N_2O IN NO REDUCTION BY CO OVER Pt/NaX ZEOLITE

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Dedicated to Dr Karel Mach on the occasion of his 60th birthday.

Pt/NaX zeolite (3 Pt atoms per unit cell) was prepared by vacuum decomposition of $[Pt(NH_3)_4]^{2+}$. NO + ^{13}CO and N_2O + ^{13}CO reactions were studied under static conditions at 180, 205 and 230 °C and followed by temperature programmed desorption (TPD) of surface species adsorbed in zeolites during the reaction. The effect of different NO/CO ratios and of the added oxygen was examined for the former reaction. The experimental results agree with the assumption that N_2O (and $^{13}CO_2$) is (are) the primary product(s) released into the gaseous phase below 230 °C; above 205 °C, the complete reduction to N_2 occurs. N_2O could be a very rapidly decomposing surface intermediate for this complete reduction, and can act together with the recombination of N atoms. Nitrous oxide released into the gas phase cannot serve as the reaction intermediate, because its reduction by CO proceeds much more slowly than that of NO. The formation of nitrous oxide in the NO + CO reaction is, in addition to low temperatures, enhanced by the increased NO/CO ratio and by the presence of oxygen. The latter effect can be due to the occupation of Pt active sites by adsorbed oxygen and/or by the oxidation of NO to higher oxides which decompose, yielding N_2O (together with NO and oxygen).

Key words: NO + CO reaction; Pt/NaX zeolite; N_2O, role of.

Removal of NO from exhaust gases still remains a permanent challenge, as the decrease of its level concentration is continuously demanded. Direct NO decomposition to harmless nitrogen and oxygen is the subject of many studies, but to date, the stage of practical utilization has not yet been reached[1,2]. In contrast, the reduction of nitrous oxide by various reductants (*e.g.* ammonia, CO, hydrocarbons) is widely spread[1–4]. In many cases, the formation of nitrogen oxides (*e.g.* N_2O, NO_2) as products[4,5] or reaction intermediates[6–9] has been reported. N_2O is the most frequently observed reaction product. Its release into air is undesirable because it is known as one of the greenhouse gases and as a destroyer of the ozone layer.

The present study deals with the formation of N_2O during the NO reduction by CO over Pt/NaX zeolite; the conditions under which nitric oxide is released into gas phase are described, and its possible role in the course of the reaction $2\,NO + 2\,CO \rightarrow N_2 + 2\,CO_2$ is discussed. This is a continuation of our studies of the latter reaction over Pt, in which the effects of various Pt forms (Pt^0, Pt^{2+}, Pt_{ox}), zeolite matrix (X and Y zeolites with different alkali ions) and size of Pt clusters have been examined[10–13].

EXPERIMENTAL

Zeolites. NaX (Si/Al = 1.25) was supplied by VURUP (Bratislava). Sodium ions were from a small part (3 Pt atoms *per* unit cell) ion exchanged for $[Pt(NH_3)_4]^{2+}$ from the relevant dichloride. The ion exchange was performed at room temperature for one week. The sample was then washed with deionized water, dried at room temperature, and hydrated over the solution of calcium dinitrate. The sample weight was always related to the hydrated form. Pt content in the NaX zeolite after these treatments was 2.5%. The hydrated sample (20 mg) was placed into a small tube microreactor, and the tetraammineplatinum(II) ions were decomposed in vacuum (evacuated 2 h at room temperature, then dehydrated by increasing the temperature (2 °C/min) to 130 °C, held 1 h at this temperature and heated by the rate 5 °C/min to 380 °C. It was left at this temperature untill the release of the gaseous products had ceased – *ca* 15 min). The majority of the Pt ions was autoreduced to Pt^0 clusters whose size was between 2–4 nm (TEM and hydrogen adsorption measurements). Details of the decomposition of the ammonia complexes and of the final Pt state were reported elsewhere[10–13].

Reactants. O_2 and N_2O were supplied by Linde, NO by Messer Griesheim, ^{13}CO (99 at.% of ^{13}C) by Aldrich Chemical Company. The labelled CO was employed to separate nitrogen and CO ions, and CO_2 and N_2O ions.

Catalytic reaction. $^{13}CO + N_2O$ reaction (1 : 1 mixture, total pressure 200 Pa) was examined in a static apparatus (“batch” reactor, 500 cm^3 volume + the microreactor) at 180, 205 and 230 °C. A negligible amount of gases was lead through a needle valve to a Balzers 400 quadrupole mass spectrometer (MS). After certain time (20–30 min) the gaseous reactants and reaction products were evacuated and the TPD (with the heating rate of 10 °C/min) of species adsorbed during the reaction in zeolites was analyzed by the MS which was in this case directly connected to the reaction volume.

The reaction of ^{13}CO with NO was studied in the same way. In addition, the effect of the CO : NO ratio (1/5, 1/1, 5/1) as well as that of the oxygen (30 Pa in the same volume) was also examined.

Experimental data in Figs 1–4 are displayed as the time dependence (at constant temperature) and temperature dependence of concentrations for catalytic reactions and TPD, respectively. The concentrations of compounds were equal within 20% to the ion intensities: 28^+ for N_2, 29^+ for ^{13}CO, 30^+ for NO, 32^+ for O_2, 44^+ for N_2O and 45^+ for $^{13}CO_2$. This implied from the ion cross sections, fragmentation of primary ions, and properties of our MS.

RESULTS

N_2O + CO Reaction

The course of the reaction of N_2O with ^{13}CO at 180, 205 and 230 °C is shown in Fig. 1, left-hand side, and TPD following these isothermal reactions is in the right-hand side of this figure. It can be seen that the reaction proceeds very slowly, especially below 230 °C, and that $^{13}CO_2$ is the only reaction product. Very small amount of gases are released during TPD, and contrary to the NO + CO reaction (see below), the amount as well as the composition of the gases released does not strongly depend on the reaction temperature. CO_2 predominates in the desorbants, being accompanied by much smaller amount of the unreacted N_2O and CO; N_2 is not observed at all (the background of the ion 28^+ is not subtracted).

NO + CO Reaction

The reaction of NO with ^{13}CO and the following TPD under the same conditions as were those for N_2O + ^{13}CO are shown in Fig. 2. The reaction is much more rapid than that of N_2O + ^{13}CO. Moreover, the amount of species adsorbed in the zeolite after the

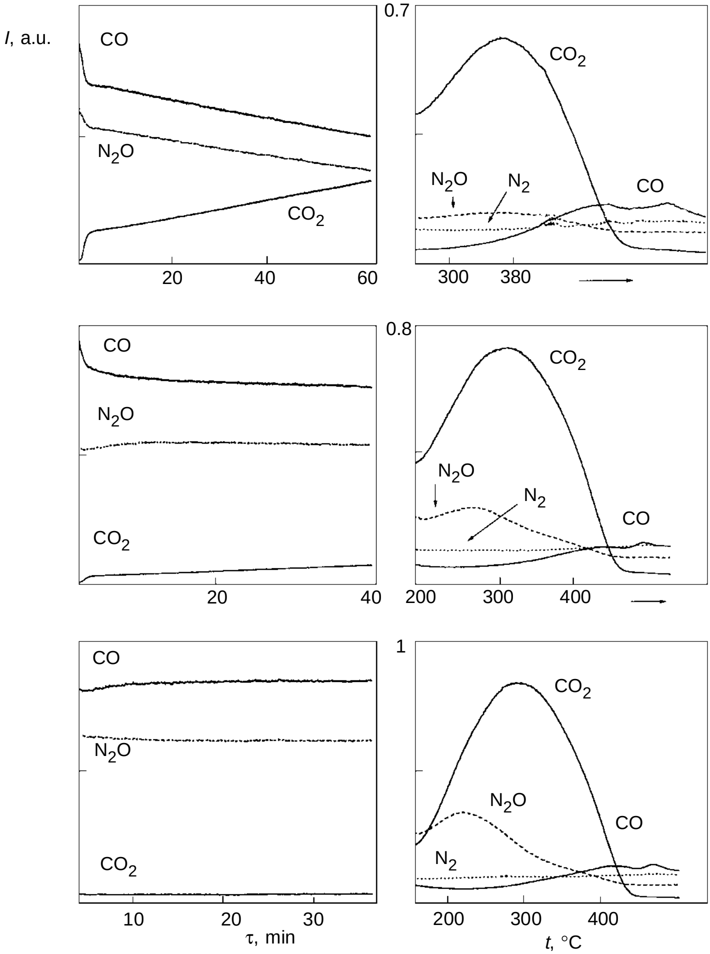

FIG.1

N_2O + ^{13}CO isothermal reactions and TPD. Left-hand side, from bottom: reaction at 180, 205 and 230 °C; right-hand side: TPD after the respective reactions; → in *x* axis means that the increase of temperature was stopped, and the reaction proceeded at 380 °C for *ca* 10 min reaction at 180 and 205 °C is high as follows from the TPD, while practically nothing is desorbed after the reaction at 230 °C. Nitrogen appears in the gas products only during the reaction at 230 °C. At the two lower temperatures it is in some form held in the zeolite and is released only during TPD. Contrary to TPD from N_2O + CO reaction, the concentration of evolved CO is the highest. The reaction NO + ^{13}CO is accompanied by the formation of N_2O, whose fraction decreases with increasing temperature (Fig. 2, left-hand side). No N_2O is released during TPD.

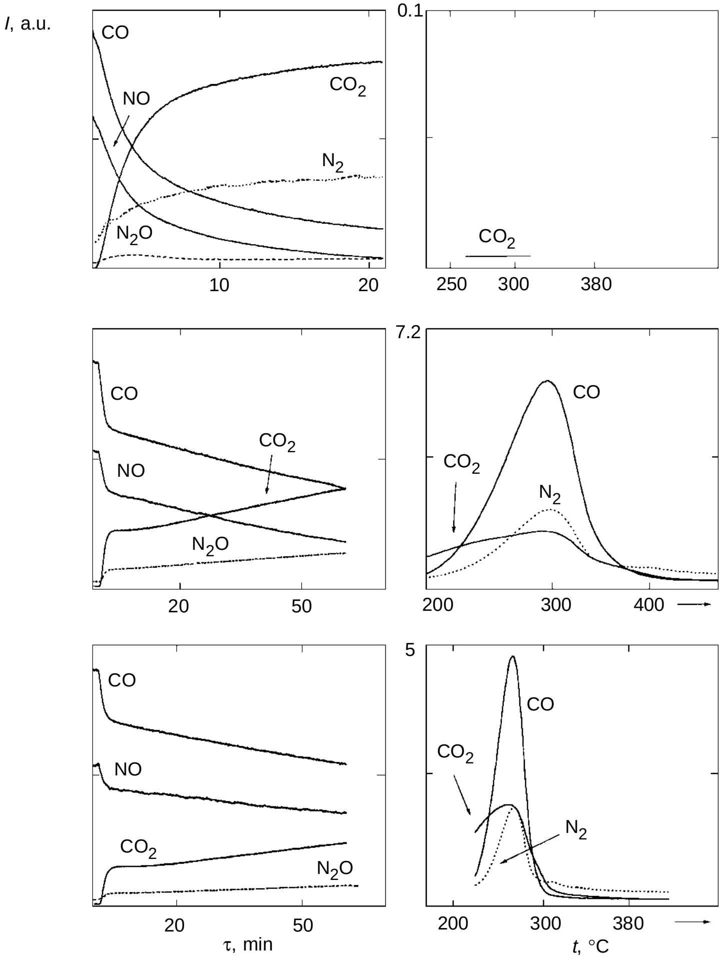

FIG. 2
NO + ^{13}CO isothermal reactions and TPD. Left-hand side, from bottom: reaction at 180, 205 and 230 °C; right-hand side: TPD after the respective reactions

NO + CO in Different Ratios

The effect of two different NO/CO ratios on the reaction course at 180 °C and on the TPD is shown in Fig. 3. The upper reaction course corresponds to the NO/CO ratio = 1/5, the bottom course to the ratio 5/1. In both cases no nitrogen is formed, similarly as for the 1/1 ratio (*cf*. Fig. 2). On the other hand, for the 5/1 ratio the fraction of N_2O in the products is considerably higher than that for the 1/1 ratio (*cf*. Figs 2 and 3 for the same temperature 180 °C). The gases released during TPD after the reaction with NO/CO ratio = 1/5 consist predominantly of CO, accompanied by CO_2 and N_2, similarly as for 1/1 ratio. For the NO/CO ratio = 5/1, the fraction of CO in the desorbed products is

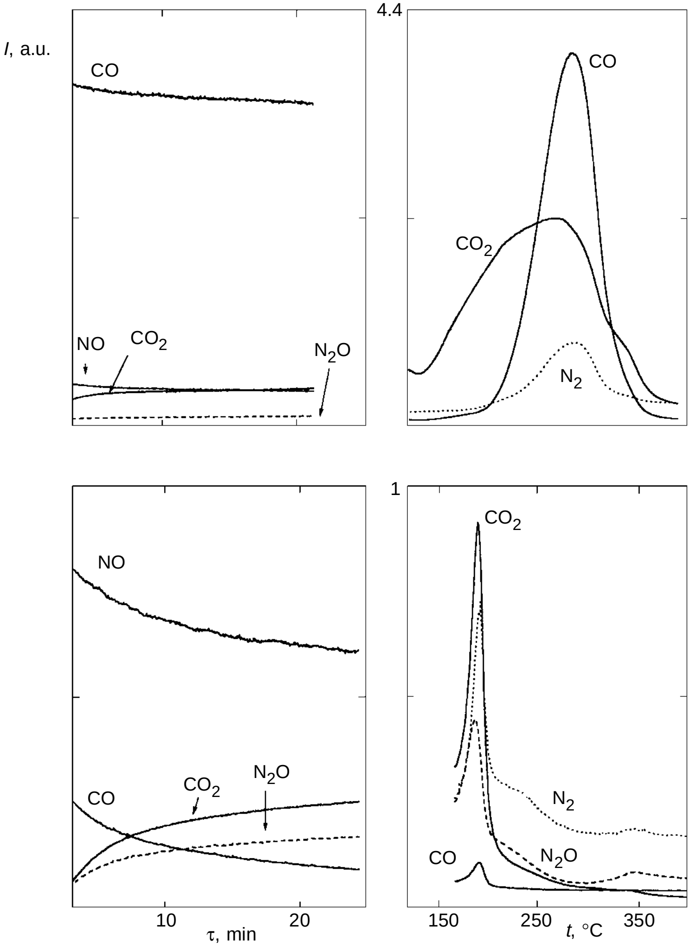

FIG. 3
Effect of different NO/CO ratios on the NO + ^{13}CO reaction at 180 °C and TPD. Left-hand side, bottom: NO/CO = 5/1, upper part: NO/CO = 1/5; right-hand side: TPD after the reactions

low, and CO_2 with N_2 prevail. In this case, also N_2O is desorbed; the amount of gases released is more than four times lower than for the 1/5 ratio, and the desorption proceeds at the lower temperature.

Effect of O_2 Addition on the CO + NO Reaction

The mixture of NO + CO + O_2 in the 1 : 1 : 1/6 ratio was allowed to react with the zeolite at 180 and 230 °C, which is shown in Fig. 4, the bottom and upper part, respec-

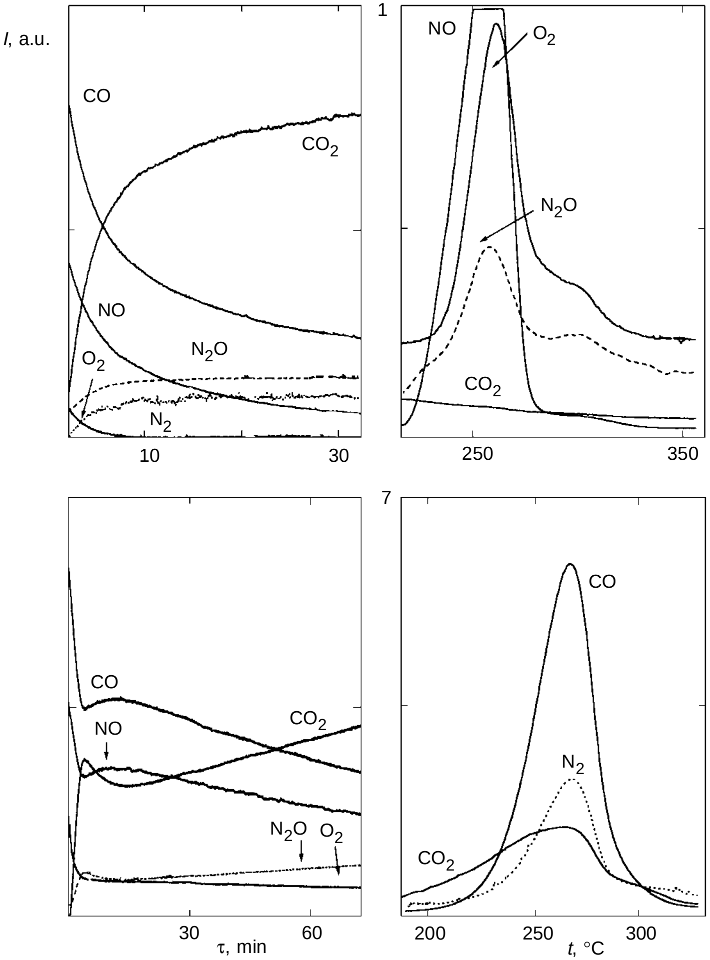

FIG. 4
Effect of O_2 addition on the isothermal reactions of NO + ^{13}CO and TPD after the reactions. NO/CO/O_2 ratio = 1/1/0.16; left-hand side, bottom: 180 °C, upper part 230 °C; right-hand side: TPD after the reactions

tively. At the beginning of the reaction at 180 °C a relatively high decrease of the reactants is observed which is accompanied by a sharp increase of CO_2. No nitrogen appears in the gas phase, only some N_2O is formed. The reaction at 230 °C exhibits much higher amount of N_2O compared to that without oxygen and smaller amount of N_2 (*cf*. Figs 2 and 4 at 230 °C). TPD after the reaction at 180 °C is similar to that without oxygen, *i.e.* with maximum yield of CO and the smaller N_2 and CO_2 yields. The amount of gases released after the reaction at 230 °C is higher than that without oxygen (though much less than after the reaction at 180 °C), and the composition of the gases released differs from all preceding desorptions. The yield of NO is the highest, followed by oxygen and N_2O, nitrogen does not appear at all and the yield of CO_2 is very low.

The reaction of N_2O + CO is not substantially changed if oxygen is added under the above experimental conditions.

DISCUSSION

The total reduction of NO by CO is given by the stoichiometry

$$2\ NO + 2\ CO = N_2 + 2\ CO_2\ . \qquad (1)$$

There are many intermediate reaction pathways proposed[14], from which the following ones predominate over Pt:

$$2\ NO \rightarrow 2\ NO_{ads} \rightarrow 2\ N_{ads} + 2\ O_{ads} \qquad (Pt^0 \rightarrow Pt_{ox}) \qquad (1a)$$

$$2\ CO \rightarrow 2\ CO_{ads} \qquad (1b)$$

$$2\ N_{ads} \rightarrow N_2 \qquad (1c)$$

$$2\ CO_{ads} + 2\ O_{ads} \rightarrow 2\ CO_2 \qquad (Pt_{ox} \rightarrow Pt^0)\ . \qquad (1d)$$

In some papers the surface reconstruction of Pt instead or together with the Pt redox cycles (shown in brackets) has been reported[15]. Both these features can lead to the oscillations found in certain temperature intervals.

The dissociation of CO has not been usually assumed. However, an evidence of its presence was reported in a recent study[16]. If this were the case, instead of route (*1b*) the dissociation of CO (*1b′*) would proceed:

$$CO \rightarrow C_{ads} + O_{ads} \qquad (1b')$$

and the following reactions could occur *via* the formation of CN or CNO intermediates[17,18]. These intermediates are often suggested in the reduction of NO by hydrocarbons[19,20].

The formation of N_2 was also assumed to occur not *via* (*1c*), but according to Simon *et al.*[5]:

$$N_{ads} + NO_{ads} \rightarrow N_2 + O_{ads} \quad . \qquad (1c')$$

Instead of route (*1a*) also the intermediate formation of N_2O has been assumed[6–8]:

$$2\ NO \rightarrow 2\ NO_{ads} \rightarrow N_2O_{ads} + O_{ads} \qquad (1a')$$

and CO_{ads} can then react with N_2O_{ads} and with O_{ads}:

$$CO_{ads} + N_2O_{ads} \rightarrow CO_2 + N_2 \qquad (1d')$$

and *via* Eq. (*1d*).

Many authors exclude this reaction route[21] because the reaction of N_2O with CO appears to be much slower than that of NO + CO (this also follows from our experiments, *cf*. Figs 1 and 2). Cho[7,8] found that the sticking coefficient of N_2O is very low and therefore also the reaction is slow. However, this does not play any role if N_2O is formed as the surface intermediate; Cho supports this possibility by theoretical calculations (for discussion of these papers see refs[22,23]).

If N_2O were not the intermediate but the reaction product, the total reaction stoichiometry would be:

$$CO + 2\ NO \rightarrow CO_2 + N_2O \quad . \qquad (2)$$

This reaction can also proceed *via* various adsorbed and dissociated intermediates.

The above list of the reaction routes is not exhausting: some other routes have also been assumed, *e.g*. through intermediate isocyanate formation.

The main difference between the reaction route (*1*) and (*2*) is the formation of nitrogen molecules in the former case, while in the latter nitrogen appears only as N_2O. According to our experiments, N_2 is not found in CO + NO reaction below 230 °C (Fig. 2), while some N_2O has been detected. This agrees with the reaction route (*2*). However, according to this equation, CO_2 and N_2O should be formed in equimolecular amounts, and the decrease of NO concentration should be twice as large as that of CO, which evidently is not the case. The composition of gases evolved during TPD after the CO + NO reaction at 180 and 205 °C shows the maximum amount of CO and a higher amount of N_2 than of CO_2. It implies that CO was most probably adsorbed on Pt in the zeolite, and, therefore, its decrease during the isothermal reaction was higher than would correspond with the Eq. (*2*). The release of N_2 during TPD can also explain the insufficient (according to Eq. (*2*)) amount of N_2O formed during the isothermal reaction.

The composition of the products and the decrease of the concentration of reactants during the isothermal reaction at 230 °C agrees with the reaction (*1*). In accordance with it, practically nothing remains adsorbed in the zeolite, as follows from TPD (Fig. 2). The prevailing operation of the mechanism (*2*) below 230 °C and (*1*) at (and most probably above) this temperature can thus be postulated. The formation of nitrous oxide instead of molecular nitrogen at lower reaction temperatures was also reported by Kudo et al.[5].

The experiments with different NO/CO ratios showed that the excess of NO results in the enhanced formation of N_2O, which appears even during TPD (Fig. 3, bottom). The insufficient amount of the reductant (CO) thus supports the uncomplete reduction of NO, so that N_2O could be the surface intermediate (Eq. (*1a′*) even at higher temperatures. If this is true, N_2O has to react very quickly with CO to N_2 and CO_2 (*1d′*), if there is enough CO), as it almost is not present in the gas phase.

The addition of oxygen increases also the contribution of uncomplete NO reduction (Fig. 4, 230 °C), which can be explained by a partial poisoning of Pt active sites by oxygen (this effect is known from literature[3]). The relatively very high yield of CO_2 found at the lower temperature (Fig. 4, bottom) can be due to the oxidation of CO by oxygen, not because of the NO + CO reaction. The special composition of the gases released during TPD after the reaction at 230 °C may be explained by the oxidation of adsorbed NO to the higher oxide and to its decomposition to NO, O_2 and N_2O (*e.g.*: $3\ NO_2 \rightarrow N_2O + 2\ O_2 + NO$).

CONCLUSIONS

Summarizing, it can be concluded that probably two temperature dependent mechanisms operate in the NO reduction by CO: below 230 °C the CO + NO reaction proceeds predominantly to give N_2O and CO_2, while at the higher temperatures the complete reduction to N_2 is preferred. In the low-temperature region, surface species are formed in the zeolite and decompose during TPD to form CO, N_2 and CO_2. The incomplete reduction is supported by the excess of NO and, even at 230 °C, by the presence of oxygen. The reaction of N_2O + CO proceeds much more slowly than that of CO + NO, and almost no surface species remain in the zeolite. The NO + CO and N_2O + CO reactions thus occur most likely by different mechanisms. However, formation of N_2O as the surface intermediate and its rapid reduction with CO to N_2 during the NO + CO reaction at higher temperatures cannot be excluded; in this way it seems to contribute to the formation of molecular nitrogen proceeding *via* recombination of adsorbed N atoms.

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