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Mechanism of Ozone-Promoted Uptake of NO$_2$ by a Si-Rich H-Type Zeolite

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We have observed significant enhancements in the rate and capacity of NO$_2$ uptake caused by the injection of ozone over the zeolite H-ZSM-5, which has a high SiO$_2$/Al$_2$O$_3$ ratio. We performed these experiments using a gas-flow system in which the profiles of NO$_2$ adsorption and subsequent temperature-programmed desorption were measured by Fourier transform infrared spectroscopy. We interpret these results in two ways: either by assuming that fast surface reactions lead to N$_2$O$_5$ formation or by considering that ozone suppresses the blockage of the reactive Brønsted-acidic protons.

1. Introduction

There is a continuing need for the discovery of effective processes to remove NOx species that are emitted from various industrial sources. In contrast to catalytic methods, such as the commercialized selective reduction with ammonia, separation of NOx using suitable adsorbents is another method that, in posse, could be effectual for a number of applications.

Among the known NOx adsorbents, zeolites are attractive because their large micropore volumes promise considerable adsorptive capacity. Poisoning and inhibition are common, however, for all NOx adsorbents. For zeolites in particular, the presence of water, which is inevitable under most practical conditions, strongly inhibits NOx removal from the gas phase.[1] Poisoning of zeolites originates from the high reactivity of NOx species within the micropores, which is induced by an adsorbent catalytic property that results in the formation of stable nitrate compounds within this adsorbent and, consequently, in its degradation.[2] The strength of zeolites as catalysts can be moderated, however, by exchanging their cations with protons so that the small H$^+$ counterions neutralize the negative Ze$^-$ skeleton that constitutes the crystalline structure of this adsorbent. The chemical resistance of H-type zeolites also can be enhanced by enlargement of the SiO$_2$/Al$_2$O$_3$ ratio.[3] In addition, an extensive degree of dealuminization can be beneficial because it weakens the strength of the zeolite's acidity and, as a consequence, moderates its catalytic activity.[4] At the same time, however, this process is associated with a significant reduction of the density of the counterprotons, which, as expected, has a detrimental effect on the rate of NO$_2$ uptake. Indeed, it has been confirmed recently that protons within zeolites play a key role in the process of NO$_2$ assimilation by these sorbents.[5] With regard to this detrimental effect, we believe that it is worth undertaking a more comprehensive investigation of the reported effects of NO$_2$ uptake by ozone-stimulated zeolites.[6] In addition, such a study should also provide additional data to validate our present knowledge of heterogeneous processes involving water, NOx, and other molecules.

The aim of the present study was to confirm and further investigate the effect of the presence of O$_3$ on the NO$_2$ adsorption by H-type zeolite, which has a high SiO$_2$/Al$_2$O$_3$ ratio.

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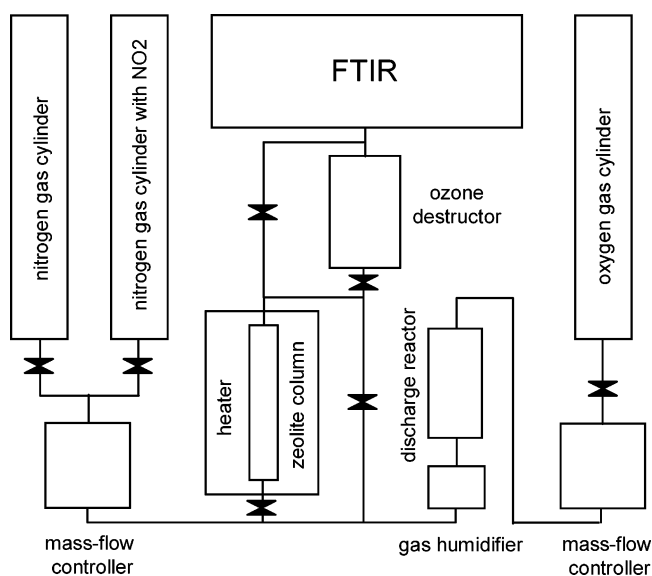
Figure 1. Block scheme of the experimental installation.

In particular, the experiments were designed in such a way as to obtain comprehensive data that increase our understanding of the mechanism of this phenomenon.

2. Experimental Section

In performing this research, we applied a gas-flow installation, depicted by a block-scheme in Figure 1, which was designated for adsorption/desorption experimentation. This apparatus consists of a number of units, including an adsorption column located within a temperature-programmed furnace and a Fourier transform infrared (FTIR) spectrometer for the analysis of a gaseous mixture at this column's outlet.

The adsorption column consists of a stainless steel tube (inner diameter, 0.6 cm; length, ca. 3.5 cm) into which was placed a sample (ca. 0.5 g) of Si-rich zeolite that had been ion-exchanged with protons. We used H-ZSM-5 zeolites for most of these experiments, but some were also performed with H-Mordenite. These adsorbents, which are produced by the TOSOH Corp., have SiO$_2$/Al$_2$O$_3$ ratios of 2100 and 15.2, respectively. During our experiments, we did not record or control the temperature of the zeolite sample; the uptake of NO$_2$ with these adsorbents was conducted at room temperature. The uptake of NO$_2$ was

usually performed at a gas-phase humidity of ca. 5 mg per standard liter (mgpsl), which corresponds to a dew point of 0 °C. To prepare a freshly packed column for investigation, nitrogen supplied from a gas cylinder was humidified also up to ca. 5 mgpsl and passed at room temperature through the column of packed zeolite for 1 h at a flow rate of 0.14 standard liters per minute (slpm). The main purpose of this procedure was to ensure that water adsorption remained under equilibrium conditions throughout the NO_2 uptake process.

The adsorption experiments were performed by passing nitrogen dioxide, carried by nitrogen gas (from a commercially prepared gas cylinder containing 1000 ppm of NO_2), into the zeolite column at a flow rate of 0.1 slpm. Oxygen, which was delivered from a gas cylinder at a flow rate of 0.04 slpm, was treated with an electrical corona-discharge reactor[7] to generate a low concentration of ozone. After ozonization, the stream of oxygen gas was humidified up to ca. 18 mgpsl; we found that humidification of the ozonized oxygen has a negligible influence on the value of the ozone concentration. The oxygen stream was then admixed into the gaseous stream of N_2/NO_2 just prior to the inlet of the zeolite column. The power supply of the electrical corona discharge was provided by a sinusoidal 50-Hz signal, having amplitudes of up to 1 kV, that was generated with a master oscillator/amplifier unit. This unit comprised a Tektronix AFG310 generator equipped with a digital control board and a TREK 20/20B amplifier. The high stability of the voltage amplitude applied to the reactor electrode and the precise adjustability of this parameter permitted us to accurately regulate the ozone concentration at the input of the zeolite column during the experiments. We measured the dependence of ozone productivity on the voltage amplitude using an Ebara Jitsugyo PG-320 ozone analyzer. To fit within the analytical range of this device, i.e., ≤ 500 ppm, the 0.04-slpm flow of oxygen that had been treated using the corona discharge reactor was diluted before measurement with N_2, the proportion of which was regulated by means of a mass-flow controller. This proportion was also verified precisely by analysis with a soap-film flow meter. The gaseous volumes of the electrical corona discharge reactor by itself and of the humidifier with the related oxygen piping were quite small (40 cm^3) and, as a consequence, the response of the ozone concentration at the inlet of the zeolite column to variations in the voltage amplitude applied to the reactor electrode was relatively fast (<1 min).

The desorption experiments were usually performed with the same samples of adsorbent that were applied in the adsorption experiments. Nitrogen was introduced into the zeolite column as the sweep gas (flow rate: 0.1 slpm) while the temperature of the temperature-programmed furnace that contained the zeolite column was raised at a constant rate of ca. 10 deg/min up to a predefined value, at which point it was then stabilized.

A detailed analysis of the gas during the sorption/desorption experiments was performed on a Bio-Rad FTS-135 FTIR spectrometer equipped with a linear MCT detector and a gas cell (Infrared Analysis Inc.; path length, 2.4 m; volume, 125 cm^3). Another gas cell, which has a path length of ca. 10 cm and a volume of just 16 cm^3, was also applied for some of the measurements described below. When the larger gas cell was used, the concentrations of NO_2 and HNO_3 were determined from the absorption peaks centered at 2918.0 and 3552.2 cm^{-1}, respectively. Each absorbance obeyed the Lambert−Beer law over the experimental concentration range we studied, i.e., $A = -\log(I/I_0) = K \times b \times c$, where A = the absorbance of a band = the negative common logarithm of its transmittance (I/I_0), K = the molar extinction coefficient, b = the path length
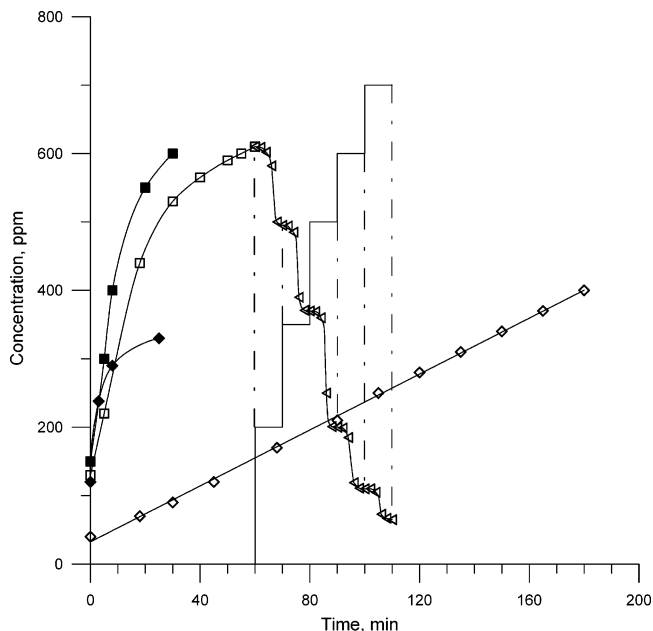

Figure 2. Profiles of NO_2 adsorption from a humid nitrogen/oxygen mixture over H−ZSM-5 zeolite (0.5 g) in the absence (□; ■) and presence (△; ◇; ◆) of ozone. The step-line relates to the ozone concentration at the inlet of the zeolite column. Profiles ◇ and ◆ relate to NO_2 sorption under conditions of stable rate of ozone introduction; its concentration at the inlet is 700 ppm. Profiles ■ and ◆ relate to the reuse of the zeolite samples after long-term temperature regeneration at 300 °C. Sorption conditions: oxygen/nitrogen flow of 0.14 slpm, humidified up to ca. 5 mgpsl; NO_2 concentration of ca. 700 ppm.

of the gas cell, and c = the concentration. The molar extinction coefficient was retrieved from the instructions (Infrared Analysis Inc.) enclosed with the gas cell. Usually, the FTIR spectroscopic measurements were performed at a resolution of 0.5 cm^{-1} over a total of 10 scans. In the case of experiments performed using stepwise injections of ozone, we measured only the NO_2 concentration by monitoring the absorbance at 2918.0 cm^{-1} by FTIR spectroscopy with the aim of accelerating the data acquisition process. Because of the extreme concentration of HNO_3 that discharged from the adsorbent after the ozone-promoted NO_2 uptake, we diluted the 0.1-slpm purge gas of nitrogen with uncontaminated N_2 before the gas inlet into the FTIR spectrometer to fit within the analytical range of this device. The degree of dilution was regulated by means of a mass-flow controller and was verified precisely by analysis with a soap-film flow meter.

To eliminate any reactions that might occur within the piping between the outlet of the zeolite column and the inlet of the FTIR spectrometer, we decomposed the ozone that passed through this column to an undetectable level at a temperature of 600 °C with the aid of a catalyst. We found that a Si-rich zeolite ion-exchanged with protons ("H−Y"; $SiO_2/Al_2O_3 = 15$; TOSOH Corp.) is an exceptionally effective catalyst for this process.

3. Results and Discussion

The results of the NO_2 uptake experiments over the zeolite H-ZSM-5 with stable ozone injection, and without any ozone admixture, together with the subsequent desorption during the temperature-programmed treatment of these adsorbents, are presented in Figures 2 and 3, respectively. In performing these experiments, we applied the gas-flow installation described in the previous paragraph and depicted by a block-scheme in Figure 1. Generation of ozone by the nonthermal plasma treatment of
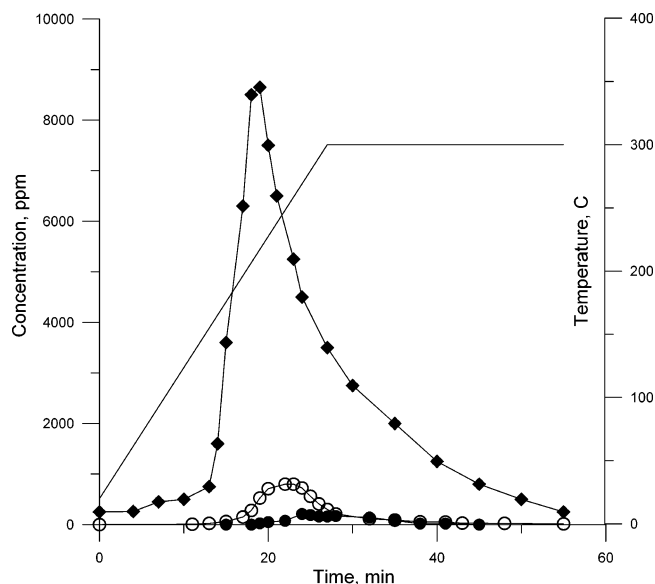
Figure 3. Profiles of the temperature-programmed desorption after NO$_2$ uptake by H-ZSM-5 in the absence of injected ozone [NO$_2$ (●); HNO$_3$ (○)] and in the presence of injected ozone [HNO$_3$ (◆)]. Adsorption conditions were the same as those described in Figure 2. Purge gas in both cases: dry nitrogen (0.1 slpm).

oxygen gas gave us high flexibility and stability when regulating its concentration at the inlet of the zeolite column. Using an FTIR spectrometer ensured high reliability for the analysis of the gas that passed through the zeolite column or was released from the adsorbent during its thermal processing. In particular, we clarified that only NO$_2$ and HNO$_3$ species (in the absence of ozone), or only HNO$_3$ (in the presence of ozone), were discharged from the zeolite during its thermal treatment after NO$_2$ uptake.

From a comparison of the curves in Figure 2, we observe that the amount of NO$_2$ that reached the chamber of the FTIR spectrometer for analysis was reduced significantly when ozone was injected. It is reasonable to suggest that, during ozone injection, an extensive accumulation of NO$_2$ species occurred only within the zeolite column, as happens also in the case when ozone was absent. Indeed, this process was evidenced by the release of extremely concentrated HNO$_3$ during the subsequent temperature-programmed desoprtion process, which is depicted in Figure 3. We do not believe that it is reasonable to suggest that NO$_2$ accumulates outside of the zeolite column. For instance, the zeolite that we used to destroy the ozone cannot be considered as an adsorbent because its temperature (600 °C) is too high for any significant uptake of NO$_2$. Moreover, because the ozone was decomposed immediately after the gas stream exited the zeolite column, we believe that this process precludes any possible NO$_2$ removal through the formation and precipitation of, e.g., nitric acid aerosol. In theory, NO$_2$ might be absorbed by liquid-phase water condensed somewhere within the experimental installation, including the surface of the zeolite, but we doubt that this phenomenon is possible because the humidity of the gas stream treated within the gas-flow installation was far below its dew point.

Intuitively, when trying to elucidate the mechanism of the enhanced removal of NO$_2$ by the zeolite column, the first plausible explanation is that NO$_2$ becomes oxidized to NO$_3$, N$_2$O$_5$, and HNO$_3$ and then these species are assimilated by the adsorbent. Actually, this mechanism is doubtful because the residence time of gas within the zeolite column (ca. 170 ms) was quite short. Indeed, when taking into account the low rate
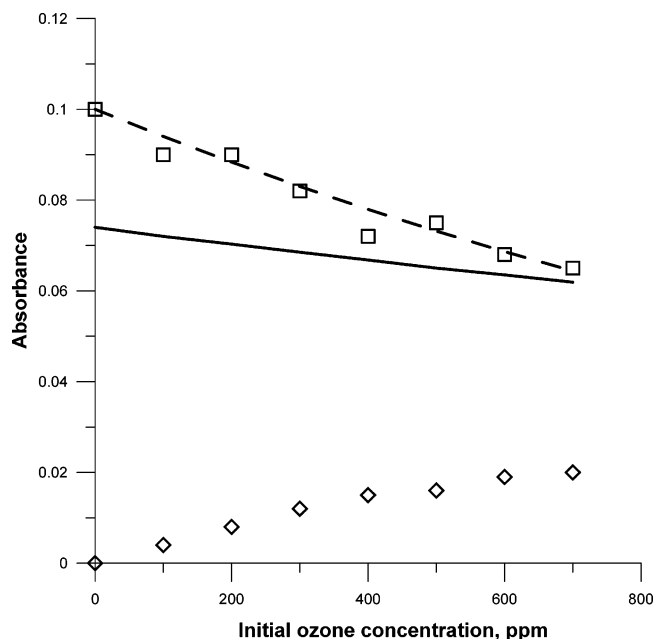

Figure 4. Dependences of NO$_2$ (□) and N$_2$O$_5$ (◇) concentrations, measured by FTIR spectroscopy, on the amount of ozone introduced at the inlet of this unit gas cell. Initial NO$_2$ concentration: 950 ppm. Gas residence time within the gas cell: 450 ms. Dotted line: calculated NO$_2$ concentration. Solid line: recalculated NO$_2$ concentration under the conditions encountered in the zeolite column (initial NO$_2$ concentration, 700 ppm; gas residence time, 170 ms).

constant of the gas-phase reaction[8]

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (k = 1.7 \times 10^{-16}\ cm^3 \cdot s^{-1})\ \ (1)$$
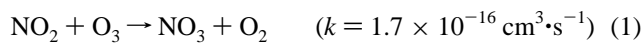
we estimate that 170 ms is not a sufficient time for transformation of a noticeable part of the NO$_2$ species into NO$_3$ and, consequently, into its successors, N$_2$O$_5$ and HNO$_3$. To support this estimation, we evaluated the amount of NO$_2$ remaining a short period of time after it had been admixed with ozone by equipping the FTIR spectrometer with the smaller gas cell. Specifically, nitrogen gas containing 1000 ppm of NO$_2$ was supplied into this cell at a relatively high flow rate of 2.0 slpm together with an oxygen effluence of 0.1 slpm admixed just prior to its inlet. We estimate that the residence time of the gases within the cell was ca. 450 ms. Additionally, we subjected this stream of oxygen to electrical corona discharge with subsequent humidification of up to 10 mgpsl before its admixture. The results of the FTIR spectroscopic measurements are presented in Figure 4 where the absorbances of NO$_2$ and N$_2$O$_5$ are related to the absorption peaks centered at 2918.0 and 743.5 cm^{-1}, respectively. From these data, we estimated that only ca. 150 ppm of NO$_2$ was eventually transformed into NO$_3$ and then into N$_2$O$_5$ through the fast gas-phase reaction[8]

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$$

$$(k = 2.7 \times 10^{-30}\ cm^3 \cdot s^{-1})\ \ (2)$$
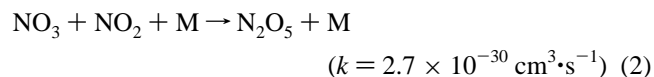
We have evaluated the kinetics of NO$_2$ oxidization using an unsophisticated numerical model based on a set of coupled ordinary differential equations and the gas-phase reactions related to NOx chemistry presented in ref 8. A good agreement exists between this model and the experimental results of NO$_2$ oxidization within the gas cell when the rate constant of reaction 1 is set to ca. 1.0×10^{-16} cm$^3 \cdot$s^{-1}. By applying this value to the model of the gas-phase oxidization of NO$_2$ within the zeolite column, we see from Figure 4 that this process is definitely an

insignificant one. Consequently, we believe that the gas phase formation of NO_3, N_2O_5, and HNO_3 within the column, followed by assimilation of these species by the adsorbent, cannot be considered as the dominant mechanism of NO_2 uptake.

On the basis of the conclusion above, we turned our attention to a study of the direct interaction of NO_2 with the zeolite surface and the impact that ozone has on this process. A detailed study of NO_2 removal by a dealuminated zeolite that had been ion-exchanged with protons[5] concluded that the dissociative surface sites of the zeolite are the primary sites of NO_2 assimilation. Specifically, the N_2O_4 dimer formed from physically adsorbed NO_2 undergoes the reaction

$$N_2O_4 \rightarrow NO^+ + NO_3^- \quad (3)$$
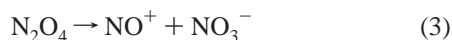
with the subsequent formation of a nitric acid-like species, HNO_3:

$$NO^+ + NO_3^- + H^+(Ze)^- \rightarrow HNO_3 + NO^+(Ze)^- \quad (4)$$
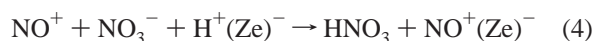
Furthermore, the reaction of $NO^+(Ze)^-$ with H_2O is believed to occur immediately:

$$NO^+(Ze)^- + H_2O \rightarrow H^+(Ze)^- + HNO_2 \quad (5)$$
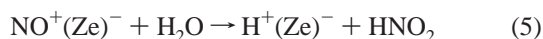
The experimentally observed simultaneous release of only NO_2 and H_2O species during thermal treatment of the adsorbent has been accounted for by the following reaction within its body:

$$HNO_2 + HNO_3 \rightarrow H_2O + 2 NO_2 \quad (6)$$
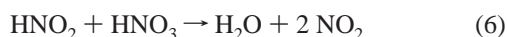
It is worth noting that the reaction path outlined above is also consistent with the results reported in a recent publication.[9]

Returning to our observations presented in Figure 3, the origin of the HNO_3 and NO_2 species discharged by the zeolite also could be accounted for by the set of reactions 3−6 presented above. With regard to our observed acceleration of NO_2 adsorption in the presence of ozone, the absence of NO_2 remittance, indicated in Figure 3, upon high-temperature treatment of the adsorbent can be considered as an argument for the formation of only HNO_3 during ozone-promoted NO_2 uptake. This fact, along with the acidic nature of the zeolite, can be posed as an argument for referring to reaction path 7−8 for the uptake of N_2O_5 by sulfuric acid aerosols:

$$N_2O_5 + H^+ \rightarrow HNO_3 + NO_2^+ \quad (7)$$

$$NO_2^+ + H_2O \rightarrow HNO_3 + H^+ \quad (8)$$
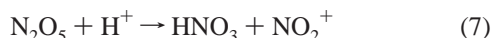
This process was reported by Robinson et al.[10] and has been discussed elsewhere.[11] Referring also to the assumption[6] that the zeolite has the necessary catalytic activity to promote, on its surface, the slow gas-phase reaction of NO_3 radical formation (1), and considering that the surface reaction of NO_3 with physically adsorbed NO_2 results in the formation of N_2O_5, we suggest that the assimilation of N_2O_5 formed on the zeolite surface is identical to the reaction path 7−8 for the uptake of N_2O_5 by sulfuric acid aerosols:

$$N_2O_5 + H^+(Ze)^- \rightarrow HNO_3 + NO_2^+(Ze)^- \quad (9)$$

$$NO_2^+(Ze)^- + H_2O \rightarrow HNO_3 + H^+(Ze)^- \quad (10)$$

In fact, the proposed reaction path 9−10 can be interpreted also

as a modification of the process 1−5 that was caused by the presence of ozone.

Actually, the formation of N_2O_5 as a result of oxidization of the N_2O_4 dimer formed from physically adsorbed NO_2 via interaction with ozone may also be suggested as a cause of the formation of HNO_3. Moreover, by following concepts based on the results of water pollutant treatment assisted by ozone and zeolites,[12,13] it is possible that the formation of N_2O_5 species occurs within some hypothetical zeolite pores where selective accumulation of O_3 takes place to a great extent. With regard to another detail of the proposed mechanism, we note that the relatively high amount of the acid-like HNO_3 species contained by the zeolite upon ozone promotion signifies that the whole micropore volume of the adsorbents is used to amass these species. This fact obviously signifies the existence of some active channel of mass transfer of these acid-like HNO_3 species within the adsorbent.

To explore the suggested mechanism of NO_2 assimilation that is promoted by ozone, we monitored the degree of NO_2 removal during a stepwise increase in the quantity of ozone injected; the results are presented in Figure 2. The ozone concentration at the inlet of the zeolite column was increased in a step-by-step manner at 10-min intervals; this time interval was almost sufficient to allow the NO_2 concentration within the gas cell of the FTIR spectrometer to reach stabilization before the next increase in ozone concentration. At the same time, we observe in Figure 2 that the NO_2 concentration decrease has some interesting features, e.g., the dramatic fall in the NO_2 concentration usually starts several minutes after the abrupt increase in the ozone concentration. Actually, the observed delays cannot be accounted for only by the transitional effects arising from gas renewal within, for example, the humidifier and the gas cell of the spectrometer. Consequently, the delays in the response of the rate of NO_2 removal after the abrupt increases in ozone concentration over the zeolite can be distinguished here as phenomena that are independent of the particular characteristics of the experimental setup.

In fact, the finding above contradicts the reaction model 9−10 of NO_2 assimilation in the presence of ozone; according to this model, the immediate response of NO_2 removal from the gas phase could be expected to be a result of variations of the ozone concentration over the adsorbent. It might be possible that the observed delays in the response of the rate of NO_2 removal to abrupt increases in ozone concentration can be explained by the concepts proposed by Fujita et al.[12,13] and mentioned earlier. Nevertheless, we proceed with our analysis by returning to reaction path 3−5 because it is consistent with reports[5,9] directly related to investigations of the process of NO_2 uptake by adsorbents such as zeolites. Following this approach, gradual blockage of the reactive, Brønsted-acidic protons and, consequently, inhibition of the reaction path 3−5 should be assumed during the NO_2 assimilation in the absence of ozone. Thus, the observations made upon the interaction with ozone could be a result of refurbishment of these active sites, so that the delays in the stabilization of the rate of NO_2 removal after the abrupt increases in ozone concentration can be explained by the gradual rise in the abundance of the reactive protons. With regard to the detailed mechanism, it could be suggested, for instance, that the HNO_2 species formed as a result of reaction 5 actually remain bonded with the reactive, Brønsted-acidic protons, i.e.,

$$NO^+(Ze)^- + H_2O \rightarrow (H_2NO_2)^+(Ze)^- \quad (11)$$

which implies a gradual blockage of these reactive sites within the vicinity of the zeolite surface and, consequently, inhibition

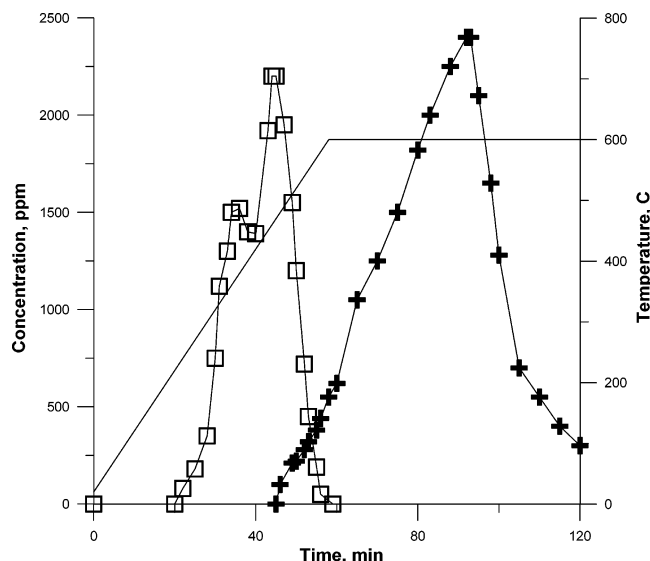**Figure 5.** Profiles of the temperature-programmed desorption after NO$_2$ uptake by H-Mordenite in the absence of ozone injection [NO$_2$ (□); HNO$_3$ (solid cross)]. Purge gas: dry nitrogen (0.1 slpm). Uptake of NO$_2$ occurred during 3 h under the gas flow conditions specified in Figure 2.

of reaction path 3−5. In turn, the refurbishment suggested above, upon the introduction of ozone, can be concretized as

$$O_3 + (H_2NO_2)^+(Ze)^- \rightarrow O_2 + HNO_3 + H^+(Ze)^- \quad (12)$$
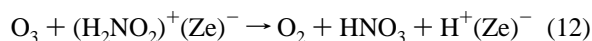
This reaction is also consistent with our experimental observation of the formation of an exceptional amount of HNO$_3$ within the zeolite as a result of ozone-promoted NO$_2$ uptake. In this manner, the significant enhancement of the rate and capacity of NO$_2$ uptake that is caused by the injection of ozone should be attributed to the prevention of blockage of the reactive protons during NO$_2$ assimilation, but not attributed to the acceleration of reaction 1 as was proposed earlier.[6]

Because the reaction path 3−5 has been suggested based on experiments with the zeolite H-Mordenite,[5] we also performed an investigation using this adsorbent to reveal whether there are any contradictions with our suggested model involving blockage of the reactive, Brønsted-acidic protons. Specifically, a sample of H-Mordenite (0.5 g) that was saturated with NO$_2$ during a 3-h flow (0.14 slpm) with a mixture of NO$_2$ (950 ppm) and H$_2$O (5 mgpsl) was heated in the same way as described previously;[5] we recorded the desorption profiles using FTIR spectroscopy. Besides the release of NO$_2$ species, when the sample of H-Mordenite was heated to 600 °C, we detected a significant discharge of HNO$_3$ into the purged gas, mainly during the following period in which the adsorbent was kept at a stable temperature of 600 °C; the results are presented in Figure 5. In the interpretation of Figure 5, the two closely disposed peaks in the NO$_2$ profile could be accounted for by the two different groups of Brønsted-acidic sites present in the structure of H-Mordenite. The relatively high amount of the acid-like species HNO$_3$ contained by this zeolite signifies that the whole micropore volume of the adsorbents is used to amass these species. Considering this assumption with regard to the reaction path 3−5, the onset of the HNO$_3$ emission that occurs almost immediately after the full decline of the NO$_2$ discharge could be accounted for by the formation and accumulation of HNO$_3$ solely within the vicinity of the surface. Actually, this pathway is compatible with the discussion above regarding the HNO$_2$ species that remain bound with the reactive, Brønsted-acidic

protons upon their formation via process 11. Specifically, the first portion of the acid-like species HNO$_3$ that emanates from the internal parts of the adsorbent probably enters into the reaction

$$HNO_3 + (H_2NO_2)^+(Ze)^- \rightarrow H_2O + 2\,NO_2 + H^+(Ze)^- \quad (13)$$
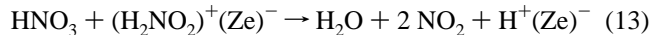
within the vicinity of the surface, which results in the intensive NO$_2$ emission recorded at the beginning of the process of heat treatment. In fact, reaction 13 can be considered as an analogue of reaction 6. The subsequent intense onset of HNO$_3$ emission into the purge gas signifies the consumption of almost all of the (H$_2$NO$_2$)$^+$(Ze)$^-$ species by reaction 13. Additionally, this bonding of HNO$_2$ with the reactive, Brønsted-acidic protons could be affirmed also by the absence of NO discharge into the gas phase during thermal treatment of the zeolite. Indeed, weak affiliation of HNO$_2$ with the adsorbent upon temperature elevation should result in the appearance of these species in the gas phase that, in turn, should give rise to the formation of NO:[14]

$$3\,HNO_2 \rightarrow HNO_3 + 2\,NO + H_2O \quad (14)$$

The simultaneous release of NO$_2$ and HNO$_3$ species observed in the case of H−ZSM-5 (Figure 3) is not in contradiction with the interpretation proposed above. Indeed, the relatively low density of (H$_2$NO$_2$)$^+$(Ze)$^-$ that exists because of the very high SiO$_2$/Al$_2$O$_3$ ratio of this adsorbent obviously results in the low probability of reaction 13 occurring and, as a consequence, in the simultaneous release of HNO$_3$ and NO$_2$. In ending this discussion concerning the blockage of the reactive protons, we must refer to a paper[9] in which mechanisms of a similar nature are considered. Specifically, it is stated that during NO$_2$ uptake by high-silica zeolite, NO$^+$NO$_2$ and NO$^+$(N$_2$O$_4$) species can be formed in the presence of H$_2$O, which, thus, has the effect of "protecting NO$^+$ from the reaction with water", i.e., it inhibits reaction 5.

We recognize that the assumptions discussed above concerning the ozone-promoted NO$_2$ sorption process are still not conclusive. Indeed, heterogeneous processes involving zeolites and only water and NO$_2$ are still far from satisfactorily understood—let alone those involving ozone. Specifically, the appearance of a noticeable amount of HNO$_3$, relative to NO$_2$, that we observed upon heating zeolite H-Mordenite after NO$_2$ uptake could signify incompleteness of the reaction path 3−5 proposed previously.[5] Actually, this reaction path suggests that we should expect equal amounts of HNO$_3$ and HNO$_2$ within H-Mordenite and, as a consequence, release of only NO$_2$ and H$_2$O species into the gas phase, as has been observed.[5] We believe that the contradiction in our experimental observations with respect to those in the literature report[5] may be ascribed, for instance, to the authors' erroneous identification of HNO$_3$ species as NO$_2$ when analyzing their system by quadrupole mass spectrometry. In this regard, we also note that the erroneous identification of HNO$_3$ as NO$_2$ obviously occurred in ref 6 when a chemiluminescent NOx analyzer was applied to investigate the desorption profiles. With regard to the complicated NOx chemistry that originates from the presence of ozone, a literature report[15] has revealed that ozone depletion is unexpectedly fast in the presence of NO$_2$ and soot particles; this finding resembles the results we presented in this paper.

To evaluate the practical applicability of this ozone-promoted NO$_2$ removal process, it is important to investigate the possibility of reusing the applied adsorbent multiple times. Unfortunately, as we see in Figure 2, despite its very high SiO$_2$/Al$_2$O$_3$ ratio

and expected chemical stability, attempts to regenerate zeolite H-ZSM-5 by long-term temperature treatment resulted in a noticeable expendability. Nevertheless, because the ozone-promoted NO_2 uptake process exhibits such features as high rates, high capacities, and the possibility of residual O_3 destruction, this process might be applicable as a base of compact installations designed for high-speed purification of large volumes of gases having low concentrations of NOx.[16]

4. Conclusions

We have studied the heterogeneous conversion of NO_2 on surfaces of Si-rich zeolites, which had been ion-exchanged with H^+, using a gas-flow installation in which gas analysis was carried out by FTIR spectroscopy.

We observed a significant enhancement in the rate and capacity of NO_2 uptake by zeolite H-ZSM-5 upon ozone injection. We have interpreted this phenomenon by considering the assumption of a fast surface reaction leading to N_2O_5 formation. Alternatively, we believe that blockage of the reactive (i.e., Brønsted-acidic) protons usually occurs during NO_2 uptake and that the enhancement of NO_2 uptake can be considered to arise from the ozone's suppressing of the above blockage effect.

The high capacity of the zeolite during ozone-promoted NO_2 uptake was proven by the concentrated release of HNO_3 into the gas phase detected during temperature-programmed desorption. During a short period, the concentration of HNO_3 in the purge gas exceeded 8000 ppm.

We encountered a noticeable expendability of zeolite H-ZSM-5 during the second application of this sorbent in the ozone-promoted NO_2 uptake process after it had undergone long-term, high-temperature treatment.

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