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Experimental and density functional theory study of the adsorption of N_2O on ion-exchanged ZSM-5: Part II. The adsorption of N_2O on main-group ion-exchanged ZSM-5

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Abstract

The adsorption and desorption of N_2O on main-group ion-exchanged ZSM-5 was studied using temperature-programmed desorption (TPD) and density functional theory (DFT) calculations. TPD experiments were carried out to determine the desorbed temperature T_{max} corresponding to the maximum mass intensity of N_2O desorption peak and adsorption capacity of N_2O on metal-ion-exchanged ZSM-5s. The results indicated that T_{max} followed a sequence of $Ba^{2+} > Ca^{2+} > Cs^+ > K^+ > Na^+ > Mg^{2+}$and the amount of adsorbed N_2O on main-group metal cation followed a sequence of $Ba^{2+} > Mg^{2+} > Ca^{2+} > Na^+ > K^+ > Cs^+$. The DFT calculations were performed to obtain the adsorption energy (E_{ads}), which represents the strength of the interaction between metal cations and the N-end or O-end of N_2O. The calculation results showed that the N-end of the N_2O molecule was favorably adsorbed on ion-exchanged ZSM-5, except for Cs-ZSM-5. For alkali metal cations, the E_{ads} of N_2O on cations followed the order which was the same to that of T_{max}: $Cs^+ > K^+ > Na^+$. The calculated and experimental results consistently showed that the adsorption performances of alkaline-earth metal cations were better than those of alkali metal cations.

Key words: N_2O adsorption; ZSM-5; DFT; ion-exchanged zeolites

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Introduction

Nitrous oxide (N_2O) is a greenhouse gas that has been proved to contribute to ozone destruction in the stratosphere (Ravishankara et al., 2009; Stott et al., 2002). Although N_2O is not the major contributor to global warming (ca. 6%), its effects are much more potent than those of CO_2 and CH_4. In addition, the destructive effects of N_2O are compounded by the fact that N_2O is a major stratospheric source of NO*x*. Anthropogenic practices, have led to a rapid increase in atmospheric N_2O concentrations, with an annual growth rate of 0.2%–0.3% (Stott et al., 2002). Therefore, the control of N_2O emissions from stationary and mobile combustion processes and from chemical processes has become a significant concern.

For decades, the catalytic decomposition of N_2O to N_2 and O_2 has been widely investigated on transition-metals ion-exchanged zeolites (Pirngruber et al., 2006; Li and Armor, 1992; Waclaw et al., 2004). N_2O adsorption on zeolites was observed in the catalytic decomposition of N_2O and in the reduction of N_2O by hydrocarbons (Kapteijn et al., 1996; Pérez-Ramírez et al., 2003; Xue et al., 2007a, 2007b). Since N_2O adsorption can be performed at room temperature and does not consume any additional energy, it can be regarded as an economic and environment-friendly method for N_2O removal, particularly at low temperatures and/or at low emitted concentrations of the gas. Centi et al. (2000) studied the N_2O adsorption on various ion-exchanged ZSM-5, X and Y zeolites. They concluded that Ba-ZSM-5 has a better adsorption capacity for N_2O than other zeolites even in the presence of larger amounts of water. To develop new materials for N_2O adsorption, the rules of adsorption for N_2O on ion-exchanged zeolites require further research.

The calculations of the N_2O adsorption were mainly focused on the transition-metal and noble metal cations, such as copper-, iron-, cobalt-, silver- gold- palliadium-exchanged ZSM-5 (Kapteijn et al., 1996; Rakic et al., 2005; Zhanpeisov et al., 2003; Kameoka et al., 2001; Ates and Reitzmann, 2005a, 2005b; Lzumi et al., 2001; Yahiro and Iwamoto, 2001). Only one study on the adsorption of N_2O over main-group ion-exchanged zeolites

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was published (Solkan et al., 2007). In this study, the activation energies for N_2O dissociation on Ga-ZSM-5 and GaO-ZSM-5 at the B3LYP/6-31+G* level (Becke's three-parameter hybrid method with the Lee, Yang and Parr gradient-corrected correlation functional, 6-31+G(d) basis set) were calculated by two full 10-membered zeolite rings model, and the possible reaction pathway for the catalytic dissociation of N_2O was proposed. Lund (2006) used two models including 5T cluster model and two full 10-membered zeolite rings to calculate the minimum energy structures of surface intermediates on Fe/ZSM-5 catalyst. The results demonstrated that the 5T cluster is sufficiently accurate for calculating energies of structure, while the two full 10-membered zeolite rings are preferred for calculating the accurate geometries of the sites. Additionally, they concluded that the longer-range interactions between surface species and the ZSM-5 zeolite channel wall do not significantly affect the energies of the mechanistic steps. Moreover, previous studies (Heyden et al., 2005a, 2005b, 2006; Ryder et al., 2002) used 5T cluster model and the first principles to simulate the reaction mechanism of N_2O dissociation over Fe-ZSM-5. They proved that the calculation can provide a satisfactory basis for simulating all of the experimental works. Therefore, 5T cluster model is suitable to calculate the adsorption energy of N_2O on metal ion-exchanged ZSM-5.

In this article, the experimental results of temperature-programmed desorption (TPD) were compared with the predictions made by density functional theory (DFT) calculations in an analysis of the adsorption behavior of N_2O on ZSM-5 zeolites exchanged with six main group metal cations (Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}). The aim of the research was to determine the rules governing the N_2O adsorption potential on main-group ion-exchanged ZSM-5 with respect to the influence of ionic radius, electrostatic field.

1 Experimental methods

1.1 Materials preparation and characterization

All samples were prepared by the wet ion-exchange method. Typically, 10 g H-ZSM-5 (SiO_2/Al_2O_3 = 25, Nankai University, China) was mixed with 80 mL of 0.2 mol/L nitrate salts solution at 90°C for 24 hr. After ion exchange, the samples were filtered, thoroughly washed, dried overnight at 100°C, and then calcined in air at 550°C for 4 hr to obtain cation-exchanged-ZSM-5. Several alkali and alkali earth cations were selected including Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}.

The Si, Al, and metal ions contents of these zeolites were determined by inductively coupled plasma optical emission spectrometer (ICP-OES) using an Optima 2000 spectrometer (Perkin-Elmer Co., USA)

1.2 Desorption test

TPD test was performed on a Hiden analytical instrument, equipped with a quadrupole mass spectrometry (QMS) sampling system (HPR20, Hiden Analytical Ltd., UK). Briefly, 1.0 g zeolites (mesh size: 0.5–0.25 mm) was placed in the tubular quart reactor. The 0.5-mm (OD) thermocouples measured the temperature of the absorbent bed and provided feedback to the temperature programmer. Prior to N_2O adsorption in 2% N_2O/Ar at room temperature, all zeolites were pretreated in a flow of 20% O_2/Ar at 500°C for 1 hr. After the zeolites were saturated with N_2O, the physical desorption of N_2O was performed using Ar for 1 hr at room temperature. Subsequently, the temperature was raised by 30°C/min from room temperature to 500°C. The signals of N_2O (m/z = 44) and NO (m/z = 30) were collected simultaneously by mass spectrometry.

2 Model development and calculation

In this study, the 5T cluster model is identical to that used in previous publications (Heyden et al., 2005a, 2005b, 2006; Ryder et al., 2002). The portion of the cluster describing the zeolite contains an Al-atom in the T12 position of the framework surrounded by shells of O- and Si-atoms. The terminal Si-atoms are fixed in their crystallographic positions, as reported by Olson et al. (1981). Dangling bonds are terminated by H-atoms.

The first-principles DFT calculations were carried out using the DMol3 package (Delley et al., 1990, 2000). The generalized gradient approximation (GGA) with PW91 functional (Perdew and Wang, 1992) was used to describe the exchange-correlation (XC) effects. The double numerical with polarization functions (DNP) basis set was used in the expanded electronic wave functional. Therefore, all of calculations were performed by using spin-restricted methods by choosing suitable spin multiplicity for different cations. The convergence criterions in energy and force were set to 10^{-5} eV and 2×10^{-3} eV/Å, respectively.

The adsorption potential energies were calculated according to the following equation:

$$E_{ads} = E_{complex} (E_{ZSM\text{-}5} + E_{adsorbate})$$

where, E_{ads} is the adsorption energy; $E_{complex}$ is the total energy of the ZSM-5 with the adsorbate; and $E_{adsorbate}$ and $E_{ZSM\text{-}5}$ are the energies of isolated adsorbate and ZSM-5, respectively.

3 Results and discussion

3.1 Desorption test

N_2O-TPD experiments were carried out to study the adsorption and desorption behaviors of N_2O on main-group metal ion-exchanged ZSM-5s. The desorbed temperature T_{max} corresponding to the maximum mass intensity of N_2O desorption peak was used to evaluate the strength of N_2O adsorption onto cations. The amount of adsorbed N_2O was calculated from TPD profiles to estimate the adsorption capacity of the various zeolites.

Figure 1 illustrates that desorption of N_2O occurred at temperatures below 200°C on all of the ion-exchanged ZSM-5 zeolites. For HZSM-5, only trace amounts of N_2O desorbed in the TPD experiment. The dramatic increase in

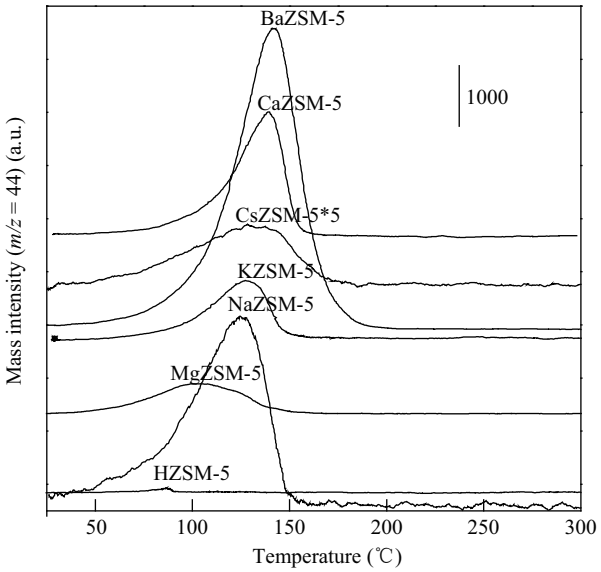

Fig. 1 Temperature-programmed desorption of N_2O on main-group metal ion-exchanged ZSM-5.

the adsorption of N_2O on ion-exchanged ZSM-5 indicates that metal cations play a crucial role in N_2O adsorption. There was only one desorption peak in each TPD profile and areas of these peaks were quite different from each other. Thus, it is concluded that the nature of the metal cation in ZSM-5 significantly influenced the adsorption behavior. T_{max} and amounts of adsorbed gases obtained from TPD profiles are summarized in Table 1.

As shown in Table 1, T_{max} and the amount of adsorbed N_2O on per main group metal cations followed the order of $Ba^{2+} > Ca^{2+} > Cs^+ > K^+ > Na^+ > Mg^{2+}$ and $Ba^{2+} > Mg^{2+} > Ca^{2+} > Cs^+ > Na^+ > K^+$, respectively. These results indicate that the adsorption performances of alkaline-earth metal cations were better than those of alkali metal cations. Ba-ZSM-5 exhibited the best adsorption behavior, including the highest desorption temperature and adsorption capacity, which is consistent with published work (Centi et al., 2000). For N_2O adsorption capacity of zeolites, the amount of absorbed N_2O is 10^{-6} mol N_2O/g zeolite which is less than the value of 6×10^{-5}–14.9×10^{-5} mol N_2O/g zeolite reported by Groen et al. (2002). In our study, the pretreatment of zeolites and the adsorption of N_2O were performed in the flow of 2% N_2O/Ar in ambient pressure. In contrast, experiments were performed *in situ* vacuum system in the literature (Groen et al., 2002). Therefore, the great deference in these results suggests that the flow decrease the trapped N_2O in the channel of zeolites.

The electrostatic field of the cation exchanged into the zeolite is important for the interaction between cation and adsorbate (Blatter and Frei, 1993, 1994). As mentioned in literature, if main-group cations were exchanged into the zeolites, a strong electrostatic field could highly polarize the N_2O molecule into the $N = N^+–O^-$ resonance form which may be favorable for stabilizing the N_2O molecule in zeolite channels (Centi et al., 2000). Cations with small radii interact strongly with N_2O at a short distance. On this basis, the T_{max} of Mg^{2+}, which has a small radius of 72 pm, should be the highest. However, the T_{max} of Mg^{2+} at 102°C is the lowest among all of the studied cations. It can be considered that the large ionic radius can increase the effective action area between the cation and N_2O, which is positively related to the strength of their interaction. Accordingly, Ba^{2+} and Cs^+, with the largest radii in their group, exhibited the best strength of adsorption. For Mg^{2+}-exchanged zeolites, the very small effective action area between Mg^{2+} and N_2O molecule probably weakened their interaction, thereby inducing the lowest T_{max}. Therefore, to the same main group cations, large radii can promote the interaction between cation and N_2O.

Table 1 Adsorption of N_2O on various ion-exchanged ZSM-5 samples at room temperature

Me-ZSM-5	T_{max} (°C)	Exchange level[a] (%)	Absorption amount[b] (10^{-6} mol N_2O/ g zeolite)	Molar ratio of N_2O/Me[c] $\times 10^{-2}$
Mg^{2+}	102	14.9	9.1	7.8
Na^+	125	100	15.2	2.2
K^+	129	100	11.35	1.47
Cs^+	135	10	0.21	2.4
Ca^{2+}	136	22.5	11.8	5.72
Ba^{2+}	140	41.2	250.3	94.9

[a] The exchange level is estimated on the basis of the Me^{n+}/Al molar ratio; [b] the maximum adsorbed moles of N_2O on per gram of zeolite are estimated from the area of TPD peak; [c] the mole ratio of N_2O and cations reflect the amount of adsorbed N_2O on per 100 metal cations (Me).

3.2 Calculations

In order to rationalize the experimental results, DFT calculations were performed to investigate the adsorption energy, geometric and electronic properties of N_2O on various main-group metal ion exchange ZSM-5 zeolite.

Figure 2 shows the optimized configuration of the N_2O molecule absorbed on Mg-ZSM-5, with the N-end (Fig. 2a) and the O-end (Fig. 2b). Similar configurations were adopted for the other ion-exchanged ZSM-5s. The bond lengths of N–N and N–O in N_2O as well as the adsorption energies of N_2O adsorbed on ion-exchanged ZSM-5s were calculated based on the above models. As presented in Table 2, geometrical and energetic changes took place during the adsorption process of N_2O on metal-ion-exchanged ZSM-5. For example, the calculated values of the N–N and N–O bond lengths in the free N_2O molecule are 1.12 and 1.18 Å, respectively. When N_2O is adsorbed onto various ion-exchanged ZSM-5s through its

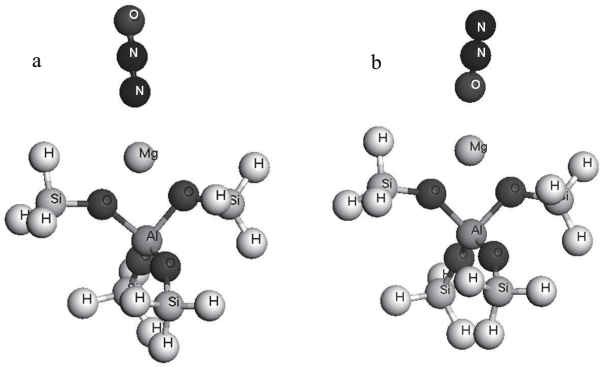

Fig. 2 Optimized configuration of N_2O molecule absorbed on Mg-ZSM-5 through N-end (a) or O-end (b).

N-end, the N–N bonds elongate, according to the calculation results. The adsorption energies of N_2O molecules on several ion-exchanged ZSM-5s are compared in Fig. 3.

From the data provided in Table 2 and Fig. 3, it is apparent that the N-end is more favorable for N_2O adsorption on various ion-exchanged ZSM-5s, except for Cs^+-ZSM-5. For most of ion-exchanged ZSM-5, adsorption of the N-end of N_2O and NO was favored, consistent with the results of previous calculations (Ghosh et al., 2003; Rakic et al., 2005; Yajima et al., 2000; Zhanpeisov et al., 2003; Miyamoto, 2000). There was no corresponding work on the adsorption of N_2O on Cs^+-ZSM-5. We analyzed N-end adsorption, as presented and discussed in the following sections. According to the E_{ads} (N-end N_2O) value, the adsorption strength of N_2O on the main-group ions followed the order: $Mg^{2+} > Ca^{2+} > Cs^+ > K^+ > Ba^{2+} > Na^+$.

Compared with the T_{max} order, $Ba^{2+} > Ca^{2+} > Cs^+ > K^+ > Na^+ > Mg^{2+}$, it is found that the adsorption strength between the alkali earth cations and N_2O is basically higher than that of alkali cations. For the elements in the similar radius, i.e., Na^+ (102 pm) and Ca^{2+} (100 pm), K^+ (138 pm) and Ba^{2+} (135 pm), the valence of cations is important to the association between N_2O and cations.

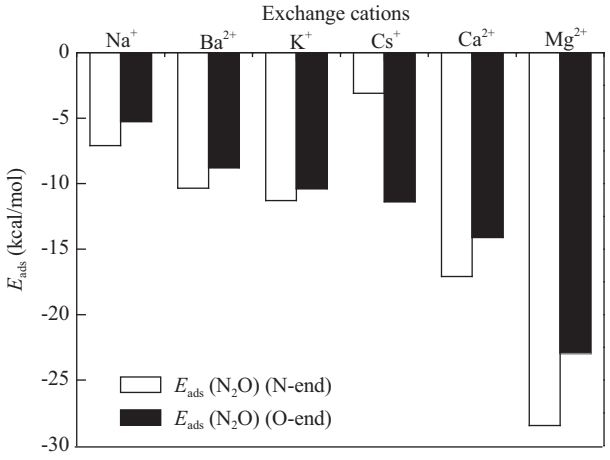

Fig. 3 Adsorption energies of N_2O on various ion-exchanged ZSM-5s (N-end and O-end).

Table 2 Adsorption energies of N_2O on various ion-exchanged ZSM-5s and bond length of N–N and N–O in N_2O molecule adsorbed on zeolites with O-end

Metal ion (ionic radius (pm))[a]	E_{ads} (kcal/mol)		Bond length of N_2O adsorbed with N-end (Å)	
	N-end	O-end	N–N (1.12 Å)	N–O (1.18 Å)
Mg^{2+} (72)	28.46	22.97	1.14	1.16
K^+ (138)	11.33	10.38	1.14	1.19
Na^+ (102)	7.1	5.26	1.14	1.18
Cs^+ (167)	3.1	11.37	1.14	1.12
Ba^{2+} (135)	10.35	8.77	1.21	1.18
Ca^{2+} (100)	17.08	14.11	1.14	1.17

[a] The ionic radius data quote from Wikipedia, the free encyclopedia.

According to experimental and calculation results, the electrostatic force of cations $F = k\frac{z}{r^2}$ (z is charge and r is radius of cation) was considered to be responsible to the rules of T_{max} and E_{ads}. The relationship between T_{max}, E_{ads} and electrostatic force is shown in Fig. 4. For the elements in the same group, T_{max} is inversely related with the electrostatic force between cations and N_2O molecular (Fig. 4a). It indicates that the cation radius plays a key role in the association between N_2O and main-group cations. Accordingly, Ba^{2+} and Cs^+, with the largest radii in their group, exhibited the best strength of adsorption. In Fig. 4b, for alkali earth cations, the E_{ads} value is proportional to F, while the converse occurred in alkali cations. For alkali cations, the E_{ads} of N_2O on the cations follows the order which is absolutely same to that of the T_{max}: $Cs^+ > K^+ > Na^+$. However, to alkali earth cations, the order of T_{max} converses to that of E_{ads}, suggesting that the

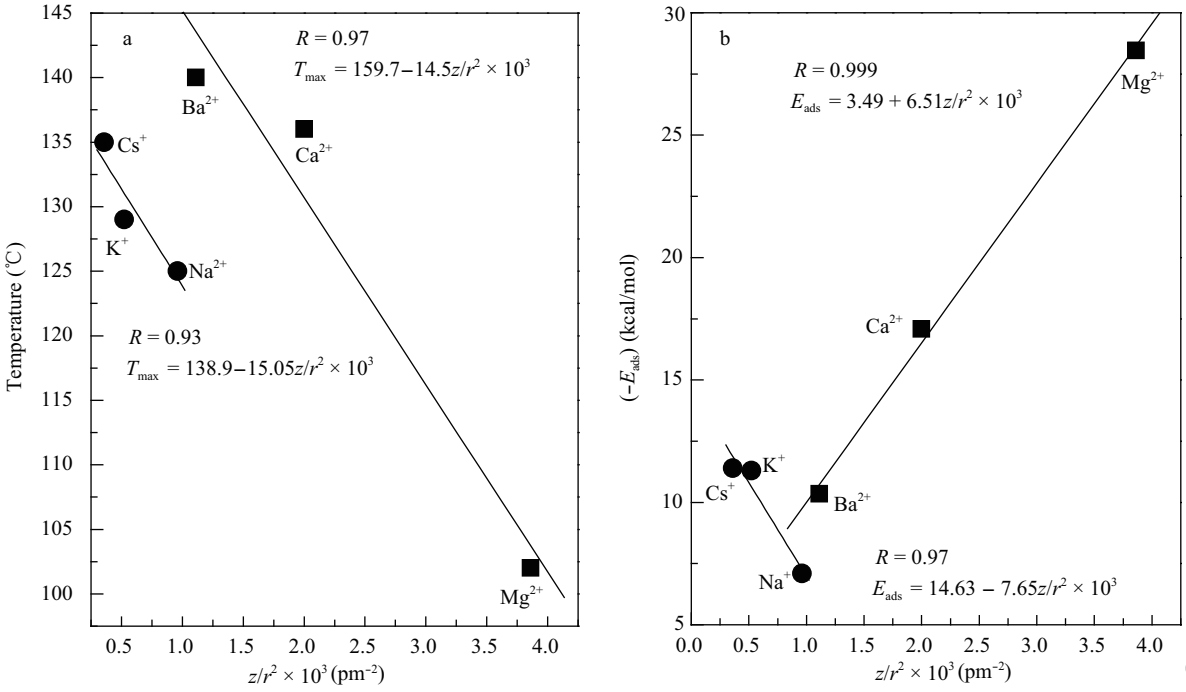

Fig. 4 Relationship between T_{max} (a) and E_{ads} (b) with electrostatic force.

current calculated method is probably unsuitable to study the adsorption behavior of gas molecular, or other factor need to be considered. The research of the calculation on the adsorption of N_2O over alkali earth cations will be developed.

On the basis of the above analysis of the data, it is found that the radius has two conflicting aspects influencing the adsorption strength of cations. On one hand, a small radius can increase the Coulombic force between main-group-metal cations and N_2O. On the other hand, a large radius can increase the effective action area of these cations and N_2O promoting the association between cations and N_2O. Experimental results undoubtedly prove that the effective action area of the cations is the main determinant of adsorption strength.

4 Conclusions

Experimental results showed that high valence and a large radius favor the strong interaction of main-group-metal cations with N_2O, Ba-ZSM-5 exhibited the best adsorption behavior, including the highest desorption temperature and adsorption capacity. The DFT calculation results showed that the N-end of N_2O is favorable in the molecule's adsorption on a set of ion-exchanged zeolites except in the cases of Cs-ZSM-5. The behavior of N_2O adsorption on main-group-metals ion-exchanged ZSM-5 is influenced not only by the valence of these cations but also by their ionic radius. Theoretical and experimental results consistently indicated that the alkali earth cations were more favorable adsorption for N_2O than alkali cations. For the alkali cations, the E_{ads} of N_2O on cations follows the order which is absolutely same to that of the T_{max}: $Cs^+ > K^+ > Na^+$. While the inverse rule of E_{ads} and T_{max} of alkali earth cations proved that the present calculation method is unsuitable to study the adsorption behavior of N_2O on alkali earth metal ion-exchanged ZSM-5.

Acknowledgments

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