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Effect of O_3 on NO_2 Sorption from Gas over H-Y Zeolite: Supposition on the Nitrate Anion Formation with NO_2 and O_3 as Coreactants

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The effect of O_3 presence on NO_2 sorption over Y-type zeolite ion exchanged with H^+ was studied. The experiments with a gas-flow system have been performed where the profiles of NO_2 sorption and temperature-programmed desorption were registered. Nitrogen dioxide was removed from a stream of humid air with dew point 0 °C by the sorbent saturated with moisture. The distinct influence of ozone presence on the characteristics of NO_2 sorption/desorption has been observed. Significant enhancement of NO_2 uptake has been obtained by the injection of O_3, which has brought about, as it seems, the formation of stable nitrate anions within the sorbent. Also, the probability of the practical application of the observed effect has been considered.

1. Introduction

It is well-known that an inexpensive sorbent with efficient sorptive characteristics would be useful in NO_x control for numerous types of emission sources. Particularly, application of zeolite for this aim is rather attractive, and for this reason, it has been studied for a long time.[1] It has been revealed that NO_x molecules are highly reactive within zeolite, and it results in disproportionation reactions. Particulary, the number of stable species, such as NO^+, NO_2^+, NO_2^-, and NO_3^-, have been found within Cu-MFI zeolite as a result of NO sorption.[1] Besides, the species N_2O, NO_2^-, NO_2^+, N_2O_3, and NO_3^- have been identified within Na-Y after sorption of NO and mechanisms of the disproportionation reactions have been proposed.[2]

Research on the disproportionation reactions of NO_x within zeolite is urgent for foundation of de-NO_x technology. Moreover, it is especially important for practical application to clarify the influence of such compounds, as O_2, H_2O, CO_2, etc., whose presence is inevitable under the above conditions. Particularly, it has been found that sorption of NO_x over zeolite with metal cations and preadsorbed molecules of water results in formation of stable nitrate compounds within the sorbent and, as a consequence, in degradation of its structure. Therefore, it is preferable to use the zeolite ion exchanged with proton because NO_x molecules are inactive within it and affiliated, mostly, on the basis of weak physical interactions.[2,3] Unfortunately, it is difficult to provide sufficient capacity and rate of NO_x sorption by the above type of zeolite for the most part of practical conditions.

To find a way to improve the situation, it seems worthy to turn to the original result described in ref 4. Particularly, it has been revealed, through an experiment, that in the presence of NO_2 and soot particles, ozone depletion proceeds faster, as expected. One of the reasonable suggestions is that the slow gas-phase reaction[5]

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad k = 1.7 \times 10^{-16}\ \mathrm{cm^3\ s^{-1}} \qquad (1)$$

is accelerated on the solid surface, where the formed NO_3 radicals are unstable, and subsequently, results in formation of NO_2 and O_2. We assumed that such a solid compound, as zeolite ion exchanged with proton, is able to exhibit the same activity as soot particles and that the formed NO_3 radicals are stabilized through formation of nitrate anions and are stored within the sorbent. Indeed, as it was mentioned above, nitrate anions have been detected within zeolite, and this can justify our supposition. Moreover, the nitrate anions are affiliated by zeolite on the basis of a strong ionic interaction and, therefore, it is expected that in the presence of ozone the intensification of NO_2 uptake over zeolite can be observed. Indeed, the intensive interaction between nitrate anion and zeolite is demonstrated in ref 1, where the species of reversible adsorption within Cu-MFI was attributed to NO^+, while those of irreversible adsorption were attributed to NO_2^+, NO_2^-, and NO_3^-.

The aim of the present study is to research the ozone influence on NO_2 uptake over zeolite. Suggested intensification of NO_2 separation in the presence of ozone can be useful for practice, even though ozone is harmful. Indeed, the consumption of one ozone molecule for the uptake of one NO_2 is expected here and, therefore, in that case it is possible to minimize the slip of ozone by keeping balance between both pollutants. Besides, ozone is an unstable molecule, and its residue can be catalytically decomposed to molecular oxygen.[6] In addition, it is worth mentioning, that the application of such a harmful matter, as NH_3, for NO_x reduction to nitrogen and water, did not restrict the wide expansion of this technology in industry and, possibly, ozone will be useful, too, for some de-NO_x applications.

2. Experimental Section

The analysis of sorption profiles and profiles of subsequent temperature-programmed desorption, obtained from the experiment with the gas-flow system, has proved suitable for the above purpose. To perform research, the installation with block-scheme depicted in Figure 1 was used. About 5 g of zeolite was packed into a stainless steel tube of 0.6 cm in inside diameter and about 30 cm in length. The samples of Si-rich Y-type zeolite ion exchanged with H^+ used for research had brand names of HSZ-360HUD1C and HSZ-390HUD3C. These sorbents were produced by TOSOH Corp., where SiO_2/Al_2O_3 ratios are, respec-

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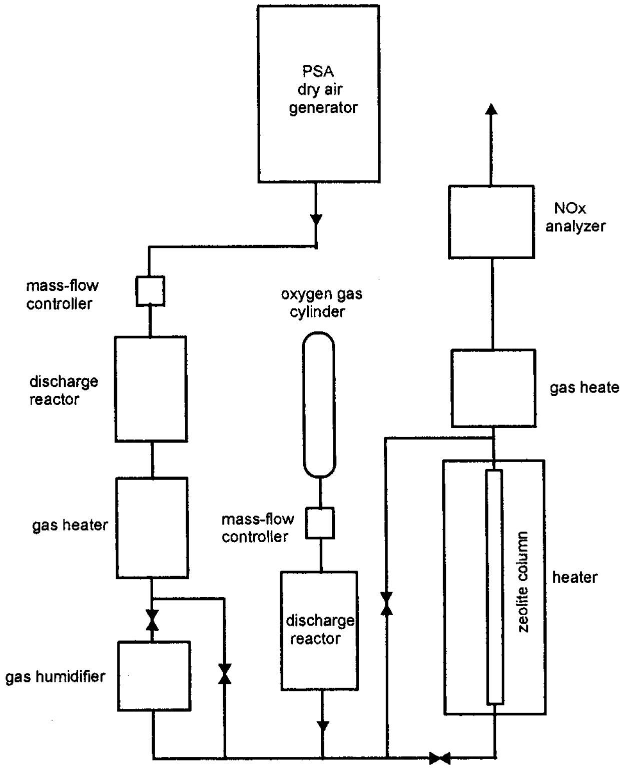

Figure 1. Block scheme of the experimental installation.

tively, 15 and 360. Also, the zeolite 320NAD1A with Na cations and SiO_2/Al_2O_3 ratio 5.7 was studied. Initially, generated by the PSA system, the clean air with a dew point −60 °C was humidified up to a dew point 0° C and introduced into the zeolite column for 1 h at a flow rate of 3.0 standard liters per minute (slpm). The main purpose was to obtain full saturation of the sorbent by moisture and, therefore, to get results of NO_2 sorption under conditions close to practical. Besides, the promotion of the suggested effect was expected, because, as has been pointed in ref 7, the preadsorbed molecules of water can stabilize nitrate anions through hydration and facilitate its diffusion. Subsequently, nitrogen dioxide was generated from air by means of silent discharge[8] in the reactor depicted in ref 9, where the NO_2 concentration reached ∼10 ppm and, generated together with NO_2, ozone was decomposed by high-temperature treatment in the outlet of the reactor. Oxygen supplied from a gas cylinder was admixed at a flow rate 0.3 slpm into the air stream, just before entering the zeolite column. This stream of oxygen was supplied through the second discharge reactor, and therefore, it was possible to generate[8] and inject low concentrated ozone into the zeolite column together with NO_2 generated from air. Detailed control of NO_x concentration in the outlet of the zeolite column was carried out by using the chemiluminescent NO_x analyzer YANACO SAE−6599. To exclude the influence of the slipped ozone on the NO_x measurements, the former one was decomposed by high-temperature treatment just before entering the NO_x analyzer. The experiments of desorption were performed with the same samples of sorbent, used before, to perform the sorption experiments. Clean air with a dew point −60 °C and flow rate 1 slpm was introduced into the zeolite column as a sweep gas, and simultaneously, the temperature of this column was raised at a constant rate of about 10 °C /min to 250 °C. The identification of desorbed species was accomplished by the chemiluminescent NO_x analyzer. During the experiments, such gaseous compounds as O_3 and H_2O (including NO_x) were, occasionally, analyzed by the gas inspection tubes GASTEC.

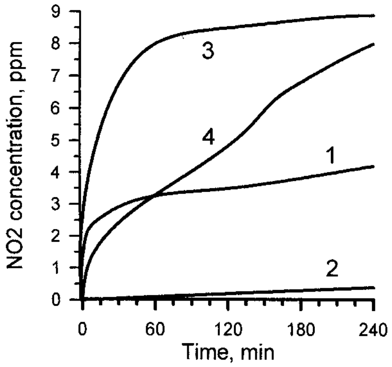

Figure 2. Profiles of NO_2 sorption from humid air over 5 g of zeolite HSZ-360HUD1C (without ozone injection, 1; with ozone injection, 2) and over 5 g of zeolite HSZ-390HUD1C (without ozone injection, 3; with ozone injection, 4). Sorption conditions: air fluent, 3.3 slpm; inlet NO_2 concentration, 9 ppm; inlet concentration of ozone, 60 ppm; air humidity, about 5 mg/L.

There is a need to mention here the systematic disagreement revealed between NO_x measurements with the chemiluminescent analyzer and the inspection tubes. Therefore, we want to point out that the present research is mainly qualitative, rather than quantitative, and subsequent experiments with more precise measurements are in progress now. Below are presented the data obtained by the chemiluminescent NO_x analyzer, which, in our opinion, seem to be more reliable.

3. Results and Discussion

In Figure 2, the experimental results of NO_2 uptake over the zeolite HSZ-360HUD1C with and without ozone injection are presented. From a comparison between curves it follows that the ozone injection substantially increased a rate of NO_2 uptake by zeolite. Another plausible channels of NO_2 removal have been considered and found as negligible. Particularly, the supposition about oxidation of NO_2 up to N_2O_5 with subsequent N_2O_5 crystallization or nitric acid formation within the zeolite column has been found as unreasonable. Indeed, the residence time of gas in the column was ∼0.1 s, which is not sufficient, even for the first step of NO_2 oxidation to N_2O_5, i.e., formation of NO_3 via the gas-phase reaction 1.

Taking into account that H-Y is almost inactive as a catalyst of the disproportionation reactions, a type of species affiliated by zeolite without O_3 should be described as the physically bonded NO_2 molecules. As to the removal of NO_2 in the presence of O_3, it appears that the zeolite really has the catalytic activity suggested above, to accelerate the slow gas-phase reaction of NO_3 radical formation with NO_2 and O_3 as coreactants (1). Apparently, subsequent electron transmission from zeolite to this radical results in the formation of nitrate anions that are stable within the sorbent and are affiliated due to strong ionic interaction with charged sites within it.[2] Evidently, it accounts for the detection of a substantially enhanced rate of NO_2 uptake by zeolite due to ozone injection, obtained through the experiment.

The proposed mechanism of formation of nitrate anions is not, of course, conclusive, and further research is necessary to reach the complete understanding. Only few experiments aimed at the above purpose have been performed and are presented below.

In Figure 3 the results of NO_x desorption from the samples, used before for the experiments described above, are presented.

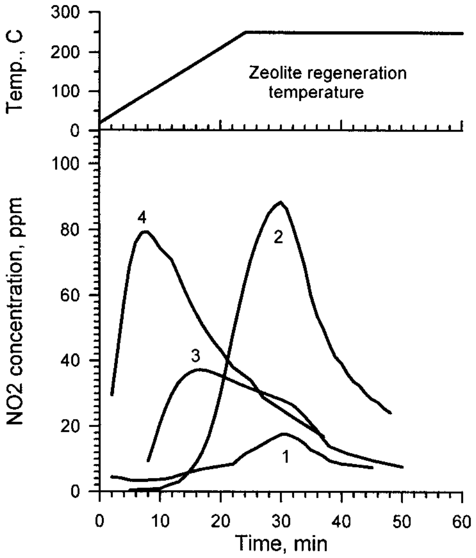

Figure 3. Profiles of NO_2 temperature-programmed desorption from zeolite HSZ-360HUD1C (NO_2 uptake before desorption: without ozone injection, 1; with ozone injection, 2). Profiles of NO_2 temperature-programmed desorption from zeolite HSZ-390HUD1C (NO_2 uptake before desorption: without ozone injection, 3; with ozone injection, 4). Sweep gas in both cases: dry air 1 slpm. Sorption condition as described in Figure 2.

The gas-phase analysis indicated that mainly nitrogen dioxide was released from both samples. For the sorbent used for removal of NO_2 without ozone injection, the subsequent release of stored species was obtained just by introduction of the sweep gas, and it, obviously, points to the presence of physically bonded NO_2 molecules. Whereas for the sample used for removal of NO_2, with ozone injection, such species have not been identified, and desorption was obtained only after heating the sorbent over 100 °C. Therefore, it appears that nitrate anions were stored within the sorbent and bonded with it due to strong ionic interaction. Besides, after sorption with ozone injection the amount of desorbed NO_2 molecules was highest. It is, surely, a consequence of the highest amount of NO_x species stored within the zeolite. It appears that this fact is in agreement with the conclusion that the ozone injection only enhanced the process of NO_2 uptake by zeolite and did not cause any other processes of NO_2 removal, whatsoever.

It has been suggested above that the formed nitrate anions are affiliated by zeolite because of the strong ionic interaction with positively charged sites within it. Such charged sites, as it is known, are formed by cations with a rather small electrostatic field within H-Y compared with other cationic forms of sorbent. The reason is that a proton, actually, forms a OH group by reacting with a lattice oxygen.[2] Dealumination of H-Y is suggested to enhance the ionic character of H atoms, thus shifting the electron density from the proton to the oxygen atom. Therefore, the OH bond within Si-rich zeolites becomes more ionic and the acid strength of zeolite rises. The quantum-chemical calculations confirmed that the acid strength of zeolites increases with the decrease of the Al content. At the same time, theoretical research failed to predict that the severe dealumination weakens the strength of the acidity of OH groups, which was confirmed by experimentation.[10]

The above considered dependence between the acidity of OH groups and the Al content within zeolite correlates with the effect of nitrate anion formation, suggested here. Indeed, the strong dealumination is expected to diminish the ionic character of the H atoms thus shifting the electron density from oxygen to the proton. It will, obviously, weaken the ionic interaction between the nitrate anion and zeolite, which are supposed to be formed, during sorption of NO_2, in the presence of ozone. Consequently, it is possible to predict that the presence of ozone will not strongly enhance the sorption of NO_2 over extremely dealuminated zeolite.

To confirm this prediction, the adsorption/desorption experiments have been performed. These experiments were the same as the ones described above, except that the zeolite HSZ-360HUD1C was exchanged to HSZ-390HUD3C with a high SiO_2/Al_2O_3 ratio 360. Figures 2 and 3 show variations in NO_2 concentrations of the outlet gas during the sorption experiments carried out with and without ozone injection and, also, during the subsequent processes of desorption. Indeed, as has been predicted above, the effect of ozone on the sorption rate of NO_2 is not so distinct as in the above described experiments with zeolite HSZ-360HUD1C. The rather slow rate of NO_2 sorption, with ozone injection, can be interpreted here as the consequence of diminished ionic character of H cations. At the same time, such interpretation still cannot be conclusive because the cation density within zeolite becomes lower with zeolite dealumination, and it can be the main reason that the higher rate of NO_2 uptake was not possible to achieve due to ozone injection. This doubt can be removed, if one takes into account rather an intense desorption process after uptake of NO_2 in the presence of ozone, obtained by relatively low temperature treatment. This feature, as it seems, directly proves the above prediction that, under the afore described conditions, the ionic interaction between the formed nitrate anions with the extremely dealuminated zeolite will be weak.

The same set of adsorption/desorption experiments has been performed, where to sorb NO_2 from humid air the zeolite 320NAD1A with Na cations has been applied. The gas-phase analysis indicated that, mainly, nitric oxide was released from the zeolite used before for NO_2 sorption without ozone injection. The zeolite with metal cations is known as an active catalyst of the disproportionation reactions, and obviously, affiliation of NO_2 resulted in the formation of various NO_x species within this sorbent.[2] Therefore, a certain part of affiliated NO_2 molecules has transformed into NO species released from the sorbent by the sweep gas, where the concentration of NO reached 30 ppm. The species with the highest oxidation states of nitrogen, obviously, remained within the sorbent, and this also is in accordance with the results of the mentioned above research.[1] Notice that the uptake of NO_2 by the zeolite 320NAD1A has been significantly enhanced by ozone injection, but it was impossible to remove any NO_x species, whatsoever, from the sorbent, even by raising its temperature to 250 °C. This result is also the confirmation of the proposed above effect of nitrate anion formation. Indeed, it seems like the only stable species formed within zeolite were NO_3^-, which are very difficult to remove in the case of metal cations present within the zeolite.[1,3]

It is also worth making additions to the considered de-NO_x application of this effect. Particularly, it is important to note that the collected nitrate anions can result in NO_2 release, when the thermal treatment of the sorbent is undertaken. During such thermal desorption the back-process of nitrate anion formation within sorbent is, obviously, impossible and, therefore, extremely concentrated NO_2 in the sweep gas can be obtained. Hence, the subsequent process of NO_x reduction by ammonia can be simplified[7] and, moreover, the thermal or catalytic decomposition of NO_x to N_2 and O_2 [11,12] will be possible.

In addition, it is necessary to note that sorption in the present system is basically a gas−solid reaction and, therefore, the removal capacity of NO_2 can be expected as large, which should be verified in practice, together with the predicted possibility of formation of a high concentration of NO_2. Besides, the acid strength and the density of protons within the sorbent can be increased, as compared with the present experiments, by reducing the SiO_2/Al_2O_3 ratio from 15 to around 5.[10] The above measure will, likely, result in achieving the highest adsorption rate and capacity. Also, to make more conclusive interpretations, it is desirable to consider the mass-balance of ozone and NO_2 molecules during the sorption process, and the application of IR spectroscopy is essential for the direct confirmation of all the above presented considerations.

4. Conclusion

The experimental investigation of the effect of O_3 presence on the affiliation of NO_2 by the Y-type zeolite ion exchanged with H^+ was performed. Humid air with due point 0 °C was used as a carrier of nitrogen dioxide, and its uptake has been accomplished in a gas-flow system by the sorbent saturated by moisture. The sorption profiles of NO_2, with and without ozone injection, as well as the profiles of subsequent temperature-programmed desorption have been recorded. It has been found that the ozone presence can substantially enhance the rate of NO_2 uptake by zeolite. It has been suggested that the zeolite appears to be catalytically active to accelerate the slow gas-phase reaction of NO_3 radical formation with NO_2 and O_3 as coreactants. Subsequent electron transmission from zeolite to this radical presumably results in the formation of nitrate anion. Such anion is stable within the sorbent and is affiliated within it due to strong ionic interaction. The practical application of this effect is possible.

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