 (1996).
- 4 Q.H. Xu and J.H. Zhu, *Acta Phys. Chem.*, **31**,181 (1985).
- 5 B. Shen, Y. Chun, J.H. Zhu, Y. Wang, Z. Wu, J.R. Xia, and Q.H. Xu, *Phys. Chem. Comm.*, **3**, E9902666 (1999).
- 6 B.E. Saltzman, *Anal. Chem.*, **26**, 1949 (1954).
- 7 J. Eng and C.H. Bartholomew, *J. Catal.*, **171**, 14 (1997).