REACTION OF NITRIC OXIDE ADSORBED ON PLATINUM CLUSTERS IN X ZEOLITES. EFFECT OF CLUSTER SIZE AND NATURE OF ALKALI CATIONS

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Adsorption and temperature-programmed desorption of NO was studied over Pt/alkali zeolites. Platinum clusters of three different sizes were prepared by different decomposition routes of $[Pt(NH_3)_4]^{2+}$ partially ion-exchanged in NaX zeolite. The effect of various alkali ions (Li, Na and K) was also examined. Similarly to platinum supported by alumina, the conversion of adsorbed NO to nitrogen increases with increasing Pt particle size. Increasing electropositivity of the alkali cations shifts the desorption to lower temperatures.

Key words: NO; Zeolites; Pt/X; Platinum clusters; Adsorption; Alkali cations; Heterogeneous catalysis.

The NO adsorption and temperature-programmed desorption (TPD) have been extensively investigated over pure platinum crystals[1–5]; however, much less attention has been paid to NO on supported platinum[6,7]. The former studies report on the NO dissociation over various crystallographic planes, especially Pt(111) (refs[1–3]). Gorte *et al.*[2] found that this plane, if perfect, is quite inactive. Pt(100) and Pt(110) were reported to be only slightly active[1,2], whereas the (210) and (410) planes exhibited the highest activity[5]. According to ref.[6], the NO dissociation over supported platinum increased with decreasing Pt dispersion. Studies concerning effects of platinum dispersion in zeolites on NO dissociation have not been published yet, in contrast to the interaction of CO with platinum clusters in zeolites: both strengthening of the Pt–C bond and weakening of the C–O bond with decreasing Pt particle size were reported[8,9]. This could be explained by an increase in the density of negative charge on small Pt clusters. A similar effect, weakening of the C–O bond, has been assumed for CO adsorbed on alkali zeolites and Pt/alkali zeolites with increasing electropositivity of alkali cations (Li < Na < K < Cs), for example in ref.[10]. The increase in basicity of zeolite oxygens occurs in the same sequence[11–15]; the back-donation of the negative charge to 2π* antibonding orbitals of CO resulting in the weakening of the C–O bond was assumed[16–18]. The aim of the present contribution is to address these problems, *i.e.*, the effects of the Pt particle size and of the nature of alkali cations in Pt/alkali X zeolites on the NO dissociation.

EXPERIMENTAL

Catalysts. NaX zeolite with Si/Al 1.25 was supplied by Serva, Germany. Li and K were introduced by ion exchange from the respective nitrates. The alkali cations were ion-exchanged with $[Pt(NH_3)_4]Cl_2$ (Aldrich Chemicals) for eight days at room temperature (RT). The catalyst composition is given in Table I. The Pt zeolite used for the ammine decomposition and subsequent reaction with NO was *ca* 30 mg keeping constant the Pt amount of 3.85 μmol.

Decomposition of the $[Pt(NH_3)_4]^{2+}$ complex in alkali X zeolites. Three ways described in refs[19–22] were used, leading to Pt clusters of defined size:

a) Slow decomposition in an oxygen stream followed by H_2 reduction leading to small Pt clusters (1–2 nm). Decomposition of the $[Pt(NH_3)_4]^{2+}$ complex was carried out in an oxygen stream using the temperature increase of 2 °C/min to 380 °C, at which temperature the sample was held for 4 h. Then, after purging oxygen and argon, the sample was reduced in a hydrogen stream at 350 °C for 2 h.

b) Vacuum decomposition leading to medium Pt clusters (1–4 nm) in LiX, NaX and KX. The samples were evacuated until the pressure dropped below 0.5 Pa (measured by an MKS Baratron). Then they were dehydrated by heating to 130 °C (2 °C/min) until the pressure dropped below 0.2 Pa. The decomposition of the $[Pt(NH_3)_4]^{2+}$ complex was performed by heating at 5 °C/min to 380 °C. The majority of Pt^{2+} ions was autoreduced[23,24] during this procedure to Pt^0, the remaining Pt^{2+} was reduced *in situ* with hydrogen, after combustion of some carbon deposits in low-pressure oxygen atmosphere.

c) Rapid decomposition in hydrogen stream giving large Pt particles (>5 nm), partially located at the outer surface of zeolitic grains. They were prepared from the $[Pt(NH_3)_4]^{2+}$ complex by a heating rate of 10 °C/min to 380 °C in a hydrogen stream for 2 h.

TABLE I
Pt content and ion exchange in zeolites

Zeolite	Pt, wt%[a]	Pt atoms/unit cell	Ion exchange, %	
			Pt	alkali
Pt/LiX	3.2	3.0	7	57
Pt/NaX	2.5	2.5	6	86
Pt/KX	2.6	2.8	7	84

[a] In undried sample.

The size of Pt clusters prepared in NaX and KX by two former procedures was checked by TEM (Philips EM420 at the University of Bremen)[23]; the ratios of the irreversibly bonded NO to Pt (Table II) confirmed the decreasing Pt particle size prepared by the three procedures. The Pt clusters will be denoted in the following text by subscripts S for small, M for medium, and L for large Pt particles.

Adsorption of NO. NO (99.5%) was supplied by Messer Griesheim. The amount of NO adsorbed at an equilibrium pressure of 90–180 Pa and NO amounts gradually desorbed at RT were measured volumetrically using MKS Baratron for a pressure range 0.02–200 Pa. The amount of the irreversibly adsorbed NO ($NO_{irr} = NO_{ads} - NO_{des}$) was calculated from these measurements.

TPD. Pt/alkali X with calculated NO_{irr} were heated in vacuum at 10 °C/min to 380 °C. Gas products were fed directly to a Balzers QMG 420 mass spectrometer. An auxiliary diffusion oil pump was employed. The pressure during TPD was lower than 0.1 Pa. Intensities of the molecular ions of NO ($m/z = 30$), N_2O (44), N_2 (28) and O_2 (32) were approximately proportional to the pressure of these gases. The peak at m/z 30 was corrected for the contribution of the fragment ion NO^+ from the molecular ion N_2O^+. The background of CO ($m/z = 28$) was negligible. CO_2 ($m/z = 44$) desorbed below 100 °C. Therefore this part of N_2O curves was omitted.

RESULTS

Effect of the Nature of Alkali Cations on the Irreversible NO Adsorption and on the Composition of TPD Products. Pt_M Clusters

Table II displays values of the ratios of NO_{irr}/Pt (adsorption checked by volumetric measurements at RT), conversion of NO_{irr} calculated as 2 (N_2 +

TABLE II
NO_{irr} over medium Pt clusters in X zeolite containing Li, Na and K cations; NO_{irr} over small, medium and large Pt clusters in NaX zeolite

Zeolite	NO_{irr}/Pt[a]	Conversion[b]	N_2/N_2O[b]	N_2 yield[c]	O/Pt[d]
Pt_M/LiX	0.23	70	3	0.12	0.14
Pt_M/NaX	0.35	75	2	0.18	0.22
Pt_M/KX	0.34	70	2	0.16	0.20
Pt_S/NaX	0.74	40	1.5	0.18	0.24
Pt_M/NaX	0.35	75	2	0.18	0 22
Pt_L/NaX	0.15	90	8	0.12	0.13

[a] Volumetric measurements of irreversible NO adsorption at RT. [b] From integrated TPD curves. [c] Desorbed N/Pt ratio. [d] Oxygen adsorbed on Pt during TPD.

N_2O)/(2 N_2 + 2 N_2O + NO) from integrated TPD curves, yield of N_2, N_2/N_2O ratios and O/Pt ratios (calculated from the NO_{irr}/Pt ratio, conversion of NO_{irr} and N_2/N_2O ratio). It follows that the amount of NO_{irr} is almost the same for Pt/NaX and Pt/KX; Pt/LiX exhibits a lower value. The extent of NO_{irr} conversion is almost the same for all the samples, the amount of nitrogen exceeds that of nitrous oxide more in Pt/LiX than in the two other zeolites, and the oxygen left per Pt is, due to a small NO_{irr} amount, lower for Pt/LiX. Also the yield of nitrogen is a little lower over Pt/LiX than over the sodium and potassium forms.

The TPD curves for the three catalysts are shown in Fig. 1. Unreacted NO is released from Pt/LiX in one "low-temperature" peak, while from both Pt/NaX and Pt/KX a second, "high-temperature" peak, is found. The first maximum occurs below 100 °C, the second below 200 °C, for Pt/KX at lower temperature than for Pt/NaX. The desorption of nitrogen also occurs in one peak for Pt/LiX and in two peaks for sodium and potassium zeolite forms. The temperature maxima are shifted to lower temperatures going from Li to K ("low-temperature" maximum at 160, 140 and 130 °C, respec-

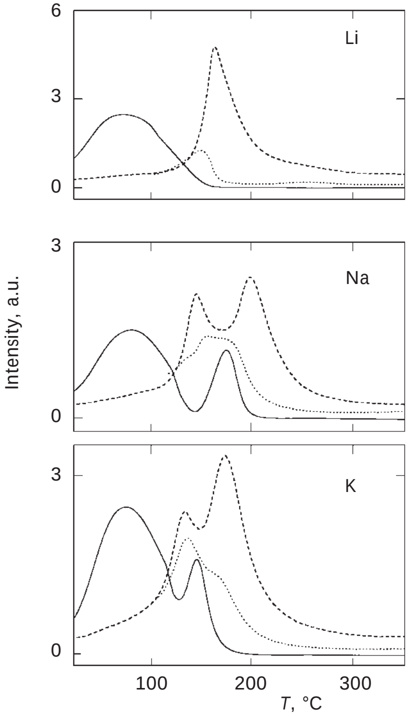

FIG. 1
Effect of various alkali cations in Pt_M/X zeolite on the reaction of NO_{irr} during the TPD; — NO, ····· N_2O, – – – N_2

tively, "high-temperature" maximum at 200 and 170 °C for Pt/NaX and Pt/KX, respectively). The desorption of N_2O corresponds with that of N_2.

It is worth mentioning that the above described features are those of reduced Pt clusters (Pt^0). The NO_{irr}/Pt ratio was the same over oxidized Pt clusters (PtO_x); however, the NO_{irr} conversion was low.

Effect of the Size of Pt^0 Clusters in Pt/NaX Zeolite

Table II lists the same items for Pt_S, Pt_M and Pt_L clusters in NaX zeolite as are those for Pt_M clusters in X zeolite with various alkali cations (the row for Pt_M/NaX is repeated for comparison). It can be seen that the NO_{irr}/Pt ratio decreases with increasing size of Pt^0 particles, while the NO_{irr} conversion and the N_2/N_2O ratio increase. The O/Pt ratio correlates approximately with the yield of nitrogen although the N_2/N_2O ratio varies.

The corresponding TPD curves are given in Fig. 2. The high conversion of small amounts of NO_{irr} over Pt_L results in a very low amount of unreacted NO_{irr} in one "low-temperature" peak; the "high-temperature" peak is com-

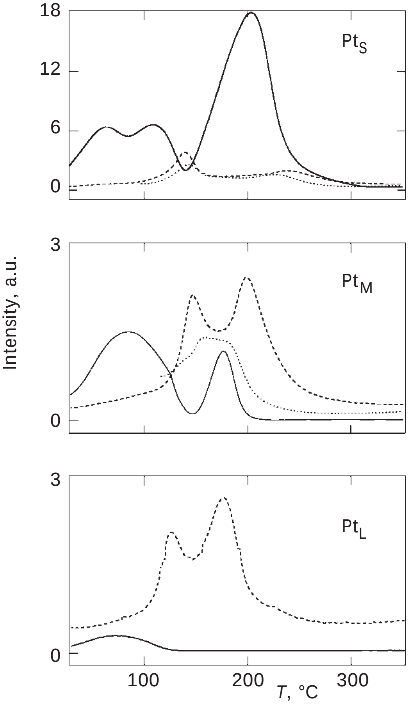

FIG. 2
Effect of Pt cluster size in NaX zeolite on the reaction of NO_{irr} during the TPD; — NO, ····· N_2O, – – – N_2

pletely converted to nitrogen. Two to three maxima of unreacted NO_{irr} can be seen for NaX with Pt_S and Pt_M. Their peakening proceeds at lower temperature over Pt_M than Pt_S. The desorption of nitrogen occurs in two maxima, the proportion in the "high-temperature" one increases from Pt_S to Pt_L. Both maxima are shifted to lower temperatures in the same sequence: the "low-temperature" peak from 140 to 125 °C, the "high-temperature" from 240 to 170 °C.

The O/Pt ratio suggests partial oxidation (chemisorption of oxygen?) of platinum during the conversion of NO_{irr}. It is interesting that after the first adsorption and TPD run over Pt_S, oxygen occupying *ca* 25% of Pt (Table II) almost completely poisons the active sites, so that the repeated run (NO adsorption and TPD) yields virtually no nitrogen. This is not the case with Pt_M and Pt_L clusters, over which the runs can be repeated with NO_{irr} conversion decreasing with repetitions. After four to five successive runs, Pt_M clusters are already poisoned by oxygen while Pt_L clusters still exhibit a considerable conversion. In all three cases, the Pt deactivation is indicated by an increase in the "high-temperature" NO peak. This peak increases very slowly just over Pt_L clusters.

DISCUSSION

It should be mentioned that the above results can be related to the presence of platinum clusters in the zeolites; similar experiments with pure alkali zeolite showed only negligible NO adsorption without detectable conversion to nitrogen or nitrous oxide.

Effect of Alkali Ions on Pt_M Clusters in X Zeolite

The increase in basicity of zeolite oxygens with increasing electropositivity of charge-balancing alkali cations was confirmed by many authors using different experimental and theoretical methods[11–15]. The negative charge on framework oxygens is expected to be transferred to Pt clusters, which, interacting with CO, back-donate the electrons to the vacant $2\pi^*$ antibonding orbitals of CO, strengthen the Pt–C bond and weaken thus the C–O bond[16–18]. If this also holds for the vacant $2\pi^*$ orbital of NO molecule[18], easier dissociation of NO (resulting in the desorption of nitrogen at lower temperature) can also be expected in the sequence Pt/LiX → Pt/NaX → Pt/KX. This order was actually found, as follows from Fig. 1 and as was also reported for the NO–CO reaction over these catalysts[25]. The desorption of unreacted NO occurring from all three samples within the low-temperature maximum below 100 °C can be assigned to physically adsorbed species. This is immediately followed by evolution of nitrogen and nitrous oxide, which might be partially due to the desorption of unreacted N_2O (whose presence is supported by the IR spectra frequencies found at 2 248 cm^{-1}, unpublished results) and partially to its decomposition by the reaction

$$N_2O \rightarrow NO + 1/2\ N_2 \quad . \qquad (1)$$

The NO formed *via* this reaction can be present in Pt/LiX in the descending TPD curve of NO which is broader than those from Pt/NaX and Pt/KX. The "high-temperature" desorption peak of nitrogen can be assigned to the direct decomposition of more firmly bonded NO to N_2, and oxidation of platinum:

$$NO \rightarrow 1/2\ N_2 + Pt\text{–}O \quad . \qquad (2)$$

Desorption maxima of products, corresponding to reactions (*1*) and (*2*), are shifted to lower temperatures with increasing electropositivity (and dimensions) of the alkali ions and, consequently, with increasing basicity of zeolitic oxygens. If the reaction scheme is correct, the more pronounced reaction (*2*) going from lithium to potassium Pt/X can be explained by higher fractions of more strongly held Pt–NO species with more weakened N–O bond.

Effect of Pt^0 Cluster Size on the Conversion of NO_{irr} Over Pt/NaX

While the effects of various alkali ions on the conversion of NO reasonably agree with the weakening of N–O bond due to back-donation of electrons into the antibonding $2\pi^*$ orbitals of NO with increasing basicity of framework oxygens, the effects of the size of Pt clusters seem to contradict these conclusions. It has been found that the increased Pt dispersion leads to the increased negative cluster charge[8,9]. If this is the only and governing factor, the opposite behaviour to that shown in Fig. 2 and Table II should occur. However, it appears that the conversion of NO_{irr} increases from small to large Pt clusters. This finding agrees with the results of Altman and Gorte[6], as well as with the Pt particle size effect on the CO–NO reaction reported, *e.g.*, in ref.[26]. The increased conversion of NO_{irr} is accompanied by a larger "high-temperature" proportion of nitrogen and by a shift of both N_2 desorption peaks to lower temperatures, similarly to the effect of more electropositive alkali cations. These controversial results (Pt/alkali X *vs* Pt cluster size) can be explained either by a false assumption of the strong electron back-donation in the case of small Pt clusters or by an "ensemble effect", overwhelming the different charges on the Pt clusters of different size. This "ensemble effect", *i.e.*, the presence of neighbouring active sites (or suitable crystallographic planes, see above) necessary for the NO dissociation, might be present on larger but not on smaller Pt particles.

The irreversibly adsorbed NO (or at least longer contact times at higher temperatures) seems to be the necessary condition for the NO conversion. Large Pt clusters allow not only very high conversion (Table II), but also repeated cycles (NO adsorption and TPD) with N_2 yield slowly decreasing[7]. Such repetition is also possible on Pt_M but not over Pt_S. This can be explained by two ways:

a) The density of sites active in NO dissociation decreases with the Pt cluster size.

b) Surface oxygen, formed by NO dissociation and blocking the active sites, moves to Pt sublayers the number of which decreases with the Pt cluster size. There are no sublayers in small Pt clusters <1 nm (dispersion = 1).

Another factor which cannot be associated with the charge on Pt^0 clusters is the location of these clusters[20]: the Pt_L clusters must be located either in a partially destroyed zeolite structure or even in the surface grains, and thus could more readily convert the adsorbed NO. If this is the only case, it cannot be simply applied to the effect of alkali ions, which do not bring about such drastic changes in Pt location.

CONCLUSIONS

a) The increasing electropositivity of the alkali cations (Li < Na < K) and, consequently, the higher basicity of zeolitic oxygens, result in a more negative charge on Pt clusters and thus in the weakening of the N–O bond and in the enhanced NO dissociation.

b) The higher conversion of irreversibly adsorbed NO over larger Pt clusters is due either to a higher number of active sites or to the penetration of surface oxygen into the Pt bulk.

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