



Attempt to adsorb *N*-nitrosamines in solution by use of zeolites

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Abstract

The strong adsorption of zeolite for *N*-nitrosamines in solution was first revealed by use of adsorption, and temperature programmed surface reaction (TPSR) techniques. *N*-nitrosodimethylamine (NDMA) and *N*-nitrosopyrrolidine (NPYR) as well as *N*-nitrosohexamethyleneimine (NHMI) can be adsorbed on zeolite Y, ZSM-5 and A in the solution of methylene chloride or water, which will be helpful for removal of the *N*-nitrosamines pollution in environmental protection. The equilibrium data were fitted to Freundlich-type isotherms, but the adsorption capacity of zeolites mainly depended on their pore size, surface area and acid–basic properties. Molecular size of adsorbate and solute–solvent interaction also strongly affected the adsorption of *N*-nitrosamines on zeolite in solution. The extraordinary adsorption properties of NaA zeolite for *N*-nitrosamines in aqueous solution is first reported and discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Zeolite; *N*-nitrosamines; Adsorption; TPSR

1. Introduction

N-Nitrosamines are probably the most widespread contributors to the total burden of carcinogens, which exist in tobacco smoke and beer as well as effluents from rubber industrial production etc., most of them can cause carcinogens even in trace amount. In order to exclude the contamination of *N*-nitrosamines, it is necessary to separate them from environment and adsorption is a predominated method. Activated carbon was reported to adsorb *N*-nitrosamines from aqueous solution (Mikhailovskii et al., 1979), but its application was hindered since active carbon is burnable and, therefore, difficult to be regenerated. Zeolite and molecular sieves are the more attractive alternative, because of their ability of recognizing, discriminating, and organizing molecules with precisions that can be less than 0.1 nm (Breck, 1974). Containing uniformly sized

pores in the range of 0.4–1.3 nm, zeolite and zeolite-like molecular sieves have been exploited by the petrochemical industries to perform many large-scale, shape-selective hydrocarbon reactions. Recently, we revealed a special function of zeolite adsorbing *N*-nitrosamines in gaseous phase at high temperature close to that of cigarette burning zone. For instance about 80% of *N*-nitrosodimethylamine (NDMA) or *N*-nitrosopyrrolidine (NPYR) could be adsorbed by zeolite NaY at 453 K (Shen et al., 2000). On the other hand, cigarettes enclosed zeolite was tried in order to decrease the emission of toxic chemicals including *N*-nitrosamines during cigarette burning, and about 50–70% of *N*-nitrosamines was thus, removed from cigarette smoke (Meier and Siegmann, 1999; Meier and Wild, 1996; Wang et al., 1999). However, it is unclear if zeolite can adsorb the *N*-nitrosamines from solutions that are different from the cigarette smoke, since only trace amounts of *N*-nitrosamines exist in cigarette smoke but the concentration of *N*-nitrosamines in organic or aqueous effluents is relatively high (Fine, 1982; Spiegelhalder and Preussmann, 1983). Also, the zeolite enclosed in cigarette could be activated when the cigarette

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is burning. Hence the pre-adsorbed impurities such as water or CO_2 molecules are removed and the adsorption sites thus, explored prior to adsorption of *N*-nitrosamines. For those zeolite adsorbents used in solution, however, no activation but a competitive adsorption of solvent molecules occurs, which may be harmful for adsorption of *N*-nitrosamines. Up to date there is almost no systematic study concerning adsorption of *N*-nitrosamines on zeolite adsorbents in liquid phase, which prompts us to explore the possibility of adsorbing *N*-nitrosamines in solution by use of zeolite. In this paper three commonly used zeolite, Y, ZSM-5 and A, were employed to adsorb NDMA, NPYR and *N*-nitrosohexamethyleneimine (NHMI) from methylene chloride or aqueous solution at high concentration. Investigation is focused on examining how the structure of adsorbate and adsorbents along with competition of solvent molecules influence on the adsorptive properties, as well as whether this could be determined from the adsorption isotherms.

2. Experimental

2.1. Materials

NDMA, NPYR and NHMI were purchased from Sigma. To prepare *N*-nitrosamines standard solution, 5 ml *N*-nitrosamines was dissolved in 100 ml methylene chloride and the corresponding concentration was thus, 50,000 mg/l. Zeolite NaY and NaZSM-5 as well as NaA used as adsorbent in the studies were commercially available powder, and their properties are listed in Table 1. Sample HZSM-5 was obtained by an ion exchange method from the parent zeolite NaZSM-5 as described previously (Xu and Zhu, 1985). For comparison, silica with a surface area of about 350 m^2/g and alumina with a surface area of 177 m^2/g were also employed to adsorb *N*-nitrosamines.

2.2. Methods

The adsorption of *N*-nitrosamines was performed as follows: 0.020 g zeolite adsorbent was activated at 500°C for 2 h, then was introduced in a flask bottle

followed by injecting 1 cm^3 of methylene chloride or distilled water at 20°C. A given amount of the *N*-nitrosamines standard solution was added to each bottle, in order to prepare different initial concentration (C_0) of solutions varied from 500 to 7500 mg/l. To avoid evaporation of methylene chloride solvent during the adsorption process, the flasks were kept in an incubator at 10°C. After adsorption of 24 h, the residual concentration (C_e) of the *N*-nitrosamines solution in each flask was measured in the manner described previously (Shen et al., 2000). *N*-nitrosamines were chemically denitrosated with HBr in glacial acetic acid to liberate the denitrosated product NO (Drescher and Frank, 1978). Being purged in N_2 carrier gas stream, the NO was purified through three successive NaOH traps and oxidized to NO_2 by passing through a CrO_3 tube. After being adsorbed in a solution of sulfanilamide and *N*-1-naphthylethylenediamine dihydrochloride (Saltzman, 1954), NO_2 was converted to NO_2^- and then the amount of NO_2^- was detected by use of a 722 model spectrophotometer (Shanghai Analytical Instruments Factory) at 540 nm. Based on these data of C_e , the amount of *N*-nitrosamines adsorbed on zeolite adsorbent could be calculated and the isotherms at 10°C were obtained. For comparison, adsorption of *N*-nitrosamines on zeolite from aqueous solution was carried out at 10°C in the manner similar to that from methylene chloride solution as mentioned above.

Temperature programmed surface reaction (TPSR) of adsorbed *N*-nitrosamines was carried out in a flow reactor (Shen et al., 2000). A zeolite sample of 40 mg, adsorbed *N*-nitrosamines from methylene chloride solution as described above, was purged with N_2 at 40°C for 20 min, then heated to 500°C at a rate of 10°C/min to degrade or desorb *N*-nitrosamines. The N–N bond in *N*-nitrosamines is the weakest, so that thermal decomposition of *N*-nitrosamines is usually accompanied with the liberation of NO_x . By use of spectrophotometer the amount of NO_x was detected and represented as the amount of *N*-nitrosamines decomposed. The desorbed *N*-nitrosamines were collected in citrate-phosphate buffer as reported by Caldwell and Conner (1990), then were chemically denitrosated and analyzed also by use of spectrophotometer (Shen et al., 2000).

Table 1
Properties of zeolite adsorbents

Zeolite	Si/Al	Crystalline size (μm)	Surface area (m^2/g)	Pore size (nm)
NaY	2.9	2.3	766	0.74
NaZSM-5	22.5	6.5	346	0.54–0.56
HZSM-5	22.8	6.8	359	0.54–0.56
NaA	1.0	1.4	444 ^a	0.42

^a Data is quoted from (Mao et al., 1991).

3. Results and discussion

3.1. Adsorption isotherms

The Freundlich equation is known to have the general form (Slejko, 1985)

$$Qe = K_F \cdot Ce^{1/n}, \quad (1)$$

where K_F and $1/n$ are characteristic constants. Eq. (1) linearizes in logarithmic form

$$\log Qe = \log K_F + 1/n \log Ce \quad (2)$$

for convenience of data fitting and parameter evaluation. K_F is taken as a relative indicator of adsorption capacity, while $1/n$ is indicative of the energy or intensity of the reaction as well as the favorability and capacity of the adsorbent/adsorbate system. Values of $n > 1$ represent favorable adsorption conditions according to the theory (Slejko, 1985).

Figs. 1–3 show equilibrium adsorption isotherms at 10°C for three *N*-nitrosamines on the four-zeolite adsorbents. Drawing from these experiments, it is clear that *N*-nitrosamines in methylene chloride solution could be selectively adsorbed by zeolite. Among the zeolite adsorbents used, NaY exhibited the largest adsorption capacity for *N*-nitrosamines in methylene chloride solution, and the amount of adsorption (Qe) increased as the Ce was raised. As the adsorbate changed from NDMA to NPYR or NMHI, the difference between the amount of *N*-nitrosamines adsorbed on NaY and other zeolites became more and more obvious. For comparison, the isotherms of NDMA and NPYR adsorbed on silica and alumina are also shown in Fig. 4. However, the amount of NDMA or NPYR adsorbed on

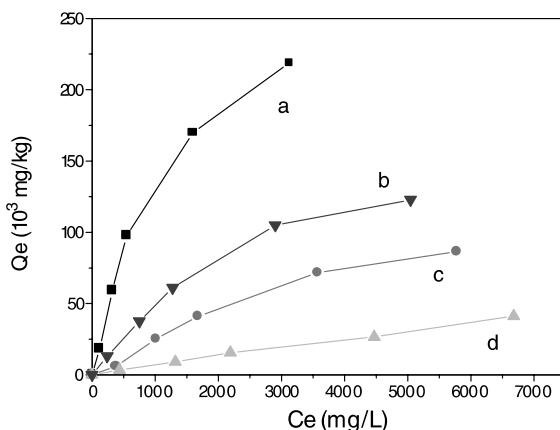


Fig. 1. Equilibrium adsorption isotherms of *N*-nitrosodimethylamine (NDMA) on zeolite adsorbents in the methylene chloride solvent at 10°C: (a) NaY, (b) HZSM-5, (c) NaZSM-5, (d) NaA.

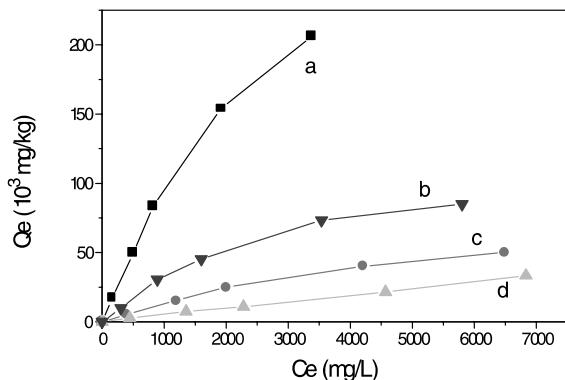


Fig. 2. Equilibrium adsorption isotherms of *N*-nitrosopyrrolidine (NPYR) on zeolite adsorbents in the methylene chloride solvent at 10°C: (a) NaY, (b) HZSM-5, (c) NaZSM-5, (d) NaA.

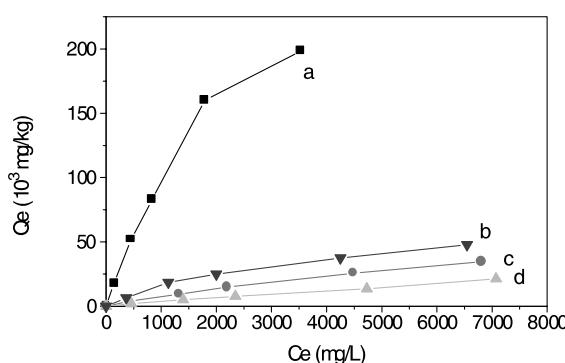


Fig. 3. Equilibrium adsorption isotherms of *N*-nitrosohexamethyleneimine (NHMI) on zeolite adsorbents in the methylene chloride solvent at 10°C: (a) NaY, (b) HZSM-5, (c) NaZSM-5, (d) NaA.

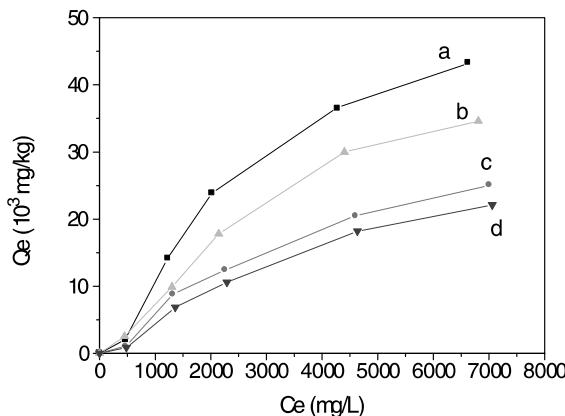


Fig. 4. Equilibrium adsorption isotherms of *N*-nitrosodimethylamine (NDMA) or *N*-nitrosopyrrolidine (NPYR) on silica and alumina adsorbents in the methylene chloride solvent at 10°C: (a) NDMA on SiO_2 , (b) NPYR on SiO_2 , (c) NDMA on Al_2O_3 , (d) NPYR on Al_2O_3 .

these two adsorbents was much smaller than that on zeolite NaY under similar conditions. For example, in the case of that the C_e of NDMA was around 2000 mg/l, the Q_e value on NaY zeolite (about 175,000 mg/kg) was estimated to be much higher than that on SiO_2 (about 25,000 mg/kg) or Al_2O_3 (about 10,000 mg/kg). One may try to attribute this difference to the different surface area of adsorbent, since zeolite NaY had a larger surface area ($766 \text{ m}^2/\text{g}$) than SiO_2 ($350 \text{ m}^2/\text{g}$) or Al_2O_3 ($177 \text{ m}^2/\text{g}$). However, the difference in the Q_e value (7–17 times) was higher than that in surface area (2–4 times). Moreover, the Q_e of NaZSM-5 was near 50,000 mg/kg via the C_e of 2000 mg/l as estimated from the curve c in Fig. 1; it was still larger than that of SiO_2 though two adsorbents had similar surface area. Owing to the special pore structure and existence of geometric and energetic fields (Su and Barthomeuf, 1995), zeolite is proven to be the better adsorbent than silica or alumina to adsorb *N*-nitrosamines in solution.

The experimental equilibrium data have been correlated with the Eq. (2). Fig. 5 shows typical Freundlich plots of the three *N*-nitrosamines on zeolite NaA, and 12 regression equations established from the experimental data and the corresponding constants K_f and n are listed in Table 2. These equations are reliable since all the correlation coefficients R are greater than 0.97, and most of them are greater than 0.99. It can be concluded that the Freundlich adsorption law explains the data presented. Adsorption is predicted in all the experimental cases performed i.e., exponential are $n > 1$.

3.2. Effect of adsorbent structure on adsorption

It is evident from the plotted adsorption isotherms and n values in the corrected Freundlich equations that the adsorption properties of the three zeolite adsorbents are quite different. Zeolite NaY demonstrated the

Table 2
Regression equations of $\log Q_e$ vs. $\log C_e$ for Freundlich isotherms conditions: 10°C, in methylene chloride solution

Adsorbate	adsorbent	K_f	n	R
NDMA	NaY	0.710	1.355	0.971
	NaZSM-5	0.023	1.022	0.975
	NaA	0.014	1.107	0.999
	HZSM-5	0.243	1.331	0.987
NPYR	NaY	0.271	1.200	0.994
	NaZSM-5	0.046	1.235	0.992
	NaA	0.014	1.110	0.999
	HZSM-5	0.179	1.368	0.981
NHMI	NaY	0.442	1.302	0.991
	NaZSM-5	0.036	1.280	0.999
	NaA	0.012	1.196	0.999
	HZSM-5	0.145	1.497	0.989

highest adsorption capacity for all the *N*-nitrosamine compounds, while zeolite NaA the lowest, and NaZSM-5 and HZSM-5, the intermediate. In order to explain the difference, the typical properties of the above-used zeolites are described in Table 1. In general, adsorbents are solids that possess high specific surfaces. The surface area with respect to pore size generally is the primary determinant of adsorption capacity. From Table 1, we can see that zeolite NaY has the largest surface area ($766 \text{ m}^2/\text{g}$) and the largest pore size (0.74 nm), so it is predictable that zeolite NaY will be the most effective adsorbent. The surface area of NaZSM-5 is only $346 \text{ m}^2/\text{g}$, less than one half of NaY and smaller than that of NaA $444 \text{ m}^2/\text{g}$ (Mao et al., 1991), but it does not display the lowest adsorptive ability because of its intermediate pore size. Clearly the effect of pore size is stronger than that of surface area on the adsorption of *N*-nitrosamines on zeolite, since the external surface of zeolite is below 10% of the total surface area and most of the adsorption occurs inside the channel of zeolite.

N-Nitrosamines have a weak basicity and adsorb favorably on acidic materials (Ma et al., 2000a,b), therefore, the surface acid–basicity of zeolite becomes an important factor on the adsorption of *N*-nitrosamines. Zeolite HZSM-5 has a surface area and pore size almost same as that of NaZSM-5 (Table 1), but adsorbs more *N*-nitrosamines under the same conditions as demonstrated in Figs. 1–3, resulting from its relative strong acidity (Xu and Zhu, 1985). Another evidence for the important role-played by the surface state of adsorbent in the adsorption of *N*-nitrosamines came from mesoporous molecular sieve SiMCM-41. SiMCM-41 had a large surface area of $990 \text{ m}^2/\text{g}$ and a pore size of 2 nm, but adsorbed little NDMA or NPYR owing to lack of adsorption centers (Shen et al., 2000), also because there was not enough acid–basic sites on its surface. On the other hand, modified zeolite such as ZrO_2/NaY , having both acidic and basic sites on it, exhibited a much better

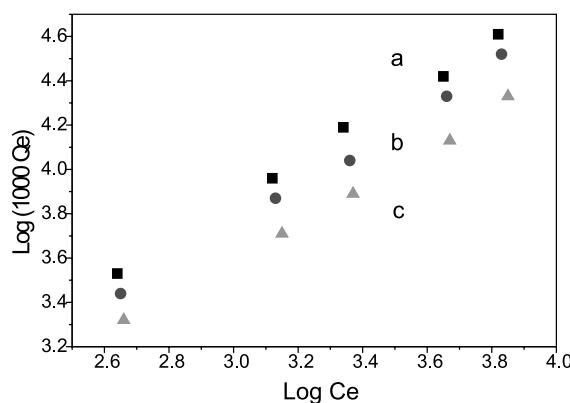


Fig. 5. Freundlich analysis of the adsorption of three *N*-nitrosamines on zeolite NaA in the methylene chloride solvent at 10°C: (a) NDMA, (b) NPYR, (c) NHMI.

adsorption and degradation properties for *N*-nitrosamines than parent zeolite as expected (Ma et al., 2000a,b). The main reason was that a suitable chemical environment was generated on the sample to promote the decomposition of the worst carcinogenic compounds.

An approximate quantitative relationship was found between adsorption parameters and adsorbent properties such as surface area and pore size as well as surface acid–basicity. These factors together could tentatively explain most of the experimental data, but there are still some unknown factors affecting adsorption of *N*-nitrosamines on zeolite in solution. Zeolite NaA is well-known to have a pore size of only 0.4 nm so nitrogen molecule cannot enter the channel. However, NaA can adsorb *N*-nitrosamines from solution as demonstrated in Figs. 1–3, and a high temperature near 500°C is desirable for desorption and degradation of the adsorbate (Shen et al., 2000; Ma et al., 2000a,b). How does the *N*-nitrosamines molecule enter the channel of zeolite NaA? Does it inert with the characteristic group of $-\text{N}=\text{N}-\text{O}$? What interaction between zeolite NaA and *N*-nitrosamines adsorbate makes the adsorption so strong? Whether a new zeolite material with the pore size smaller than NaA but a higher surface area will be worthwhile investigating as an improved adsorbent? Up to date these questions are not clear yet and a further investigation is thus required.

Competitive adsorption of solvent molecules seems to be another factor that affect the adsorption amount of *N*-nitrosamines. Through comparison of Figs. 1 and 6, it is clear that more NDMA can be adsorbed on NaY zeolite when the adsorbate is dissolved in methylene chloride than in water. For e.g., 59,000 mg/kg of NDMA was adsorbed at C_e of 320 mg/l in the organic solution, but only about 1050 mg/kg of NDMA adsorbed at C_e of 478 mg/l in aqueous solution. Similar difference was also observed in the adsorption of NPYR as demonstrated in

Figs. 2 and 7. The hydrophilic nature of zeolite NaY seems to be a main reason to cause these differences because water can be favorably adsorbed on the zeolite. There is not enough experiment evident yet to distinguish if *N*-nitrosamines and water molecules in general adsorb significantly differently and/or competitively for the same affinity sites. However, it could at least be estimated that adsorption of water solvent molecules on zeolite would block the channel and hinder the successive adsorption of *N*-nitrosamines. On the other hand, the solute–solvent interaction of the *N*-nitrosamines might be the one very important variable. In the standard solution of adsorbate, *N*-nitrosamines were dissolved in methylene chloride. When the standard solution was added to methylene chloride solvent, only the dilute process results in a uniform distribution of adsorbate in the solution. Moreover, the methylene chloride solvent molecules did not have much competition with *N*-nitrosamines for the adsorption on the hydrophilic zeolite NaY. Different situations can be imagined when the standard solution of *N*-nitrosamines was added in water. Owing to the intrinsic property of *N*-nitrosamines, less NDMA or NPYR exists in aqueous phase than in organic phase. For those *N*-nitrosamine molecules in organic phase, the water phase might hinder them from contacting with the adsorption sites on zeolite adsorbent, but the adsorption of those in aqueous phase was also hindered because of the competitive adsorption of the water molecules on the hydrophilic zeolite. Consequently the hydrophilic adsorbent is not suitable for adsorption of *N*-nitrosamines in aqueous solutions. NaA zeolite is another hydrophilic adsorbent, but the difference between the two solvents is smaller in the case of adsorption of NDMA comparing with that on NaY. For instance, 3390 mg/kg of NDMA was adsorbed at C_e of 432 mg/l in the organic solution, and about 836 mg/kg

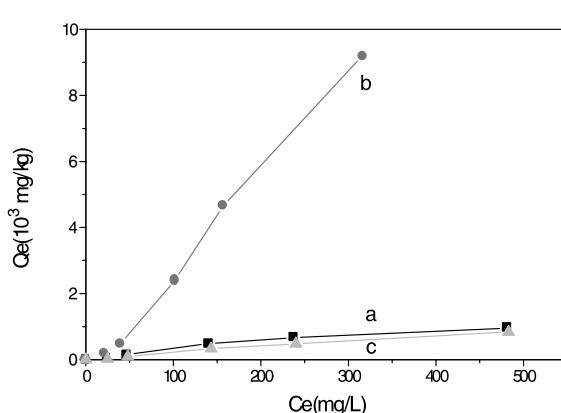


Fig. 6. Equilibrium adsorption isotherms of *N*-nitrosodimethylamine (NDMA) on zeolite adsorbents in the water solvent at 10°C: (a) NaY, (b) NaZSM-5, (c) NaA.

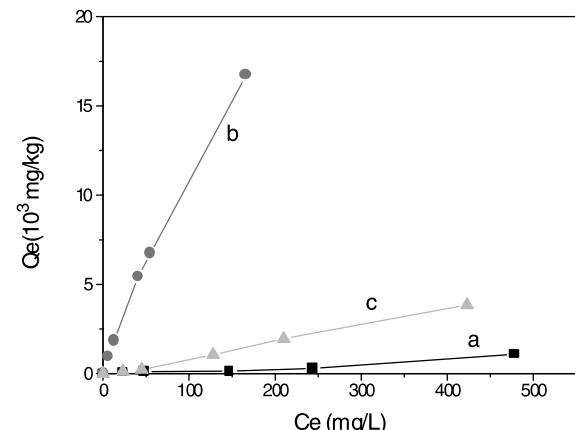


Fig. 7. Equilibrium adsorption isotherms of *N*-nitrosopyrrolidine (NPYR) on zeolite adsorbents in the water solvent at 10°C: (a) NaY, (b) NaZSM-5, (c) NaA.

adsorbed at C_e of 478 mg/l in aqueous solution as demonstrated in Figs. 1 and 6. Furthermore, more NPYR could be adsorbed on NaA zeolite in aqueous solution (3800 mg/kg) than that in methylene chloride solution (2800 mg/kg) in the case of low C_e (423 mg/l), as listed in Table 3. Although the true reason is unknown and needs to be explored in future, the discovering of such property of NaA promoted application of zeolite adsorbent for removal of *N*-nitrosamines from aqueous solution, and about 70% of the worst carcinogenic compounds can thus be removed from beer (Wang et al., 2000). On the other hand, reverse difference was observed when NDMA and NPYR were adsorbed on zeolite NaZSM-5. As it is evident in Table 3, larger amount of Q_e was observed on NaZSM-5 zeolite when the adsorbate is dissolved in water instead of in methylene chloride, resulting from the hydrophobicity of the zeolite. Without the competitive adsorption of methylene chloride, more NDMA or NPYR can be adsorbed on NaZSM-5 zeolite. Based on these results, it is favorable to use hydrophobic zeolite to remove *N*-nitrosamines from aqueous solution while using hydrophilic zeolite for separate *N*-nitrosamines from organic solutions.

3.3. Effect of adsorbate properties on adsorption

In order to compare the adsorbing properties of *N*-nitrosamines, Table 4 lists the equilibrium adsorption capacities Q_e of the three compounds from methylene chloride solution on zeolite adsorbents at the same residual concentration $C_e = 1000$ mg/l. (The values of Q_e

are not obtained directly from experiment, but calculated from the adsorption isotherms for convenience of comparison).

As the data in Table 4 shows that for all the four zeolite used in this study, the adsorption capacity of *N*-nitrosamines on zeolite was strongly affected by the molecular size of the adsorbate. The molecular dimensions of *N*-nitrosamines were 0.45 nm for NDMA, 0.56 nm for NPYR and 0.59 nm for NHMI, and these critical dimensions are comparable with the pore size of zeolite (Shen et al., 2000). With the smallest molecular diameter among the three *N*-nitrosamines, NDMA was adsorbed more strongly on all four adsorbents, while NHMI with a seven-member ring and the relative largest molecular size (0.59 nm), was adsorbed with a lesser effect on all four adsorbents. Therefore, adsorption capacities of all four zeolite decreased in following: NDMA > NPYR > NHMI, revealing the "sieve effect" of zeolite for adsorption of *N*-nitrosamines in solution. Based on the results in Table 4 combined Figs. 1–3, it is clear that ZSM-5 zeolite is expected to be the selective adsorbent for separation of these three *N*-nitrosamines in methylene chloride solution, because the adsorption capacity for each adsorbate is so different. However, in some cases with relative low C_e of *N*-nitrosamines, this difference would become indistinct. For e.g., the amount of NDMA adsorbed on NaZSM-5 was 5955 mg/kg at the C_e of 380 mg/l, while 5285 mg/kg of NPYR was adsorbed on the same adsorbent at a C_e of 394 mg/l as shown in the curve a in Figs. 1 and 2. Therefore, a further modification on zeolite ZSM-5 is desirable to

Table 3
Equilibrium adsorption capacity Q_e for *N*-nitrosamines on zeolite adsorbents

Adsorbate	Adsorbent	C_e (mg/l) ^a	Q_e ^b (mg/kg)	Q_e ^c (mg/kg)
NDMA	NaY	480.9	1080	78100
	NaZSM-5	316.0	9200	5500
	NaA	483.3	800	3300
NPYR	NaY	478.3	1050	45500
	NaZSM-5	165.9	16700	1800
	NaA	423.0	3800	2800

^aCalculated data instead of the value obtained directly from experiment were used for convenience of comparison.

^bAdsorption in aqueous solution.

^cAdsorption in methylene chloride solution.

Table 4
Equilibrium adsorption capacity Q_e for *N*-nitrosamines in methylene chloride solution on zeolite adsorbents. $C_e = 1000$ mg/l

Adsorbent	Adsorbate	Q_e (mg/kg)	Adsorbent	Adsorbate	Q_e (mg/kg)
NaY	NDMA	129300	NaA	NDMA	8200
NaY	NPYR	95500	NaA	NPYR	5400
NaY	NHMI	92300	NaA	NHMI	4200
NaZSM-5	NDMA	25200	HZSM-5	NDMA	50200
NaZSM-5	NPYR	13600	HZSM-5	NPYR	32700
NaZSM-5	NHMI	9100	HZSM-5	NHMI	22200

prepare effective adsorbents for adsorption and separation of *N*-nitrosamines in solution. With the largest pore size among the three types of zeolite, NaY had a distinguished large capacity for adsorption of NDMA but that for NPYR and NHMI was similar (Table 4). Contrarily zeolite NaA exhibited different capacity for adsorption of three *N*-nitrosamines though the capacities were relative small. It is difficult to explain how the *N*-nitrosamines were adsorbed on zeolite NaA based on known knowledge, because even the molecular size of NDMA (0.45 nm) was comparable to the pore size of NaA (0.40 nm). Probably, distortion of adsorbate occurs during the adsorption but a picture of such process cannot be drawn yet.

It is noteworthy to point out that the effect of molecular size of *N*-nitrosamines adsorbate is not the same in aqueous solution. On zeolite NaY the adsorption amount of NPYR (1050 mg/kg) was close to that of NDMA (1080 mg/kg), while on zeolite NaZSM-5 the former amount exceeded the latter one (Table 3). An obvious variation was observed on NaA zeolites where the amount of adsorbed NPYR (3800 mg/kg) was three times higher than that of NDMA (800 mg/kg). The larger adsorbate molecule had the higher degree of adsorption in aqueous solution, which may cause the suspicion that if this had something to do with the solute–solvent interaction. It is unclear whether the larger molecules such as NPYR might disrupt water to a greater extent, thus increasing the entropy contribution to the Gibbs Free Energy of aqueous solution of sorption or not, due to the lack of enough experiment evidences. Besides, NaA zeolite played a rather extraordinary role in the adsorption of NPYR in aqueous solution and adsorbed more NPYR than zeolite NaY (Table 3). This fact implied existence of some unknown factors with the influence stronger than the sieve effect on the adsorption of *N*-nitrosamines in solution, and a further investigation is required to explore them in detail.

To explore the adsorption strength of *N*-nitrosamines on zeolite, temperature programmed surface reaction (TPSR) is employed (Shen et al., 2000; Ma et al., 2000a,b). On the sample of zeolite NaY that adsorbed about 6320 mg/kg of NPYR, only about 2% of the adsorbate desorbed during the TPSR experiment from 40°C to 500°C. In contrast, most of them had been degraded on the zeolite and NO_x was thus liberated as products. This fact indicates the efficiency of zeolite used as adsorbent for removal of *N*-nitrosamines from environment; since the *N*-nitrosamines cannot escape from the zeolite so no secondary pollution will occur. Fig. 8 shows the NO_x desorption in the TPSR profiles of NPYR on zeolite NaY, NaZSM-5 and NaA. On the three zeolite adsorbents NPYR decomposed above 280°C and NO_x could be detected even at 500°C during the TPSR process. Pore size of zeolites seems to affect

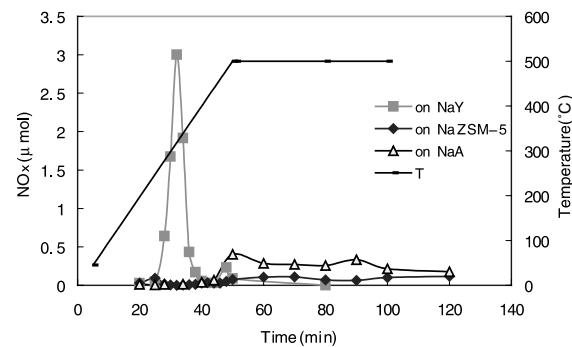


Fig. 8. The NO_x desorption in the TPSR profiles of NPYR over zeolite NaY, NaZSM-5 and NaA via the temperature (*T*) and run time.

the decomposition of *N*-nitrosamines, coincided with that in the adsorption of *N*-nitrosamines in methylene chloride solution as mentioned earlier. In the TPSR of NPYR around 320°C, gaseous effluent NO_x amount over zeolite NaY was 3.0 μmol, while about 0.4 μmol was found over NaA near 500°C. In general, the easy decomposition of adsorbate on zeolite adsorbent is beneficial to successive adsorption (Zhu, 1997). However, the TPSR results cannot be used to predict the adsorption of *N*-nitrosamines in solution yet, because the experiment conditions are so different that no simple equation parallel to the Freundlich equation is found. It should be pointed out that the NO_x could be detected even at 500°C during the TPSR process on zeolites as demonstrated in Fig. 8, but there was no literature on the adsorption of NO or NO₂ on zeolite over 200°C (Eng and Bartholomew, 1997). Consequently it is reasonable to infer that the big amount of NO_x liberation at 500°C is from the in situ degradation of the adsorbed *N*-nitrosamines instead of the desorption of the NO_x adsorbed on zeolites (Shen et al., 2000), which indicates the strong adsorption of NDMA and NPYR on zeolite Y and ZSM-5.

4. Conclusions

From the above experimental facts it is clear that zeolite NaY, NaZSM-5 and NaA can adsorb *N*-nitrosamines from methylene chloride or aqueous solution. The equilibrium adsorption isotherms in methylene chloride solution correlate with the Freundlich equation. The values of adsorption capacities depend on the structure of adsorbents involving surface area, pore size, particle size along with surface acid–basicity; they are also strongly affected by adsorbate structure, solute–solvent interaction of the *N*-nitrosamines along with competitive adsorption of solvent molecules. However, through modifying the geometric structure and/or sur-

face state of zeolite to adjust the adsorption properties of the adsorbent, it is possible to accomplish a selective adsorption of *N*-nitrosamines in solution.

Zeolites can be used to adsorb *N*-nitrosamines with a higher efficiency than silica or alumina, and the adsorption is proven to be quite strong. Most of the adsorbate was decomposed on zeolite above 280°C while only few of them can desorb at elevated temperature. This feature of zeolite seems to be useful for removal of *N*-nitrosamines from liquid phase such as beer along with industrial effluents.

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References

- Breck, D.W., 1974. *Zeolites Molecular Sieves*. Wiley, New York.
- Caldwell, W., Conner, J.M., 1990. Artifact formation during smoke trapping: an improved methods for determination of *N*-nitrosamines in cigarette smoke. *J. Ass. Off. Anal. Chemists* 73 (5), 783–789.
- Drescher, G.S., Frank, C.W., 1978. Estimation of extractable *N*-nitroso compounds at the part-per-billion level. *Anal. Chem.* 50 (14), 2118–2121.
- Eng, J., Bartholomew, C.H., 1997. Kinetic and mechanistic study of NO_x reduction by NH₃ over H-form zeolites. *J. Catal.* 171 (1), 14–26.
- Fine, D.H., 1982. Nitrosamine in the general environment and food. *Banbury Report*, 12 (Nitrosamines and Human Cancer), 199–209.
- Ma, L.L., Shen, B., Zhu, J.H., Xia, J.R., Xu, Q.H., 2000a. Modifying NaY zeolite with metal oxide by microwave irradiation: influence on the adsorption and decomposition of *N*-nitrosamines. *Ch. Chem. Lett.* 11 (7), 649–652.
- Ma, L.L., Shen, B., Zhu, J.H., Xu, Q.H., 2000b. Temperature programmed surface reaction of *N*-nitrosamine on zeolite catalysts. *Ch. J. Catal.* 21 (2), 138–142.
- Mao, R.L.V., Sjariel, B., Dunnigan, J., 1991. Asbestos-derived zeolites as water-retaining materials in soils. *Zeolites* 11 (6), 804–809.
- Meier, W.M., Siegmann, K., 1999. Significant reduction of carcinogenic compounds in tobacco smoke by the use of zeolite catalyst. *Microporous and Mesoporous Mat.* 33 (2), 307–310.
- Meier, W.M., Wild, J., 1996. Scanlan F. Smoker's article. EP 0740907A1.
- Mikhailovskii, N.Ya., Iinitskii, A.P., Korolev, A.A., 1979. Hygienic effectiveness of the removal of *N*-nitroso compounds from water. *Kazan. Med. Zh.* 60 (6), 65–68.
- Saltzman, B.E., 1954. Colorimetric microdetermination of nitrogen dioxide in the atmosphere. *Anal. Chem.* 26 (12), 1949–1955.
- Shen, B., Ma, L.L., Zhu, J.H., Xu, Q.H., 2000. Decomposition of *N*-nitrosamines over zeolites. *Chem. Lett.* 4, 380–381.
- Slejko, F.L., 1985. *Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application*. Marcel Dekker, New York.
- Spiegelhalder, B., Preussmann, R., 1983. *Analysis of airborne *N*-nitrosamines, environmental carcinogens selected methods of analysis, Volume 6, *N*-nitroso compounds*, WHO, IARC Scientific Publications, Lyon, No. 45, 41–50.
- Su, B.L., Barthomeuf, D., 1995. Adsorption sites for benzene in KL zeolite: An infrared study of molecular recognition. *Zeolites* 15 (3), 470–474.
- Wang, Y., Huang, W.Y., Xia, J.R., Zhu, J.H., 2000. New method to remove *N*-nitrosamines from beer. CN00112109.x.
- Wang, Y., Zhu, J.H., Shen, B., Chun, Y., Xu, Q.H., 1999. An additive for lowering content of *N*-nitrosamines in cigarette smoke and the cigarette enclosed the additive. CN1228945A.
- Xu, Q.H., Zhu, J.H., 1985. Ethylation of toluene on HZSM-5 zeolites prepared without organic compounds. *Acta Phys. Chem.* 31 (1–2), 181–187.
- Zhu, J.H., 1997. Different behaviors of HZSM-5 zeolites synthesized in different procedures in loading of MoCl₅ and methanol to gasoline (MTG) reaction. *React. Kinet. Catal. Lett.* 62 (1), 39–46.