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NOTE

The Effect of Adsorbates on N_2O Formation in Pulsing NO over a Pt/ZSM-5 Catalyst

Selective catalytic reduction of NO_x by hydrocarbons in the presence of oxygen (SCR-HC) is presently studied for diesel and lean-burn engine exhaust purification (1). Among various catalysts proposed in the past, supported platinum belongs to the most promising ones due to its activity at low temperatures and its stability against poisons such as SO_2 and H_2O (2–6). On the other hand, N_2O is formed over Pt-based catalysts, which is known to contribute to both stratospheric ozone destruction and greenhouse warming (7); therefore, N_2O emissions must be avoided in any NO_x reduction process.

An excellent review on kinetics and mechanisms of SCR-HC over platinum group metal catalysts has recently been given by Burch and Millington (8). The authors concluded that the predominant reaction pathway over Pt-based catalysts involves NO dissociation on reduced Pt sites adjacent to adsorbed hydrocarbonaceous species. They further suggested that N_2 is formed from two dissociated molecules, whereas N_2O stems from the interaction of one N atom with molecularly adsorbed NO (8, 9). Very little is known, however, about the circumstances which favor or suppress undesired N_2O formation over Pt-based catalysts. In this note, the effects of (i) adsorbed NO molecules and (ii) adsorbed oxygen atoms on N_2O formation over a Pt/ZSM-5 catalyst are reported.

Pt(0.9 wt%)/ZSM-5 was prepared by a conventional ion-exchange procedure applying the parent H-ZSM-5 (Conteka, Si/Al = 25), followed by hydrogen reduction at 673 K; the XRD spectrum of the catalyst showed peaks assignable to the ZSM-5 structure and to metallic platinum, which obviously had formed on the outer zeolite surface in the course of the calcination and reduction process. The activity of the catalyst for a feed of NO, C_3H_6, and O_2 was reported previously (10); a maximum NO conversion to N_2 and N_2O of approximately 60% at 535 K was observed.

A vacuum pulse technique applying the temporal-analysis-of-products (TAP) reactor, which has been described in detail elsewhere (11, 12), was used to study NO decomposition on differently pretreated catalyst surfaces. Pt/ZSM-5 ($m_{\mathrm{Cat}} = 0.1$ g, $d_{\mathrm{p}} = 250$–$355\ \mu$m) was charged into the catalytic microreactor between two layers of quartz sand; it was then temperature programmed heated to 500 K in vacuum (10 K min^{-1}). Prior to the experiments, the catalyst was reduced in a flow of hydrogen for 30 min at 500 K to remove adsorbed oxygen from the surface. It was ascertained that a longer reductive treatment did not lead to any change of the experimental results.

First, the effect of NO partial pressure on N_2O formation was studied. NO was pulsed at 500 K over the prereduced catalyst; the pulse intensity was varied between 4×10^{14} and 2×10^{16} molecules in order to alter the NO concentration in the gas phase and, therefore, also on the surface. To improve the signal-to-noise ratio, 10 pulses were averaged; the responses of N_2 ($m/z = 28$) and N_2O ($m/z = 44$) were measured alternately. After each experiment, the catalyst was again reduced by hydrogen; the results were highly reproducible after this treatment.

Second, the effect of adsorbed oxygen was examined. Pulse sizes amounted to 2×10^{16} molecules NO and 1×10^{16} molecules O_2, respectively. After pretreatment of the catalyst, NO was pulsed and the responses of N_2 and N_2O were measured. Afterward, 10 pulses of oxygen were introduced, which adsorbed irreversibly on the catalyst (i.e., no oxygen response signal was detected); in that way, the oxygen surface concentration was increased and NO was pulsed again. This procedure was repeated until the surface was completely covered by oxygen, which was indicated by the breakthrough of pulsed oxygen at the reactor outlet. Again, the responses to 10 pulses of NO were averaged.

Yields of N_2 and N_2O (i.e., the percentage of NO molecules converted to the respective products) were calculated from the areas under the response signals considering the respective calibration factors. To determine the N_2 response area, the signal at $m/z = 28$ was corrected by the fragment of N_2O at this mass number. The selectivity to N_2 was calculated as $S(N_2) = Y(N_2)/(Y(N_2) + Y(N_2O))$.

The effect of NO pulse intensity on N_2 and N_2O formation over the reduced Pt/ZSM-5 catalyst is shown in Fig. 1. A sharp increase in N_2 formation with pulse size is noted from 4×10^{14} to 6×10^{15} molecules/pulse. N_2O yields may be considered negligible up to approximately 1.2×10^{16} molecules/pulse; only a slight rise to $Y(N_2O) \approx 10\%$ is observed at the highest intensity.

Complete consumption of NO, i.e., no nitric oxide response, was observed in each experiment, irrespective of the pulse size; neither oxygen nor NO_2 were detected. This

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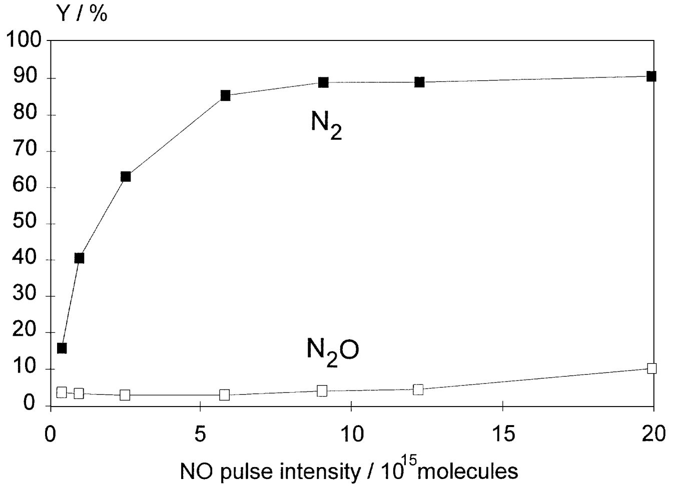

FIG. 1. Dependence of the yields of N_2 and N_2O on NO pulse intensity over prereduced Pt/ZSM-5 at 500 K.

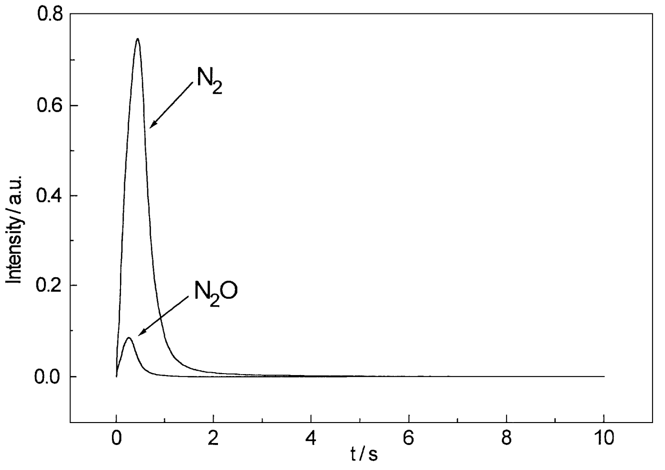

FIG. 2. Transient responses to pulsing NO over prereduced Pt/ZSM-5 at 500 K.

means that, using "small" pulses, a significant proportion of the pulsed NO molecules stays either molecularly or dissociatively adsorbed on the catalyst without reaction. It is known that the rate of NO decomposition on platinum strongly varies with crystal face (13); for instance, all adsorbed molecules could be dissociated during NO TPD from Pt(410), whereas absolutely no dissociation occurred in desorbing NO from Pt(111) (13). Furthermore, it was reported that small supported Pt particles are much less active for NO dissociation than larger ones; e.g., no N_2 formation was observed on 1.7-nm Pt particles below 500 K (14). Therefore, the low N_2 yields obtained with small pulses at 500 K were not unexpected.

The sharp increase of NO conversion with pulse intensity must be connected with an increase of NO surface concentration, since gas-phase reactions can be excluded at 500 K. Burch and Watling (15) have recently described the promoting effect of adsorbed H atoms on NO dissociation and indicated that the reaction may also be assisted by other adsorbates such as N_{ads}, C_{ads}, or $C_xH_{y,ads}$. Indeed, a surface interaction between C-containing species and NO_x, which may either be called *reaction* or *adsorbate-assisted decomposition*, was already reported by the present authors (10). Hence, it seems possible that either molecularly or dissociatively adsorbed NO facilitates the dissociation of adjacent molecules, thus leading to the observed rise in N_2 formation. On the other hand, it cannot be excluded that NO dissociates completely, irrespective of the pulse size, and the increase of N_2 yield is simply due to a higher concentration of adsorbed N atoms.

It may be concluded that N_2, and not N_2O, is the main product from NO decomposition over prereduced Pt/ZSM-5, independent on the amount of NO adsorbed on the surface; it should be noted that, during a pulse of 1×10^{16} NO molecules, the pressure inside the catalyst bed increases to approximately $p_{NO} = 40$–50 Pa, which is, compared to $p_{NO} \approx 30$ Pa in lean exhaust gases, a realistic value.

In the second series of experiments, the effect of surface oxygen concentration was studied. The responses of N_2 and N_2O to pulsing NO immediately after the reductive treatment at 500 K are given in Fig. 2. As described above, NO decomposition yields mainly N_2 and only small amounts of N_2O over the reduced platinum surface (the undoped zeolite was found to be completely inactive for NO decomposition). Again, neither NO_2 nor O_2 were detected, since oxygen from NO decomposition is retained on the surface as reported earlier (9, 10). After catalyst treatment by 60 pulses of O_2 the selectivity to N_2O rises markedly, which can be deduced from the responses shown in Fig. 3. At the same time, both products signals become

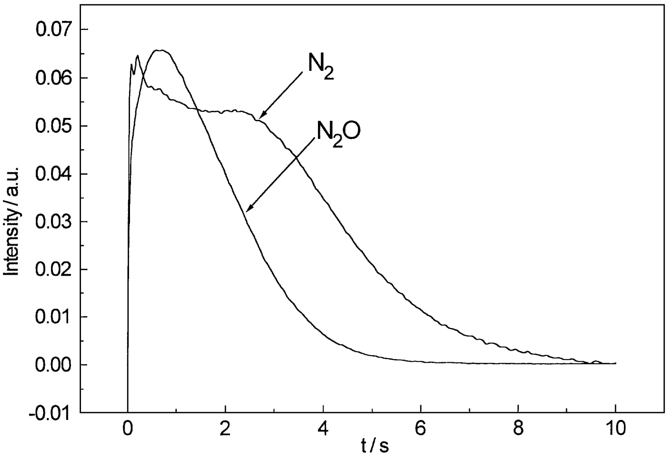

FIG. 3. Transient responses to pulsing NO over Pt/ZSM-5 at 500 K; the catalyst was prereduced and then exposed to 6×10^{17} molecules O_2.

significantly broader; i.e., the rate of product formation decreases.

The latter observation can be explained as follows: On the reduced surface, pulsed NO molecules are able to react at the entrance of the catalyst bed; the decomposition products are not (N_2) or only weakly (N_2O) adsorbed and therefore quickly detected. After introducing oxygen, however, Pt sites at the entrance of the catalyst bed are already occupied and NO molecules need longer to reach vacant sites to dissociate. During this time, they will adsorb reversibly both on oxidized Pt sites and within the zeolite support, which was observed in separate experiments (16) and reported by other authors as well (9, 17); the adsorption of NO on PtO_{ads} may proceed via the intermediate formation of adsorbed NO_2 (18), which, however, was not detected in the gas phase. In conclusion, the broadening of responses after partial catalyst coverage with oxygen is most probably due to reversible NO adsorption *before* reaction.

Furthermore, Fig. 3 reveals a broadening of the N_2 response compared to N_2O. Clearly, this effect can neither be accounted for by diffusion (since N_2 diffuses faster than N_2O) nor by adsorption effects (since N_2 was proven to behave inert, whereas N_2O is weakly adsorbed (16)). Instead, the broader N_2 curve is probably due to subsequent decomposition of N_2O, which was found to occur over reduced Pt/ZSM-5 on pulsing N_2O (16). Indeed, the N_2 response in Fig. 3 shows a maximum at approximately 0.1 s and a shoulder at approximately 3 s; this indicates that N_2 is both a primary (from NO decomposition) and a secondary product (from N_2O decomposition) under the applied experimental conditions.

The calculated yields of N_2 and N_2O as a function of the number of prepulsed oxygen molecules are given in Fig. 4.

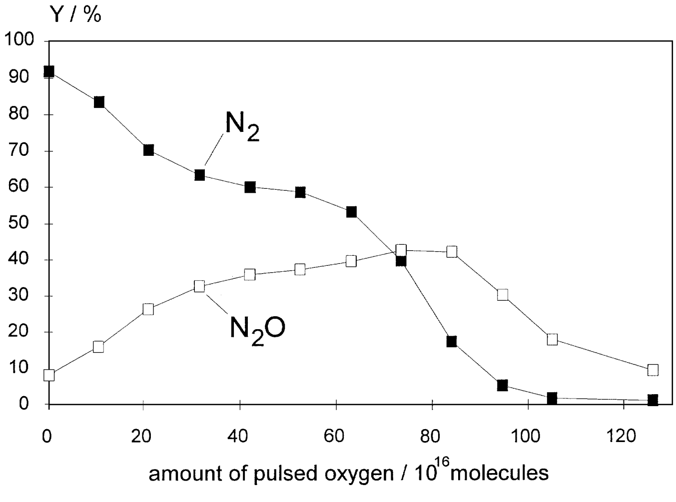

FIG. 4. Dependence of the yields of N_2 and N_2O on the amount of surface oxygen when pulsing NO over Pt/ZSM-5 at 500 K; the catalyst was prereduced and then exposed to the indicated number of oxygen molecules.

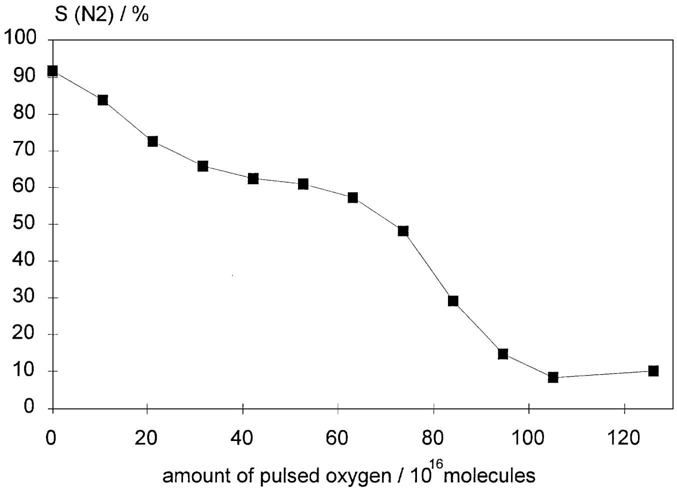

FIG. 5. Dependence of the selectivity to N_2 on the amount of surface oxygen when pulsing NO over Pt/ZSM-5 at 500 K; the catalyst was prereduced and then exposed to the indicated number of oxygen molecules.

A continuous decrease of N_2 yield with surface coverage is obvious, whereas the concomitant N_2O formation passes through a maximum. As a result, the selectivity to N_2, as shown in Fig. 5, decreases continuously.

The dependence of N_2 and N_2O formation on surface oxygen concentration becomes understandable if one assumes the following elementary reaction steps (13):

$$NO_{ads} \rightarrow N_{ads} + O_{ads} \quad [1]$$

$$2\ N_{ads} \rightarrow N_2 \quad [2]$$

$$N_{ads} + NO_{ads} \rightarrow N_2O \quad [3]$$

With increasing surface coverage by oxygen, reaction [1] is inhibited, as often reported before (e. g., 9, 19). Both steric and/or electronic reasons are conceivable. As a result, at intermediate oxygen coverages, the concentration of molecularly adsorbed NO will rise and, hence, the rate of N_2O formation (Eq. [3]) increases. Finally, the concentration of N_{ads} becomes too small and consequently the rates of both N_2 and N_2O formation (Eqs. [2] and [3]) drop off.

It may be concluded that—if the oxygen coverage is low—N_2O formation over Pt/ZSM-5 is scarcely influenced by surface NO concentration, whereas it is strongly influenced by surface oxygen concentration within the range of the applied experimental conditions. From a practical point of view, considering the excess of O_2 in lean exhaust gases, there seems to be little promise to improve the selectivity of Pt-based catalysts unless means of reducing the surface oxygen coverage are found. Investigating the effects of additional adsorbates like different HC species and of modifications of the catalyst surface are possibilities to gain further insights.

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