



Experimental and DFT study of the adsorption of N₂O on transition ion-exchanged ZSM-5



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ABSTRACT

N₂O has an adverse impact on environment as a strong greenhouse gas and stratospheric ozone depletor, and also is a biotoxic gas to human beings with the long-time exposure. Adsorption is important for N₂O removal and the catalytic decomposition of N₂O. Here, the interaction between N₂O and transition-metal ion-exchanged ZSM-5 were studied using experimental and theoretical methods. T_{\max} (desorbed temperature at peak maximum) obtained by temperature-programmed desorption (TPD) and adsorption heat (ΔH_{ads}) calculated by density functional theory (DFT) were used to determine the strength of interaction between N₂O and metal ions. It was found that the adsorption and desorption behaviors of N₂O significantly depended on the type of the ions. The TPD results indicate that T_{\max} followed the order: Mn > Fe > Co > Zn > Ni > Cu. The DFT-calculated ΔH_{ads} shows that N₂O molecule more favorably adsorbed on the transition-metal active site by O-end, and simultaneously N₂O is dissociated into gaseous N₂ and one adsorbed O atom. The electron transfer between cations and N₂O molecule strongly correlates with ΔH_{ads} . The higher electron transfers lead to the stronger N₂O chemisorption. There is a linear positive correlation between ΔH_{ads} and T_{\max} which provides an advantageous auxiliary tool for choosing suitable zeolites for N₂O removal.

1. Introduction

Nitrous oxide (N₂O) as a strong greenhouse gas has a great global warming potential which is approximately 310 and 21 times higher than that of CO₂ and CH₄, respectively [1]. In addition, when it migrated to the stratosphere, N₂O reacts with ozone, causing the ozone layer depletion and the formation of NO_x. Toxicological studies have indicated that N₂O can cause adverse effects such as reduced fertility, neurological disorders, and renal and liver disease [2]. Anthropogenic practices result in atmospheric N₂O concentrations, with an annual growth rate of 0.2–0.3% [1]. Therefore, the control of N₂O emissions from stationary and mobile combustion processes has become a significant concern.

Extensive efforts have been made to develop effective methods for elimination of N₂O [3–14]. Currently, directly catalytic decomposition of N₂O to harmless N₂ and O₂ has been considered to be the most efficient method for N₂O abatement. Transition-metals ion-exchanged zeolites catalysts are attractive catalysts for N₂O decomposition because

of their high catalytic activity, good thermal stabilities and low costs [4–12]. Additionally, N₂O is a valuable reactant in some oxidation reactions, such as selective catalytic oxidation of organic molecules and ammonia at room temperature [9–12]. Thus, an efficient removal process would be to trap N₂O with an absorbent at the end of the emission source and then recover the N₂O from the absorbent such that it could be used in industry, or to remove it by N₂O reductases [13–18]. However, little attention has been paid to the removal of N₂O with an absorbent, because the N₂O hardly adsorbs on most materials in nature [9,18]. Introduction of transition metal ions to the porous materials can lead to a remarkable increase of binding strength to N₂O [14,19]. Among of them, numerous studies have focused on ion-exchanged ZSM-5 zeolites because its special channel system prefers to entrap a large amount of N₂O and to promote N₂O catalytic decomposition in complex atmosphere [13,14,16,17]. Centi et al. [13] carried out a detailed experimental study on ion-exchanged ZSM-5, X and Y zeolites. They concluded that Ba-ZSM-5 had a significantly better adsorption capacity for N₂O than other zeolites even in the presence of large amounts of

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water in the gaseous industrial streams. Guillemot et al. also found that Ba-ZSM-5 was suitable as the workplace nitrous oxide adsorbent [14].

Density functional theory (DFT) calculation is a powerful tool for investigating the interactions of N_2O molecules with zeolites [17–24]. The factors including electric field [17], the structure of active center [18,19], the valence of exchanged ions and the framework acid-base properties [20,21], have been considered as the important properties to play the major roles in adsorption and dissociation of N_2O on zeolite catalysts. However, relatively few studies devoted to the series of common ions modified zeolites reacting with N_2O , with the purpose of exploring the rule of the interaction between these ions and N_2O . In light of that, our previous work systematically investigated the adsorption and desorption behavior of N_2O on main-group ion-exchanged ZSM-5 by theoretical and experimental methods [22], and concluded that the interaction between main-group-metals ion-exchanged ZSM-5 and N_2O was influenced not only by the valence of these cations but also by their ionic radius. The alkali earth cations were more favorable adsorption for N_2O than alkali cations.

The interaction between transition metal cations-exchanged ZSM-5 and N_2O is important for selecting the adsorbents of N_2O and studying the N_2O catalytic decomposition. In this paper, the adsorption behavior of N_2O on HZSM-5 zeolites exchanged with six transition metal cations (Mn, Co, Fe, Ni, Cu and Zn) have been investigated by the temperature-programmed desorption (TPD) experiment and the density functional theory (DFT) calculations. The adsorption potential, adsorption capacity and the electron transfer from these cations to N_2O have been examined. The aim of the research is to find the mechanisms governing the interaction strength of cations with N_2O , which will be helpful for the selection and design of highly efficient zeolites for N_2O removal.

2. Materials and methods

2.1. Materials preparation and characterization

The transition ion-exchanged ZSM-5 were prepared through our previously reported wet ion-exchange method [22]. Briefly, H-ZSM-5 ($SiO_2/Al_2O_3 = 25$, Nankai University) were mixed with 0.2 M aqueous solution of nitrate salts at 30 °C for 24 h. After ion exchange, the samples were filtered, thoroughly washed, dried at 100 °C overnight, and then calcined in air at 550 °C for 4 h to obtain cation-exchanged-ZSM-5. The aqueous solution of nitrate salts included $Co(NO_3)_2$, $Cu(NO_3)_2$, $Fe(NO_3)_3$, $Mn(NO_3)_2$, $Ni(NO_3)_2$ and $Zn(NO_3)_2$. The Si, Al, and metal ions contents of these zeolites were determined by ICP-OES using an Optima 2000 spectrometer (Perkin-Elmer Co.).

The nitrogen adsorption-desorption isotherms were obtained at -196 °C on a Quantasorb-18 automatic instrument (Quanta Chrome Instrument Co.). Prior to measurements, samples were evacuated at 300 °C for 10 h. Specific areas were computed from the sorption isotherms using the Brunauer-Emmett-Teller (BET) method.

2.2. Experiments

To determine the N_2O adsorption amount of zeolites, N_2O breakthrough curves were measured. 100 mg of catalyst was pretreated in pure N_2 for 1 h at 500 °C and then cooled down to 30 °C. Afterwards, the sample was placed into an atmosphere of 300 ppm N_2O/N_2 at 300 mL/min for 30 min. Meanwhile, the N_2O concentration was detected by an online NEXUS 670-FTIR spectrometer, and the spectra were recorded with a time interval of ~ 8 s.

Temperature-programmed desorption experiment was performed on a Micromeritics AutoChem II 2920 apparatus, equipped with a computer-controlled CryoCooler and a thermal conductivity detector (TCD). In a typical measurement, 50 mg transition ion-exchanged zeolites (mesh size: 0.5–0.25 mm) was placed in the U-type quartz reactor. Prior to N_2O adsorption at room temperature, all zeolites were pretreated in a flow of 20% O_2/Ar at 500 °C for 1 h. After the zeolites had been

saturated with adsorbed N_2O , the physical desorption of N_2O was performed using Ar for about 1 h at 50 °C. Subsequently, the temperature was raised at a ramp of 10 °C min^{-1} from 50 °C to 300 °C. The signals of N_2O ($m/z = 44$) and, NO ($m/z = 30$), N_2 ($m/z = 28$) and O_2 ($m/z = 32$) were collected simultaneously by mass spectrometry.

2.3. Computational details

The B3LYP functional [24] and 6-31G(d) basis set [25] were used for geometry optimization. Vibrational frequency calculations were performed at the same level to identify the minima and to obtain the zero-point energy (ZPE) correction and the thermal correction to enthalpy (ΔH). To improve the accuracy of electronic energies, single-point energies at the converged geometries were calculated using the 6-311G(d,p) basis set [26] for the main-group elements, and the SDD pseudo-potential and basis set [27] for the transition metals (i.e., Mn, Fe, Co, Ni, Cu, Zn) with the B3LYP functional. A double 10-membered ring ZSM-5 cluster with one Al atom at the T12 site was used as the zeolite model [17]. The transition metal ion was placed next to the Al-containing tetrahedron. The dangling bonds of boundary Si atoms of clusters were saturated with H atoms to obtain neutral clusters. All atoms except the H atoms were relaxed. The terminating H atoms were fixed to orient in the Si-O direction in the ZSM-5-type zeolite to avoid unrealistic deformation of the cluster during the geometry optimization [28,29]. The spin-unrestricted method is applied to the open-shell systems. For a given cluster, all possible spin multiplicities are tested to find the most stable electronic state. The natural population analysis (NPA) charge was calculated to estimate the charge transfer during the adsorption processes. All the DFT calculations were performed using the Gaussian 09 package [30]. Two kinds of adsorption configurations of N_2O with either N-end or O-end in metal ion-exchanged ZSM-5 were considered. The adsorption reaction enthalpy changes ΔH_{ads} was calculated as follows, $\Delta H_{ads} = H_{complex} - (H_{ZSM-5} + H_{adsorbate})$

Where $H_{complex}$ is the enthalpy of the HZSM-5 with the adsorbate, and $H_{adsorbate}$ and H_{ZSM-5} are the enthalpies of isolated adsorbate and ZSM-5, respectively.

3. Results and discussion

3.1. Adsorption and desorption test

The adsorption experiment was performed to estimate the mass of N_2O collected on ion-exchanged ZSM-5. The adsorption breakthrough curves are shown in Fig. 1, and the adsorption capacities of zeolites for N_2O adsorption are presented in Table 1. As shown in Fig. 1, the

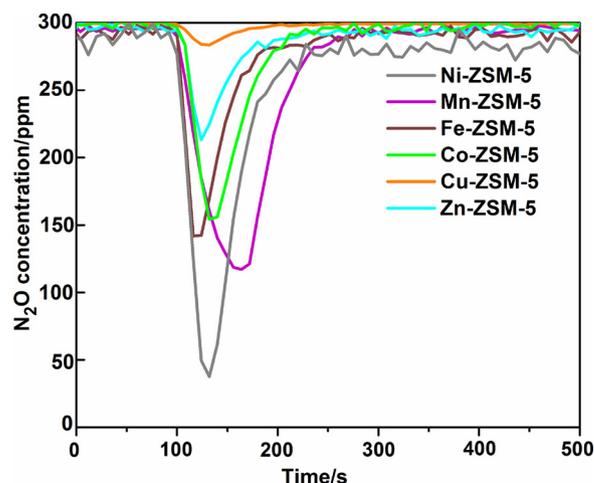


Fig. 1. Breakthrough curves for N_2O (300 ppm) adsorption on per mole ion at 30 °C, 300 mL/min.

Table 1
The behavior of the adsorption and desorption of N₂O on various ion-exchanged ZSM-5 samples.

Me-ZSM-5	T _{max} (°C)	Exchange level ^a (%)	Adsorption amount ^b (10 ⁻³ mol N ₂ O/g zeolite)	Desorption amount ^b (10 ⁻⁶ mol N ₂ O/g zeolite)	Molar ratio of N ₂ O/Me ^c
Cu	80	24.5	9.8	0.92	3.7
Ni	82	1.49	12.6	4.3	66.7
Zn	91	3.5	8.1	15.0	20.0
Co	99	3.1	7.1	13.2	20.8
Fe	104	2.0	7.9	9.3	33.3
Mn	105	3.72	17.9	24.9	43.9

^a The exchange level was estimated on the basis of the Me/Al molar ratio.

^b The adsorption and desorption amount of N₂O on zeolite was estimated from breakthrough curves (Fig. 1) and the area of TPD peak (Fig. 2).

^c The mole ratio of N₂O to cations reflected the amount of adsorbed N₂O on per 100 metal cations.

adsorption of N₂O on all of the zeolites reached at saturation within 200 s. The nature of the metal cation in HZSM-5 significantly influenced the adsorption behavior so that the amounts of desorbed gases obtained from N₂O-TPD profile are quite different. The N₂O adsorption capacities are in the order: Ni > Mn > Co > Fe > Zn > Cu. Ni-ZSM-5 zeolites shows a significantly higher adsorption capacity for N₂O than other zeolites (in Table 1). The adsorption capacity of Cu-ZSM-5 is the lowest and it is thus not suitable for N₂O removal. The surface areas and pore volume of HZSM-5 and ion-exchanged ZSM-5 are shown in Table S1. Except Cu-ZSM-5, both surface area and pore volume of the ion-exchanged ZSM-5 are lower than that of HZSM-5, indicating that the ion species were located in the channel of the zeolites. Cu-ZSM-5 with comparably high exchange level (24.5%) resulted in the aggregation of Cu oxidation clusters blocking the channels of ZSM-5. The surface area and pore volume of Cu-ZSM-5 therefore decreased significantly.

To study the desorption behaviors of N₂O on various ion-exchanged ZSM-5, N₂O-temperature program desorption (TPD) experiments were performed. The desorbed temperature at peak maximum (T_{max}) and the amount of desorbed N₂O from the ion-exchanged ZSM-5 zeolites were obtained from Fig. 2. T_{max} was used to evaluate the adsorption strength of N₂O onto cations. The amount of desorbed N₂O was calculated from TPD profiles.

Similar to the main-group ion-exchanged ZSM-5 zeolites reported in our previous study [22], there is only one desorption peak in each N₂O-TPD profile of the transition ion-exchanged ZSM-5 zeolites (Fig. 2),

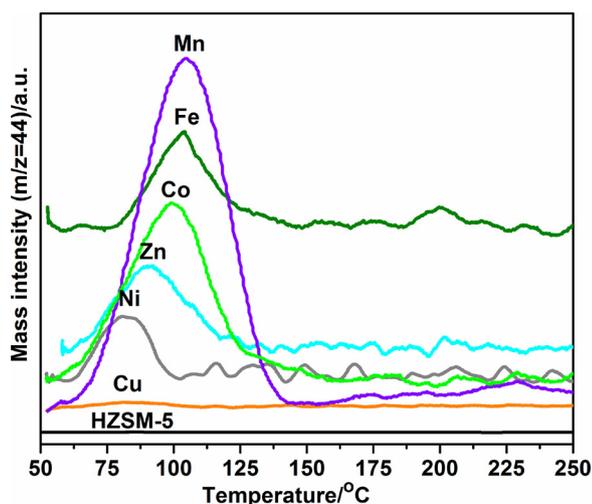


Fig. 2. Temperature-programmed desorption of N₂O on transition ion-exchanged ZSM-5.

indicating the uniform of the adsorbed sites of every ion-exchanged ZSM-5 zeolites. To estimate the adsorption behavior of zeolites in industrial condition, the pretreatment of zeolites and the adsorption of N₂O were performed in the flow of mixture under ambient pressure. According to the T_{max} values, the adsorption strength of N₂O on transition-metal ions followed the order Mn > Fe > Co > Zn > Ni > Cu, as shown in Fig. 2. Mn-ZSM-5 zeolites shows a comparatively better adsorption behavior for N₂O than other zeolites not only on the adsorption capacity but also on the adsorption strength. The adsorption capacity of Ni-ZSM-5 is good according to the adsorption amount and the molar ratio of N₂O/Me, however, its T_{max} is low. Therefore, the key to the desorbed temperature is the adsorption strength between N₂O and transition-metal ions, not the adsorption capacity of zeolites.

As shown in Table 1, the amount of the desorption of N₂O on every zeolite are quite less than their adsorption amount. The main amount of adsorbed N₂O was emitted in the process of physical desorption which was performed using Ar flow at 50 °C. It is probably that N₂O adsorbed in the channel and surface of zeolites was weak physical adsorption, and small amount of N₂O chemically adsorbed on metal site can desorb only in the temperature-programmed desorption. For Mn-, Fe-, Co-, Ni-ZSM-5, partial adsorbed N₂O dissociated to N₂ in the process of adsorption, while no detectable N₂ signal indicated that N₂O was not decomposed on Cu- and Zn-ZSM-5, as shown in Fig. 3. Therefore, the adsorption of N₂O on Mn-, Fe-, Co-, Ni-ZSM-5 were probably chemisorption. Since the dissociative adsorption of N₂O is barrierless process, it can easily occur at low temperature (50 °C in this study). For Cu-ZSM-5, the amount of adsorption and desorption of N₂O were both the least among the ion-exchanged ZSM-5, indicating that Cu has a weak affinity for N₂O molecule. According to the adsorption behavior and dissociation of N₂O on zeolites, Mn-, Fe-, Co-, Ni-ZSM-5 were suitable as N₂O adsorbents and their excellent adsorption capacity may be favorable for N₂O decomposition and the related study will be carried out in the future work.

3.2. Calculations

In order to rationalize the experimental results, DFT calculations were performed to investigate the adsorption reaction enthalpy changes ΔH_{ads} , geometric and electronic properties of N₂O on various transition-metal ion exchange ZSM-5 zeolites.

In this study, two kinds of configurations of N₂O adsorbed on metal ion-exchanged ZSM-5 with either N-end or O-end were considered. As an example, the optimized geometries of Fe-ZSM-5 are shown in Fig. 4(A–B). Both HOMO and LUMO orbitals are predominantly populated on the transition metal ions, indicating that the transition metal ions are the reactive sites for N₂O adsorption. Fig. 4(C–D) shows the

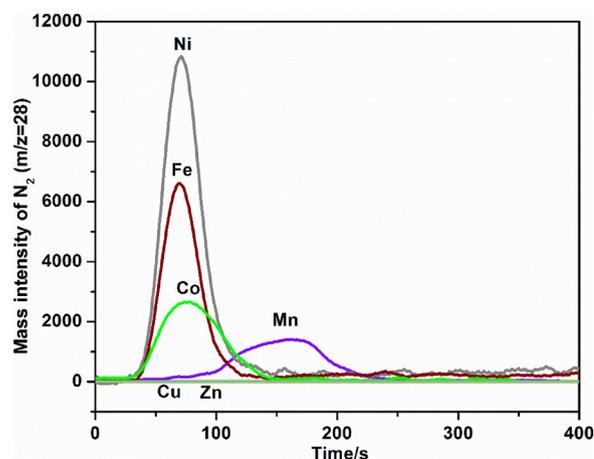


Fig. 3. Mass signal of N₂ (m/z = 28) in the process of N₂O adsorption on ion-exchanged ZSM-5 at 50 °C.

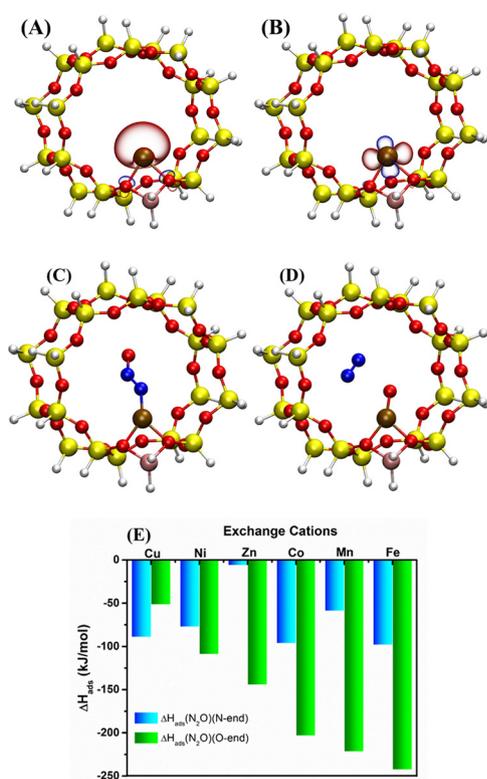


Fig. 4. HOMO (A) and LUMO (B) orbitals (isovalue = 0.05 a.u.) of Fe-ZSM-5 zeolites. Optimized configuration of N₂O molecule adsorbed on Fe-ZSM-5 through N-end (C) and O-end (D). Red, yellow, white, blue, pink, and ochre circles denote O, Si, H, N, Al, and Fe atoms, respectively. (E) Adsorption heats (ΔH_{ads}) of N₂O on various ion-exchanged ZSM-5 zeolites.

Table 2

The adsorption reaction enthalpy changes ΔH_{ads} of N₂O on various ion-exchanged ZSM-5, the bond lengths of N–M (M: transition-metal ion) and O–M, and the electron transfer from transition-metal ion to N₂O molecule.

Metal ion	ΔH _{ads} (kJ/mol)		Bond length of (Å) ^a			Electron transfer (e) ^a
	N-end	O-end	O–M	N–N	N–O	
Cu	–89.1	–51.6	1.70	1.10	3.18	0.47
Ni	–77.2	–108.8	1.64	1.10	3.21	0.55
Zn	–6.2	–144.4	1.78	1.10	3.06	0.59
Co	–96.2	–203.3	1.64	1.10	3.18	0.64
Fe	–98.1	–242.6	1.62	1.10	3.23	0.64
Mn	–58.8	–221.7	1.66	1.10	3.23	0.71

^a The N₂O adsorbed on metal ions with O-end. The optimized N–N and N–O bond length in the free N₂O molecule are 1.13 and 1.19 Å, respectively.

optimized geometries of the N₂O molecule adsorbed on Fe-ZSM-5, the other optimized geometries are shown in Fig. S1. For all of the investigated ion-exchange ZSM-5, the structure with O-end is much more stable than the one with N-end except Cu-ZSM-5 (in Table 2). In the O-end adsorption mode, the adsorbed N₂O was irreversibly decomposed into gaseous N₂ and one adsorbed O atom (Fig. 4D). This O-end adsorption mechanism has been commonly observed in the catalytic cycle for N₂O direct decomposition [31].

In the following section, we focus on the discussion of these O-end configurations. According to the ΔH_{ads} shown in Table 2, the adsorption strength of N₂O on various transition metal cations exchanged ZSM-5 followed the order Fe > Mn > Co > Zn > Ni > Cu. From experimental and theoretical results, the sequences of ΔH_{ads} matched well with those of T_{max} available experimental data. Moreover, as shown in Fig. 2, Fe and Mn has strong interaction with N₂O, probably resulting from the high electron transfer amount from the variable-valency

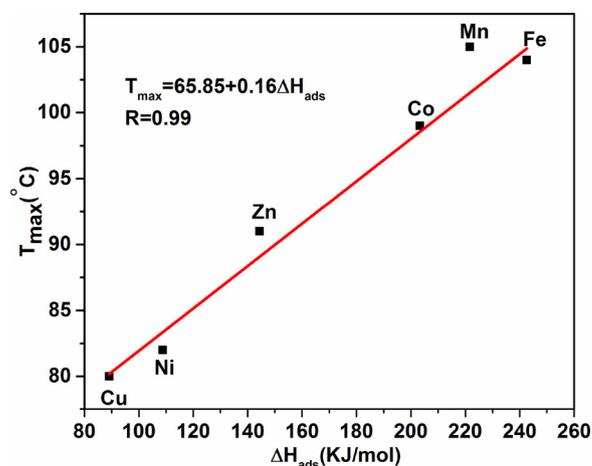


Fig. 5. Plot of -ΔH_{ads} as the function of T_{max} on ion-exchanged ZSM-5.

metals to the N₂O molecule.

As shown in Fig. 5, the calculated ΔH_{ads} values of N₂O on transition-metal cations exchanged ZSM-5 linearly correlate with the T_{max} data. The empirical equations (ΔH_{ads} (kJ/mol) = –233.4 + 4.18T_{max} (°C), T_{max} (°C) = 65.85 + 0.16ΔH_{ads} (kJ/mol)) were obtained accordingly. The highly fitting degree (R = 0.99) indicates that ΔH_{ads} is strongly and linearly correlated with T_{max}. The T_{max} and ΔH_{ads} of cations unmentioned in this studied may be estimated by these equations, which can be used as a tool to select suitable zeolites for N₂O removal. From Table 2 and Fig. 5, the more the electrons transfer from metal cations to N₂O, the stronger the bond strength between the ion-exchanged zeolite and N₂O. Therefore, the electron transfer is key to the adsorption energy and adsorption strength of N₂O on cations exchanged zeolites.

4. Conclusions

The DFT calculation results showed that the O-end of N₂O is favorable in the molecule's adsorption on a set of ion-exchanged zeolites. Theoretical and experimental results consistently indicate that the adsorption strength of N₂O on transition-metal ions followed the order: Fe > Mn > Co > Zn > Ni > Cu. The electron transfer amount from the metal cations to N₂O is a key to the adsorption energy and adsorption strength of N₂O on cations exchanged zeolites. The relationship between ΔH_{ads} and T_{max} provides an advantageous auxiliary tool for choosing suitable zeolites for N₂O removal. The T_{max} of a series of cations can be estimated using these empirical equations, providing references for the further study on the adsorption of N₂O on ion-exchanged zeolites. Furthermore, the method of associating ΔH_{ads} with T_{max} of cations can be applied in other adsorbate and ion-exchanged zeolites.

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