

PLATINUM, PALLADIUM AND RHODIUM CLUSTERS IN ALKALI X AND Y ZEOLITES. PREPARATION AND CATALYTIC ACTIVITY

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Pt, Pd and Rh ammine cations partially ion-exchanged for alkali ions of X and Y zeolites were decomposed in vacuum to metallic clusters embedded in cavities. The course of the parent ammine decomposition as well as the CO + NO reaction after the deamination to metallic clusters were compared for the individual metals. The effects of the respective metals as well as those of the zeolitic matrices are discussed.

Key words: Zeolites, Pt, Pd, Rh/alkali faujasites; Ammine ligand decomposition; NO + CO reaction; Heterogeneous catalysis.

Noble metals are able to catalyze the NO reduction by hydrocarbons and by CO. Due to this ability, they are used as components of three-way catalysts of car exhaust¹. These metals, when located in zeolitic cavities, enable to study various effects (*e.g.* metal environment, cluster dimension, adsorption/desorption/dissociation of reactants) affecting their activity. To date, zeolitic matrices have not appeared to be suitable real catalysts due to their low resistance to high temperature and presence of water vapour. However, the interest in their employment has been recently renewed because it was found that supported noble metals (by silica, alumina and in zeolites) are able to withstand the presence of oxygen in NO reduction by hydrocarbons at relatively mild temperatures in exhaust gases after the combustion of fuels enriched by oxygen²⁻⁸. A comparison of silica and alumina supported Pt, Pd and Rh activity in NO + CH₄ reaction was reported⁹: platinum was found to be the most active, followed by palladium and rhodium. A lot of papers have reported on high reactivity of rhodium due to its ability to dissociate readily nitric oxide¹⁰⁻¹³.

The aim of this study was to examine the effect of the zeolite matrix on the activity and selectivity of individual noble metals in the NO + CO reaction and, primarily, on the decomposition route of parent ammine cations. The effect of two matrices (X and Y faujasites) was examined for Pd and Rh. These zeolite types differ in basicity of framework oxygens and in the number of charge-compensating alkali cations. In addition, the role of different alkali cations was checked for Pt exchanged faujasites.

The vacuum decomposition of the ammine ligands was studied using the analysis of the gases released during the temperature-programmed heating. The CO + NO reaction was carried out isothermally at various temperatures and was followed by temperature-programmed desorption of surface species formed during these reactions. Both the reaction and the desorption products were analyzed mass spectrometrically. Although the results are obtained under conditions far from real systems, they can provide information on the behaviour of metallic clusters in different environment.

EXPERIMENTAL

Zeolites X (Si/Al = 1.25, Serva International) and *Y* (Si/Al = 2.5, VURUP, Slovak Republic) in sodium form were ion exchanged for respective chloride at room temperature for three days. The same procedure was used for the introduction of tetramminePd(II) cations; pentammineRh(III) cations were ion exchanged from the $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ solution. The amount of each metal was 3 wt.%. $[\text{Pt}(\text{NH}_3)_4]^{2+}$ was also introduced in faujasites in which the sodium had been previously ion exchanged for lithium, potassium and caesium (for details, see ref.¹⁴).

Decomposition of the metal-ammine ions was carried out in vacuum. The gas products were led directly into the vacuum system of a QMG 420 Balzers quadrupole mass spectrometer. The samples (zeolites: 4 mg, parent chlorides: 0.05 mg) were first evacuated at room temperature for 1 h, then heated in vacuum to 130 °C (Pd and Rh samples to 100 °C) by the rate of 2 °C/min to remove the majority of water. After the dehydration, the ammine decomposition was performed by the rate of 5 °C/min up to 400 °C. The ion 16⁺ was selected to represent ammonia, 28⁺ CO and N₂ (in the former case accompanied by the fragment ion 12⁺ in 2% fraction, in the latter case by the ion 14⁺ in 5% fraction), and 44⁺ for CO₂. After the decomposition, which yields predominantly metallic particles^{14–20}, the samples were treated in hydrogen at 380 °C to complete the reduction. It has been shown that the vacuum decomposition (completed with reduction) yields metallic clusters 2–4 nm in size located inside the zeolite channels^{14,16–20}. This was also confirmed for the samples employed in the present study^{14,17–19}. The local disruption of the zeolitic lattice in case of clusters exceeding the dimensions of the large cavities in faujasites (1.25 nm) proceeds, but the disturbance of the zeolitic framework is negligible because of a very small amount of metallic particles (*e.g.* for platinum: 3 wt.% roughly correspond to 3 Pt atoms per zeolite unit cell; the largest 4 nm clusters contain *ca* 1.5×10^3 Pt atoms, *i.e.* of about one disorder per 300 unit cells).

Catalytic reaction ($\text{CO} + \text{NO} \rightarrow \text{CO}_2, \text{N}_2\text{O}, \text{N}_2$; ions: 29⁺ for ¹³CO, 30⁺ for NO, 44⁺ for N₂O and 45⁺ for ¹³CO₂) was examined under isothermal conditions over 20 mg samples (after deamination procedure as described above) in a closed 500 ml reactor (predominantly at temperatures 200–260 °C); small amount of the gas phase leaked into the mass spectrometer (MS). After 20 min (in some cases after 1.5 min), the gaseous phase was evacuated at the temperature of the experiment and the temperature-programmed desorption (TPD, 10 °C/min) of the surface species was performed. In this case, the gas products were pumped off by the vacuum system of the MS. In some cases, the reaction was examined during the linear temperature increase (10 °C/min) over the samples pretreated in the same way as for the isothermal reactions; the temperatures at which the 50% NO conversion occurred were compared for the individual samples.

Gases: ¹³CO (99% enrichment, Aldrich) was employed to separate the CO ions from N₂ and CO₂ from N₂O. NO was supplied by Messer Griesheim.

RESULTS

The removal of the ammine ligands of Pt, Pd and Rh complexes in X and Y zeolites as well of the parent ammine chlorides is shown in Figs 1A–1C, respectively. It can be seen that the decomposition proceeds in several steps which are more separated in Pd and Rh containing samples than in those with platinum. The Pt and Pd tetrammine dichlorides decompose more similarly to the tetrammine complexes in Y zeolites, while

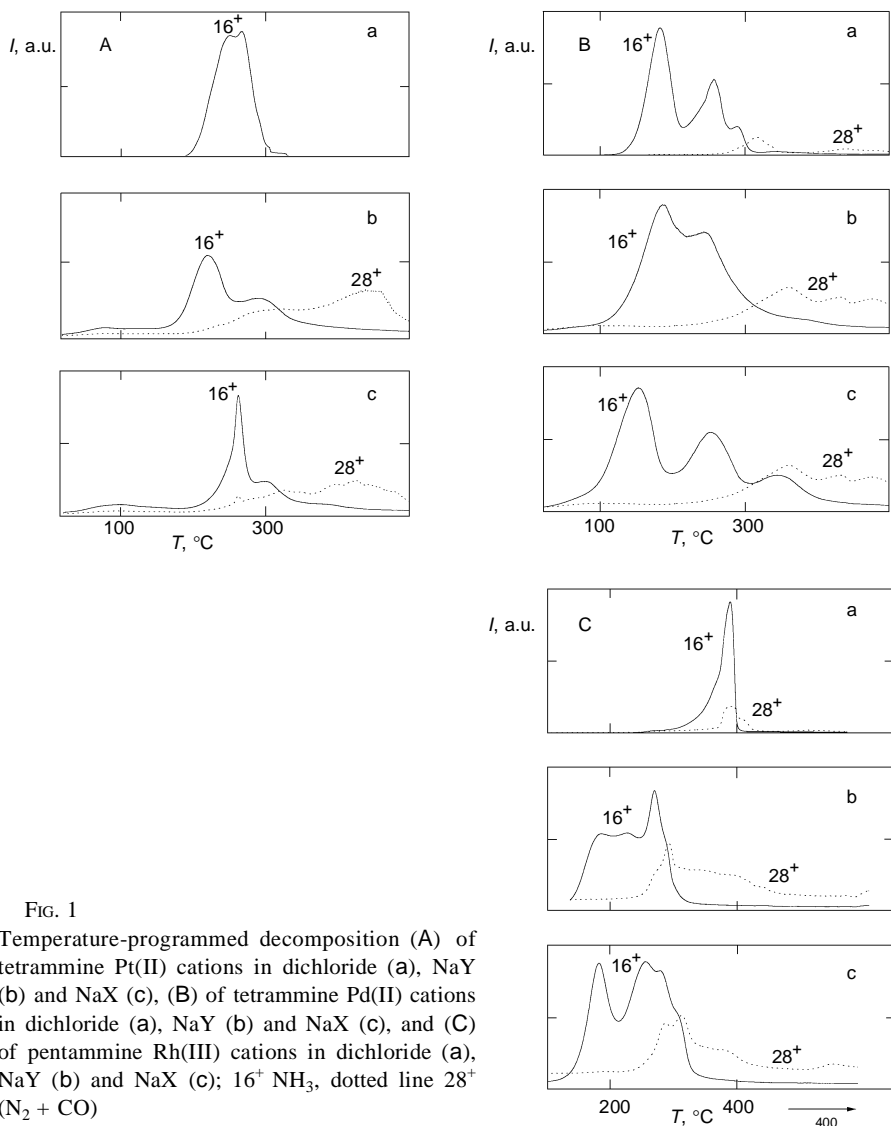


FIG. 1

Temperature-programmed decomposition (A) of tetrammine Pt(II) cations in dichloride (a), NaY (b) and NaX (c), (B) of tetrammine Pd(II) cations in dichloride (a), NaY (b) and NaX (c), and (C) of pentammine Rh(III) cations in dichloride (a), NaY (b) and NaX (c); 16^+ NH_3 , dotted line 28^+ ($\text{N}_2 + \text{CO}$)

the $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ complex decomposed at substantially higher temperature than the Rh pentammine cation in X and Y zeolites. The start of the decomposition lies at lower temperatures for Pd and Rh ammine complexes in zeolites (Figs 1B and 1C) than for those of Pt (Fig. 1A). Pt complexes in Y zeolites decompose at lower temperature compared with X zeolites. The opposite case stands for the decomposition of Pd and Rh complexes: it is more rapid in X than in Y zeolite.

Ammonia (ions 16^+ and 17^+) is the main gas product. It is accompanied by much smaller amount of ion 28^+ . The temperature dependence of the release of ion 28^+ is shown in Figs 1A–1C as a dotted line; the part which appears during the release of the first ammonia peak can be related predominantly to nitrogen, in the higher temperature region both nitrogen and CO are evolved. Some CO_2 is also released (not shown in the figure). Both carbon oxides originate from small amounts of decomposing carbonates present in the samples.

The effect of different alkali cations on the temperature of the ammonia release (the first low-temperature peak, related to the stability of the ammine ligands) is depicted in Fig. 2 for PtX and PtY zeolites. PdX and PdY sodium zeolites are also included to stress the difference from Pt sodium zeolite forms. It can be seen that for both platinum zeolite types, the deamination temperature decreases in the sequence $\text{Li} > \text{Na} > \text{K} > \text{Cs}$ and is lower for the Y than for the X zeolite (the alkali ion exchange of Cs is relatively low, especially in Y zeolite, so that the values of Cs-containing samples are not convincing). The Pd/NaX and Pd/NaY zeolites show a substantial lower deamination temperature and, opposite to Pt samples, are easier deaminated in X than in Y forms.

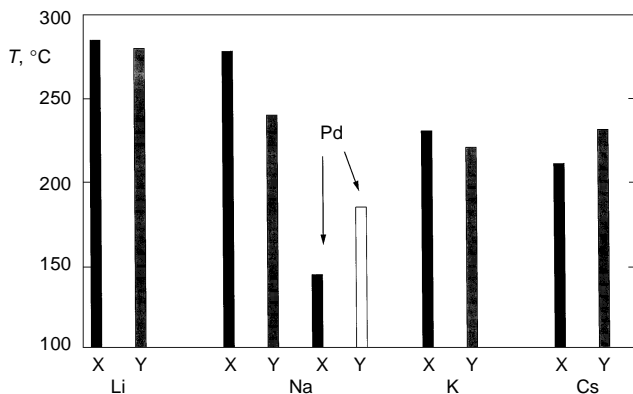


FIG. 2

Desorption temperature of the first ammonia peak in Pt/alkali X and Y zeolite; Pd/NaX and Pd/NaY shown for comparison

The NO + CO Reaction and Decomposition of the Surface Species

Pt/Alkali Faujasites

The reaction course (during the first 1.5 min, the same features are found for longer reaction times) over Pt/alkali X zeolites at 200 °C is shown in the left-hand side of Fig. 3. The decomposition of the surface species formed during this reaction is given in the right-hand side of the same figure. It follows that the reaction is accelerated in the sequence $K > Na > Li$, *i.e.*, it proceeds more readily with the increasing electropositivity and diameter of the alkali cation. Simultaneously, the increase in the amount of surface species occurs in the same cation sequence.

Figure 4 displays the course of the CO + NO reaction over Pt/NaY and Pt/NaX zeolites during 30 min at 260 °C. The higher rate over the Pt/NaX zeolite can be seen, the amount of surface species (not shown) is relatively low, especially for Pt/NaY. The effect of alkali cations and the difference between X and Y zeolite is summarized in Fig. 5, where the temperatures of 50% reduction of NO during the temperature programmed reaction are displayed. The temperature of the 50% NO reduction is much higher over Y than over X zeolite, and it decreases more rapidly from Li to K over X than over the Y zeolite.

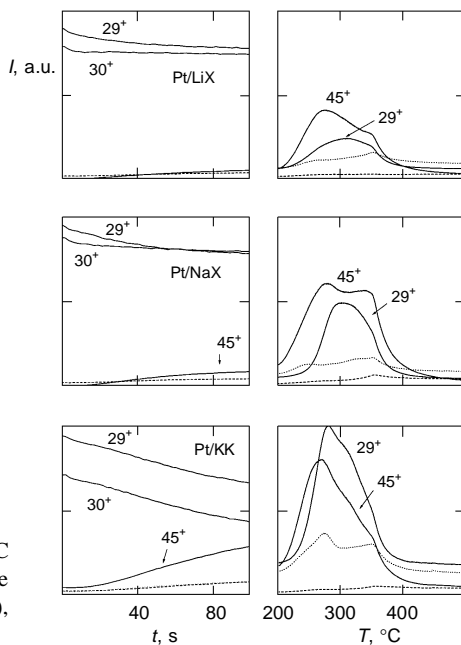


FIG. 3

The dependence of $^{13}\text{CO} + \text{NO}$ reaction at 200 °C over Pt/alkali X zeolites and TPD of surface species; left: reaction, right: TPD, ($\text{N}_2 \dots$), ($\text{N}_2\text{O} \text{---}$), ($29^+ \text{ }^{13}\text{CO}$, 30^+ NO , $45^+ \text{ }^{13}\text{CO}_2$)

Pd/Na Faujasites

The NO reduction by CO over Pd/NaX and Pd/NaY zeolites is shown in Fig. 6A at 200 °C, in Fig. 6B at 260 °C. The amount of surface species is relatively low and therefore is not depicted. A little higher conversion proceeds over the Pd/NaY than over Pd/NaX.

Rh/Na Faujasites

The reaction occurs at substantially lower temperature over Rh/NaX and Rh/NaY than over the preceding Pt and Pd zeolites: in Fig. 7, the reaction course at 200 °C is given, which is similar to those over Pt and Pd samples at 260 °C (*cf.* Figs 4 and 6B with Fig. 7).

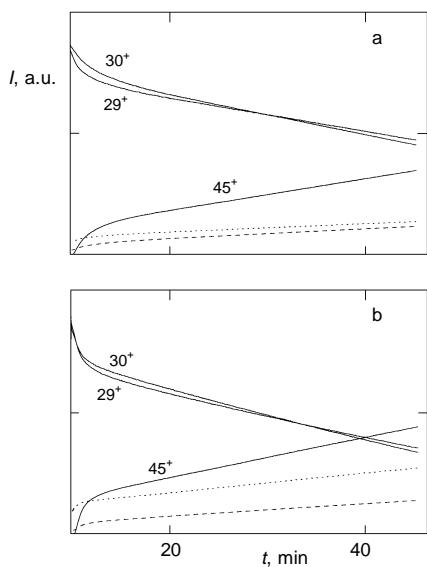


FIG. 4
The dependence of $^{13}\text{CO} + \text{NO}$ reaction over Pt/NaY (a) and Pt/NaX (b) zeolite at 260 °C; (N_2 ), (N_2O - - -), (29^+^{13}CO , 30^+NO , 45^+^{13}CO_2)

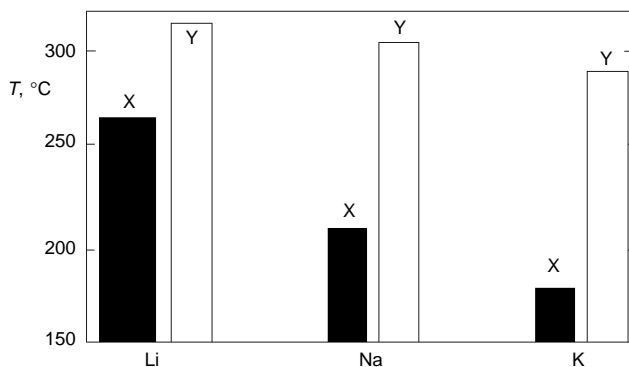


FIG. 5

Temperature of 50% conversion of NO in NO + CO reaction over Pt/alkali X and Y zeolites

As concerns *the products of the NO + CO reaction*: The only gaseous products are CO₂ (ion 45⁺) and N₂O (ion 44⁺) over Pt and Pd faujasites at temperatures below 230 °C (Figs 3 and 6A). The NO reduction to nitrogen proceeds above 230 °C, but it is still accompanied by a low yield of nitrous oxide (Figs 4 and 6B). Almost no N₂O is formed over Rh/NaX at 200 °C and above this temperature, but below 200 °C, a small fraction of nitrous oxide is also formed. A higher fraction of N₂O appears during the reaction over Rh/NaY zeolite (Fig. 7).

DISCUSSION

Removal of Ammine Ligands in Vacuum

The decomposition of the Pt and Pd tetrammine ions in zeolites during calcination was reported in review¹⁵, in vacuum in refs^{14,16-19}, and that of the Rh pentammine ions in vacuum in ref.²⁰. IR, UV-VIS and XPS spectra as well as the gaseous products released were employed to describe the deamination process. A stepwise removal of the ammine ligands, bonded after the water removal to the oxygens (not yet specified) of the

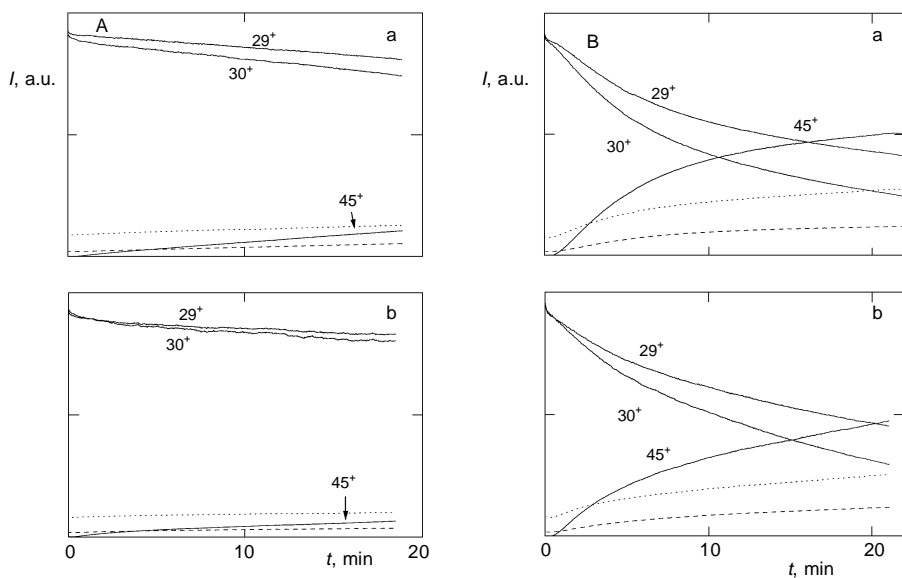
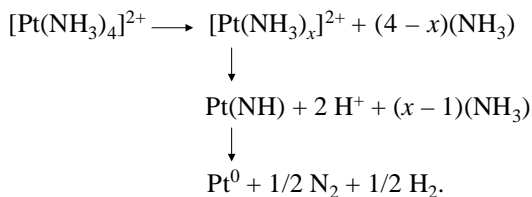


FIG. 6

The dependence of ¹³CO + NO reaction over Pd/NaY (a) and Pd/NaX (b) zeolite at 200 °C (A) and 260 °C (B); (N₂ ····), (N₂O ---), (29⁺ ¹³CO, 30⁺ NO, 45⁺ ¹³CO₂)

zeolitic framework has been found. Ammonium ions (at higher temperatures deammoniated to protons) are found to compensate the negative zeolite charge after the decomposition of the Pt, Pd and Rh ammine cations in vacuum, under which conditions most of the metallic ions is autoreduced to metallic state. Exner *et al.*¹⁶ suggested the following mechanism of the autoreduction for $[\text{Pt}(\text{NH}_3)_4]^{2+}$ complexes:



The vacuum decomposition of tetrammine Pt(II) ions in alkali X and Y examined in this study: it follows that the increasing electropositivity of the alkali cations shifts the decomposition temperature to lower values in both matrices (Fig. 2). The increasing electropositivity of alkali ions can thus weaken the bonds in positively charged $[\text{Pt}(\text{NH}_3)_4]^{2+}$. It is known that the basicity of oxygens of the zeolitic matrix increase in the sequence $\text{Li} < \text{Na} < \text{K} < \text{Cs}$ (refs²¹⁻²⁷) which also can increase the polarization of the complex and lead to its easier decomposition. However, the framework oxygens exhibit more basic features in X than in Y zeolites, which should lead, according to this simple assumption, to an easier decomposition of the complex in X zeolite. This does

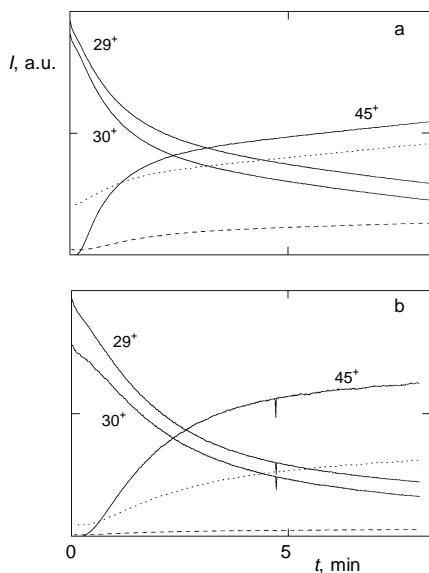


FIG. 7
The dependence of $^{13}\text{CO} + \text{NO}$ reaction over Rh/NaY (a) and Rh/NaX (b) zeolite at 200 °C; ($\text{N}_2 \dots$), ($\text{N}_2\text{O} \text{---}$), (^{13}CO , $^{13}\text{CO}_2$), (^{13}CO , NO), (^{13}CO , $^{13}\text{CO}_2$)

not agree with the higher temperature of the release of the first ammonia peak (see Figs 1A and 2; in our previous papers^{14,17-19}, no difference between these two zeolite types was reported which is correct when the temperature interval of all ammine removal is considered). In ref.²⁴ different basic strength of framework oxygens due to various location of cations is reported: *e.g.* for sodium forms it increases from sites I' to I and II in NaX compared to NaY. The IR as well as the XPS spectra show that after the removal of water ligands, different fractions of various Pt species in X and Y are formed and anchored to framework oxygens^{14,18} which is also reflected in higher fraction of "high" temperature peak in Y than in X zeolites (Fig. 1a and ref.¹⁴). Different cation location in both zeolite types can thus be responsible for the lower temperature of the beginning of deamination in PtY zeolite. Nevertheless, the ammine decomposition in Y zeolite exhibits the same dependence on the electropositivity of the alkali cations as that in X zeolite, which points to direct strong influence of the alkali cations.

The palladium and rhodium ammine complexes decompose at much lower temperature than those of platinum (Figs 1B, 1C vs Fig. 1A), which confirms less stable ligand bonds of these metals²⁸. This agrees with the literature data of the Pd and Rh decomposition of these complexes in zeolites^{16,20} in vacuum. Contrary to Pt, the Pd and Rh start of deamination proceeds more readily in X than in Y zeolites, which reflects the direct role of the enhancing activity of the basicity of zeolitic oxygens. A higher separation of the ammonia peaks with at least three maxima is seen in Fig. 1C during the deamination of Rh complexes than that reported in ref.²⁰, where two maxima of ammonia were found.

In parent dichlorides, a lower stability of the Pd tetrammine complex than of the same Pt complex was already reported²⁸. The decrease in the decomposition temperature in the sequence $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$ (ref.²⁸) agrees with the easier decomposition of the complex in more basic X zeolite (Figs 1B, 1C). The chloropentammineRh(III) dichloride behaves in quite different way than Pt and Pd tetrammine chlorides (the dissociation patterns of Pt and Pd tetrammine dichloride are similar to those in Y zeolite, see Figs 1A, 1B). The decomposition of the Rh complex alone proceeds at much higher temperature than that in zeolites, and only a small shoulder points to a two-step decomposition, while in zeolites at least three steps are clearly visible (Fig. 1C). The anchoring of Rh ammine complexes to the zeolite cavities allows thus to separate better the individual ammonia ligands removed during the temperature increase.

NO Reduction by CO

The increasing conversion in this reaction over Pt/alkali X and Y zeolites with increasing positivity of the alkali cation (Fig. 3) and, consequently, increasing basicity of zeolitic oxygens (due to these cations as well as to zeolite types) follows from Figs 3-5. The conversion can thus be related to the intermediate Sanderson electronegativity²⁹: it increases linearly with decreasing zeolite electronegativity³⁰.

The weakening of the C–O bond in the interaction of CO with transition metals due to the backdonation of metal electrons into the antibonding CO orbitals was assumed originally by Blyholder³¹ in 1964 and recently modified, *e.g.* in refs.^{32,33}. The backdonation should be higher in zeolites with more positive alkali ions²², and in X than in Y zeolites, which agrees with the above trend in the CO + NO reaction. The effect of zeolite electronegativity and classical bonding/antibonding should operate, even more strongly, also for NO molecules¹², the dissociation of which in the reaction proceeds.

As concerns the reaction products: below 210 °C, the only reaction products under the experimental conditions described are carbon dioxide and nitrous oxide ($\text{CO} + 2 \text{NO} \rightarrow \text{CO}_2 + \text{N}_2\text{O}$, Fig. 3); above this temperature, the almost complete reduction of NO to N_2 occurs, predominantly according to the scheme $\text{CO} + \text{NO} \rightarrow \text{CO}_2 + 1/2 \text{N}_2$ (Fig. 4).

The reaction course over Pd/NaX and Pd/NaY at 200 and 260 °C (Figs 6A, 6B) resembles that over platinum, but contrary to platinum, the reaction proceeds a little easier over Pd in Y than in X zeolite which can be most probably related to different electronic character of Pd.

Similarly to platinum, no nitrogen, only nitric oxide and carbon dioxide are found in the reaction products at 200 °C. A smaller fraction of N_2O at 260 °C also appears similarly to Pt/NaX and Pt/NaY (*cf.* Figs 4 and 6B).

The much lower temperature at which the CO + NO reaction proceeds over Rh/NaX and Rh/NaY agrees with the literature data. The reaction has been assumed to occur easier over Rh than over Pt and Pt due to the enhanced ability of Rh to dissociate NO (*e.g.* ref.¹) which is assigned to the Rh electronic structure¹², position of the Fermi level (NO antibonding orbitals above Fermi level for Rh, below for Pd and Pt, ref.¹⁰) or geometrical and dynamic properties¹¹. The literature data on the ability of rhodium to reduce NO_x to N_2 or N_2O are a little controversial: The reduction of NO by methane to N_2O over supported Rh was reported in ref.⁹, the reduction to dinitrogen, *e.g.*, in ref.¹. Our experiments show virtually no nitrous oxide over Rh/NaX and some N_2O fraction over Rh/NaY under identical experimental conditions (Fig. 7). The Rh environment thus seems to play a role in the completeness of the reduction of nitric oxide.

CONCLUSIONS

The decomposition of the parent ammine complexes in faujasites was found to be affected by (i) electropositivity (and number) of alkali co-cations, (ii) basicity of the framework oxygens – on the one hand influenced by the nature of the alkali cations and, on the other hand, by the zeolite Si/Al ratio, and (iii) by the noble metal itself. Deamination of platinum tetrammine complexes is enhanced by increasing electropositivity of the alkali co-cations and by the increased Si/Al ratio. It is not yet clear whether the latter factor (which should exhibit an opposite effect) can be related to the different location of alkali co-cations in X and Y zeolites. Palladium and rhodium ammine complexes are decomposed much more easier than corresponding platinum com-

plexes, which is related to the lower ligand stability of Pd and Rh complexes. The decomposition occurs more readily in X than in Y zeolites which agrees with higher basicity of framework oxygens interacting with positively charged Pd and Rh ammine complexes.

The NO reduction by CO over platinum in X and Y zeolites is accelerated by the increasing electropositivity of alkali co-cations and decreasing Si/Al ratio in faujasite, which can be related to the decreasing Sanderson intermediate electronegativity. The course as well as the composition of reaction products over palladium are similar to that over platinum except for the opposite effect of the zeolitic Si/Al ratio. The reaction over rhodium in sodium faujasites was found to proceed much easier compared with platinum and palladium in the same zeolitic matrices.

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