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Abstract: The capacity of natural zeolites (ZAPS, ZNT, and ZSL) to adsorb N_2O and NO in both static and dynamic regimes was studied experimentally. It was found that the cations present in the zeolites act as centers of adsorption for both gases, suggesting their competitive adsorption. However, a considerable difference was observed among the capacities of the zeolites to adsorb these two gases, which can be used for the separation of N_2O–NO mixtures. Adsorption of NO on the three samples showed diffusion-activated.

Keywords: Adsorption, natural zeolites, NO_x

INTRODUCTION

Many polluting agents currently affect the atmosphere in important ways. This is also the case for the nitrogen oxides, which are predominantly emitted by the transportation industry and stationary industrial sources as gas flows containing the products of incomplete combustion, such as soot and carbon monoxide. Without ignoring the production

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of nitric acid, atmospheric contamination by high concentrations of these oxides in emitted gases must be carefully considered.

Nitrogen monoxide (NO) constitutes 95% of all the nitrogen oxide emissions (1), contributing in large measure to a variety of environmental problems such as acid rain and the resulting acidification of aquatic systems, high ozone levels, and a general degradation in atmospheric visibility.

For these reasons, it is necessary to control nitrogen oxide emissions with effective catalysts. A simpler method for the elimination of nitrogen oxides is the adsorption of these gases onto porous adsorbent materials. The method mentioned above allows them to be adsorbed and subsequently desorbed separately at different temperatures for their later treatment or direct application (2). Another important function of these adsorbents is in concentrating the flows of some nitrogen oxides. A clear example of this is the selective recovery of N_2O on an adsorbent in order to produce a concentrated stream of the gas during the desorption. In fact, N_2O is a highly selective and valuable reactant in certain oxidation reactions (3). The key step in this process is the development of a new, economic, and effective technology to selectively recover N_2O from the emissions of nitric-acid production plants and other chemical processes (3). Because zeolitic materials have a regular pore structure and high void volume, they are potentially practical solids with which to entrap large amounts of nitrogen oxides. The modification of these zeolites by ion exchange with metals can provide active sites that enhance selective adsorption.

EXPERIMENTAL

Three natural zeolites from various deposits in Mexico were used as adsorbents which, for the sake of simplicity, were named thus: Erionite (ZAPS), mordenite (ZNT), and clinoptilolite (ZSL).

Characterization of the Adsorbents

The adsorbents were characterized using the classic method of N_2 adsorption at 77 K and water adsorption at 20°C, as well by powder X-ray diffraction (XRD). Obtained results were reported in previous works (4 and 5). The micropore volume V_0 (cm^3/g) was 0.1876, 0.1186, and 0.1168 for samples ZAPS, ZNT, and ZSL respectively.

Adsorption Isotherms Measurement

The adsorption isotherms were measured in a high vacuum volumetric system constructed entirely of Pyrex glass and equipped with teflon valves grease free. Vacuum was created by a mechanical pump E2M1.5 (Edwards) reaching residual pressures of 10^{-3} Torr. Pressure was registered in a digital display pressure transducer TPR 017 (Balzers) for pressures in the interval of 10^{-4} to 1 Torr, as well as in a pressure transducer CDG Gauge (Varian) Multi Gage digitally displayed for pressures that oscillate between 1 and 1000 Torr. Before the measurements were taken, around 500 mg of each one of the samples (fraction 0.38–0.54 mm) and were dehydrated in situ at 300°C in an oven constantly evacuating up to a residual pressure of 10^{-3} Torr, having maintained these conditions for 3 h. Simultaneously, the determination of weight loss of the adsorbents was evaluated by heating samples to 300°C at atmospheric pressure in a conventional oven. After dehydration, temperature from the samples was reduced until reaching the temperature of measurement, and maintained constant during at least 1 h before starting any measurement. The temperatures (20 and 60°C) were controlled by a Haake L. ultra thermostat with a precision of ±0.2°C. The 0°C temperature was created by a bath of ice water.

The reversible adsorption isotherm was measured after obtaining total adsorption isotherm, previous evacuation of the sample to the temperature of measurement, until reaching residual pressures of 10^{-3} Torr.

The adsorption of gases as a function of time t was obtained on the basis of the difference between the initial amount of gas introduced into the cell and the amount of gas remaining in the dead space of the cell at any given time t_i from $t = 0$ to t_{eq} (equilibrium). The initial pressure was 400 Torr in all experiments.

Temperature Programed Desorption

Both temperature-programed desorption, as well as the study of real mixture of the involved gases, were carried out with a gas chromatograph Auto System XL (Perkin Elmer) with a packed column with the adsorbent in study of 40 cm length and 1.3 mm of internal diameter. The dehydration of the adsorbent was carried out in situ to 300°C and with a helium flow of 20 ml/min. The temperature-programed desorption was realized at a heating rate of 5°C/min and with the same helium flow.

RESULTS AND DISCUSSION

Adsorption of N_2O

Figure 1 shows the adsorption isotherms for N_2O at 20°C with the different natural zeolites analyzed in this study. It is clear that the isotherms

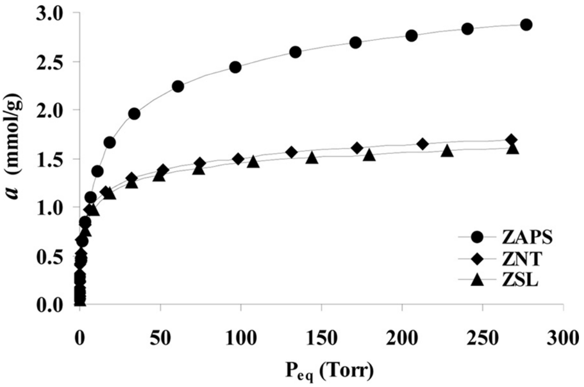

Figure 1. Total adsorption isotherms of N_2O at 20°C with natural zeolites.

are type I, according to the Brunauer, Deming, Deming, and Teller (BDDT) classification (6). Their adsorption capacities increase in the order clinoptilolite (ZSL) $\approx$ mordenite (ZNT) $<$ erionite (ZAPS). Because the kinetic diameter of the N_2O molecule is 3.3 Å and clinoptilolite, mordenite, and erionite adsorb molecules with kinetic diameters that do not exceed 3.5, 3.9, and 4.3 Å, respectively (7), it is clear that N_2O molecules can freely penetrate the entrance windows of the micropores of all three samples. Therefore, the adsorption of this gas is not influenced by esteric effects, and the adsorption behavior is mainly due to the limiting volume of the micropores (4) of the zeolites and the quantity of cations available per unit mass of the dehydrated zeolites (cationic density). The cationic density depends on the Si/Al ratio, which follows precisely the order ZSL $\approx$ ZNT $<$ ZAPS: clinoptilolites, $4.25 \leq \mathrm{Si/Al} \leq 5.25$; mordenites, $4.17 \leq \mathrm{Si/Al} \leq 5.0$; and erionites, $3 \leq \mathrm{Si/Al} \leq 3.5$ (7). In other words, the adsorption capacity of ZAPS is greatest because there is a large amount of Al in this sample. Therefore, its cationic density is greater than that of the other two samples. The similar adsorption capacities of ZNT and ZSL is attributable to the similar Si/Al ratios and micropore volumes of the two zeolites.

The adsorption behavior of this gas at 0°C was similar to that observed at 20°C, although, as expected, the decrease in temperature caused an increase in the adsorption capacities of the three samples.

The amount of N_2O adsorbed irreversibly was calculated as the difference between the total and reversible adsorption isotherms (Fig. 2) for this gas at a given temperature. An increase in irreversibility was observed in the order ZAPS $<$ ZNT $\approx$ ZSL in the range of all the equilibrium pressures studied. This finding agrees with the increasing sequence

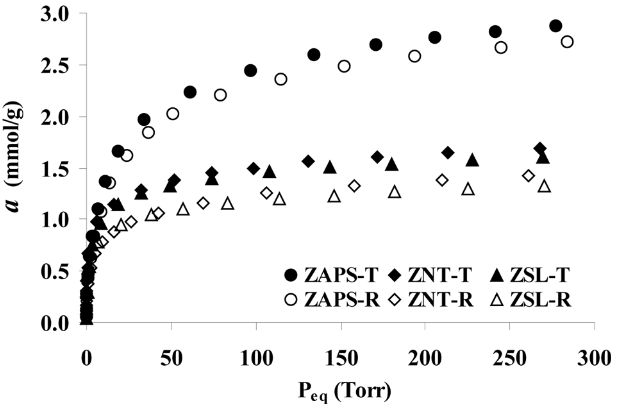

Figure 2. Adsorption isotherms of N_2O at 20°C with natural zeolites.

of adsorption characteristic energies (E) (Table 1) calculated by the Dubinin–Radushkevich equation (8); i.e., as the adsorption characteristic energy increases, the gas interaction with the surface of the adsorbent increases, and its desorbance becomes more difficult. Therefore, the proportion of irreversible adsorption also increases. The greatest proportion of irreversible adsorption shown by all three samples at low equilibrium pressures was due (in this range of pressures) to adsorption occurring at the most active adsorption sites (cations), at which desorption is most difficult because of the strong adsorbate–adsorbent interactions, as reflected in the value of Langmuir's constant K (9) (Table 1), which increases in the order $ZAPS < ZNT \approx ZSL$. It is important to emphasize that a greater interaction energy (E) or a higher level of adsorbate–adsorbent interaction (K), or both, does not mean greater adsorption. Therefore, the ZAPS sample can be considered to be a suitable adsorbent for the

Table 1. Irreversibility grade, characteristic energy of adsorption (Dubinin-Radushkevich) and Langmuir's constant (K), for adsorption of N_2O at 20°C

	Irreversibly (%)				
Adsorbent	6 Torr	85 Torr	225 Torr	E (kJ/mol)	K ($Torr^{-1}$)
ZAPS	12	6	6	16.9	0.11
ZNT	27	18	16	21.8	0.21
ZSL	28	19	16	22.9	0.19

recovery of N_2O during the desorption process because it shows a larger adsorption capacity and a lower level of irreversibility.

Adsorption of NO

As in the adsorption of N_2O, the capacities of these zeolite samples to adsorb NO at a given temperature increases in the order ZNT $\approx$ ZSL $<$ ZAPS (Fig. 3) in the range of all the equilibrium pressures studied. The fact that the cationic density of the zeolites also increases precisely in this order suggests the participation of cations as adsorptions centers for NO molecules, as Lunell et al. observed when they studied the adsorption of NO to the Na–Linde-type A (LTA) zeolite (10).

It is necessary to note that the adsorption of NO to all the samples was very slow. Because the kinetic diameter of the NO molecule is 3.17 Å, it is clear that the penetration of NO molecules into the micropores of the zeolites is not impeded, but rather that the rate of diffusion of NO into the micropores is very slow. This may result from the formation of NO dimers inside the micropores, blocking the diffusion of further NO molecules into the same pores; i.e., the presence of the new N_2O_2 molecule would give rise to NO adsorption that is influenced by esteric effects.

The possible formation of the NO dimer is supported by the facts that the dimer exists in the liquid phase and its aggregation state in the liquid and adsorbed phases is similar. Furthermore, Biglino et al. demonstrated the existence of dimeric NO complexes in the LTA zeolite using pulse electronic paramagnetic resonance (11).

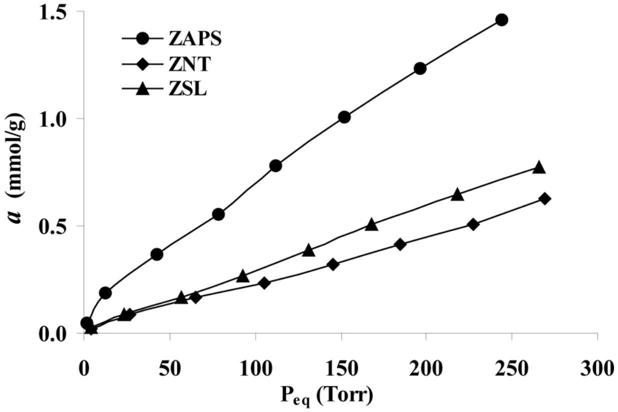

Figure 3. Total adsorption isotherms of NO at 20°C with natural zeolites.

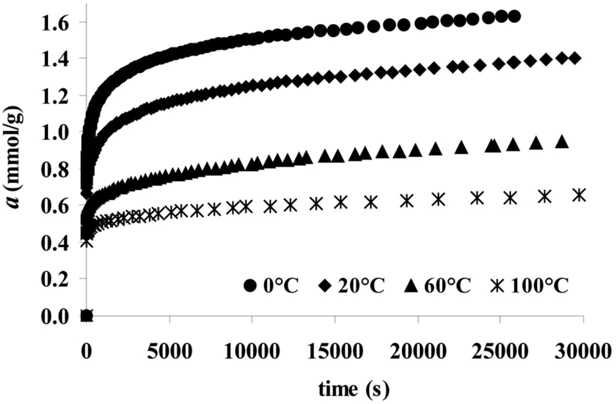

Figure 4. NO uptake curves with ZAPS at different temperatures.

A more complete analysis of this phenomenon is required to determine the adsorption kinetics of NO in all three zeolitic samples (Fig. 4). The results of this study reveal that the quantity of adsorbed substance diminishes as the temperature increases; however, an increase in the adsorption rate occurs together with an increase in temperature. In other words, the adsorption equilibrium is reached faster when the temperature is increased, which suggests that the adsorption of this gas is a process of activated type.

The Arrhenius equation ($D_0e^{-E_a/RT}$) is used to study diffusion in such a process. The activation energy can be calculated by the equation: $E_a = [(RT_1T_2)/(T_1 - T_2)]\ln(\tau_{2(0.5)})/(\tau_{1(0.5)})(12)$. Calculations revealed that the energy of activation for the NO diffusion process in ZAPS is ~24 kJ/mol. These results confirm the occurrence of esteric effects, possibly attributable to the formation of NO dimers. The ZNT and ZSL samples showed similar results, with calculated activation energies of 9 and 19 kJ/mol, respectively.

Analysis of the irreversible adsorption of NO revealed high irreversibility on all three adsorbents (Table 2). The greatest irreversibility was observed on ZAPS, possibly related to the greater number of dimeric NO complexes formed on this adsorbent (as a consequence of its greater adsorption of NO); the complexes could not be evacuated from the micropores during the desorption process at the employed temperature. This result may be attributable both to esteric effects and strong adsorbent–adsorbate interaction, as demonstrated by the theoretical constants n and K_H calculated from the Freündlich (13) and Henry (14) models, respectively.

Table 2. Irreversibility grade and n (Freündlich) and K_H (Henry) constants for adsorption of NO at 20°C

	Irreversibly (%)			n		K_H	
Adsorbent	6 Torr	85 Torr	225 Torr	Total	Rev	Total	Rev
ZAPS	87	70	55	1.46	0.93	0.0310	0.0017
ZNT	65	51	49	1.21	1.06	0.0055	0.0016
ZSL	57	49	51	1.17	1.10	0.0061	0.0023

As a consequence of the high irreversibility and the major extent of adsorbent–adsorbate interaction present in ZAPS for total adsorption, during reversible adsorption it is ZAPS that shows the weakest adsorbent–adsorbate interaction of the three samples (Table 2). Experimentally, this results in an adsorption isotherm that appears to be type III on the BDDT classification (6).

Adsorption of N_2O and NO

A comparison of the adsorption isotherm data for N_2O and NO at 20°C is shown in Fig. 5. As expected, because of the difference in the molecular weights of the gases, more N_2O was adsorbed than NO on every adsorbent studied, specially at low equilibrium pressures. From these results, it is possible to infer that if an N_2O–NO mixture is placed in contact with

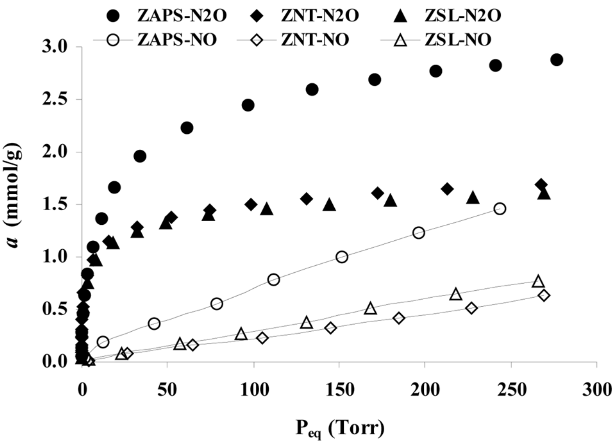

Figure 5. Total adsorption isotherms of N_2O and NO at 20°C with natural zeolites.

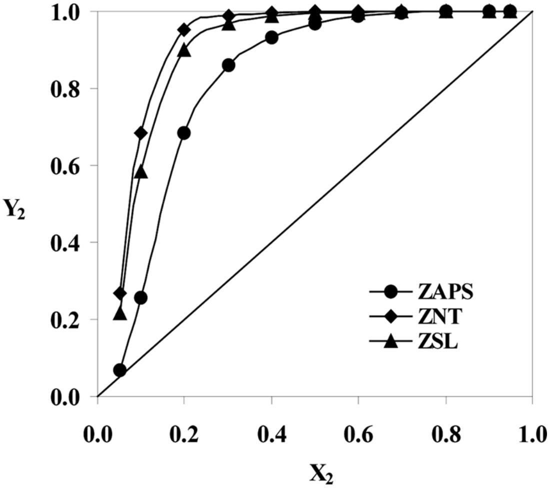

Figure 6. Estimated X–Y diagram for adsorption of NO, N_2O (1) – NO (2) mixtures at 20°C.

all three zeolites, N_2O would be preferentially adsorbed, leading to the enrichment of NO in the gas phase. This would allow the recovery of N_2O during the desorption process.

In Fig. 6, a compositional diagram of the phases is shown as $Y_2 = f(X_2)$, calculated by the Lewis method (15), where Y_2 and X_2 are the mole fractions of NO in the gas phase and in the adsorbed phase, respectively, for the adsorption of an N_2O–NO mixture. All three equilibrium curves are situated above the diagonal $Y_2 = X_2$. The separation efficiency on the three samples increases in the order ZAPS < ZSL < ZNT. The results obtained at 0°C were similar in all cases.

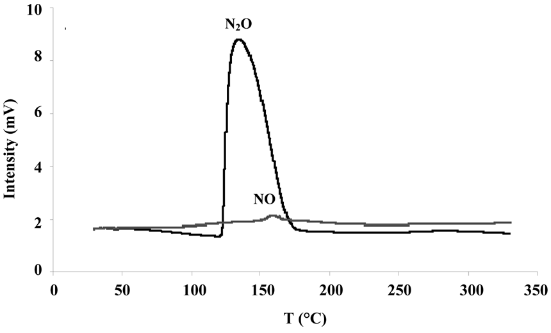

Figure 7. N_2O and NO temperature-program desorption curves from ZNT.

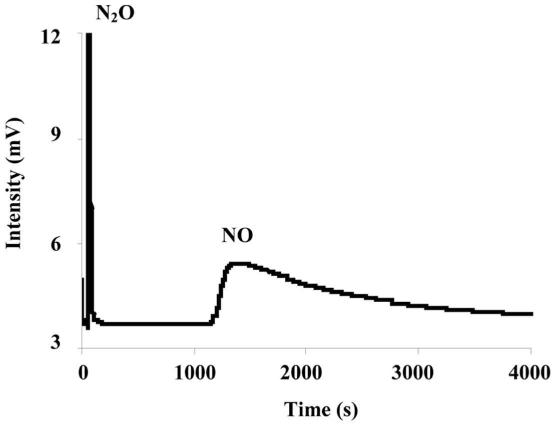

Figure 8. Chromatogram of an N_2O–NO mixture at 100°C.

Because the ZNT zeolite is the most promising adsorbent for separating N_2O–NO mixtures, the nature of the adsorption sites present in this sample that are involved in N_2O and NO adsorption was examined by temperature-programmed desorption from pure gases. The results (Fig. 7) show that the adsorption of both gases took place at only one type of adsorption site, which was common to both gases. The results for static regime adsorption showed that these adsorption sites correspond to the cations present in the zeolites. The adsorption of both gases at the same adsorption sites establishes a competitive adsorption, in which the adsorption of N_2O is favored, based on the results shown in Figs. 5 and 7. In Fig. 7, we can see that adsorbed N_2O is desorbed only at temperatures above 100°C.

The real N_2O–NO mixtures studied here were made by gas chromatography at different temperatures. The results obtained at 100°C are presented in Fig. 8, as an example. This study enabled us to confirm that N_2O adsorbs to zeolites in larger quantities and more strongly than NO. We also observed the influence of temperature on the behavior of the chromatographic separation of the mixture. At room temperature, we confirmed that N_2O mixed with NO is preferentially adsorbed onto ZNT, meaning that flows enriched in N_2O can be obtained during the desorption process. At temperatures higher than 100°C, the separation of these gases could be achieved based on time differences.

CONCLUSIONS

The adsorption of N_2O onto three natural zeolites was not influenced by esteric effects. The capacities of these samples to adsorb N_2O coincides with the zeolite type (Si/Al), and with their corresponding properties. Conversely, NO adsorption showed an activated diffusion process, attributable to the possible formation of NO dimers inside the micropores.

Because of the difference in the molecular masses of the two gases, N_2O was adsorbed on all three adsorbents in greater quantities than NO. This fact suggests that all three zeolites can be used as adsorbents in the separation of N_2O–NO mixtures, especially ZNT, either at room temperature or at temperatures above 100°C.

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