

THE INTERACTION OF NITRIC OXIDE WITH PLATINUM AND PLATINUM–SILVER CATALYSTS

K.P. DE JONG *, G.R. MEIMA and J.W. GEUS

Department of Inorganic Chemistry, University of Utrecht, Croesestraat 77A, 3522 AD Utrecht, The Netherlands

Received 23 June 1982; accepted for publication 7 September 1982

The interaction of NO with Pt/SiO₂ and PtAg/SiO₂ catalysts is investigated by infrared spectroscopy, volumetric chemisorption and mass spectrometry. Room temperature adsorption of NO on the reduced Pt/SiO₂ catalyst mainly leads to molecular adsorption, accompanied by a small N₂ production. Infrared spectra reveal absorption bands at 1780 and 1600 cm⁻¹, ascribed to the stretching vibrations of linearly and bridged bonded NO species, respectively. Furthermore, a weak band at 1935 cm⁻¹ is observed. This high-frequency band is strongly enhanced when NO is dosed at elevated temperatures and is attributed to NO bound to Pt sites in the neighbourhood of adsorbed oxygen atoms. Reaction of NO with Pt/SiO₂ at 400°C leads to a limited dissociation of NO, producing N₂ in the gas phase and leaving oxygen atoms to remain on the catalyst surface. With the PtAg/SiO₂ catalysts the 1600 cm⁻¹ band is absent, while the activity for NO dissociation has been lowered as compared to Pt/SiO₂. Alloying of Pt with Ag diminishes the amount of bridged bonded species which seem to precede dissociation, whereas linearly bonded species desorb molecularly at high temperatures. Investigations of the catalysts after oxidation at 400°C in 1 atm O₂ show the adsorption of NO to be weaker and non-dissociative even at 400°C.

1. Introduction

The importance of removal of NO as an air pollutant has stimulated the study of its adsorption and decomposition on platinum surfaces. Work with single crystals of platinum has provided detailed insight in the bonding and reactivity of NO. Techniques such as XPS [1,2], LEED and AES [1–5], TPD [3–6] and EELS [4,5,7] have established the adsorption to be molecular at room temperature. Adsorption at low temperatures followed by heating showed the dissociation of adsorbed NO to start at around 100°C [1]. Although the extent of dissociation of NO on the different crystallographic planes is a matter of considerable discussion and confusion in the literature, the role of crystallographic anisotropy on NO adsorption has been proven [6]. Gland [8] showed, moreover, that a small amount of adsorbed oxygen inhibited the decomposition of NO.

* Present address: Koninklijke/Shell-Laboratorium, Badhuisweg 3, 1031 CM Amsterdam, The Netherlands.

Working with supported platinum catalysts, several authors report on infrared spectra of adsorbed NO [9–13]. Solymosi et al. [13] established the extent of adsorption both with reduced and oxidized samples. It cannot be said, however, that the interaction of NO with supported platinum catalysts is understood in great detail.

Results obtained with small supported Pt particles are hard to interpret because of the unknown surface structure of the particles. Modification of the platinum surface cannot be achieved with supported samples as easily as with single crystals. An important procedure to modify platinum particles is by alloying with a relatively inactive IB metal. Alloying can give more information on geometric and electronic factors which influence the bonding and reactivity of adsorbed molecules [14]. Furthermore, a complete set of vibrational frequencies of NO on the low-index planes of platinum has been obtained recently [6]. Infrared spectra of NO adsorbed on the supported samples, therefore, offer a possibility to gain insight in the surface structure of the metal particles.

In this work we have investigated the interaction of NO with a silica-supported platinum catalyst and two platinum–silver bimetallic catalysts. The interaction was studied in the temperature range of 25–400°C. The catalysts were subjected to reducing and oxidizing pretreatments. The techniques used were transmission infrared spectroscopy and volumetric chemisorption combined with mass spectrometry.

2. Experimental

The platinum catalyst investigated was 6 wt% Pt-on-silica supplied by Johnson Matthey and proposed as a common standard (Eurocat). Both hydrogen chemisorption and electron microscopy revealed the surface-average particle size to be 23 Å. PtAg/SiO₂ catalysts were prepared by using the Pt/SiO₂ catalyst as a starting material. Selective deposition of Ag onto the metal particles of the Pt/SiO₂ catalyst suspended in an aqueous silver solution was effected by reduction of Ag(NH₃)₂⁺ with Formalin. This preparation technique assured a very homogeneous distribution of the alloy particles over the support. The size of the majority of the particles ranged from 20 to 50 Å. Details about the preparation method and the characterization of the catalysts have been dealt with before [15]. In this work we used PtAg/SiO₂ catalysts F2 and F6 containing 64 and 31 at% Ag, respectively.

The infrared spectroscopic investigations were performed using the pressed disk technique. Details of both the transmission infrared measurements and the vacuum system used have been described before [16,17]. The spectra were always recorded at room temperature and corrected for background absorption of the silica support. Under our conditions of temperature and pressure no adsorption of NO on the blank support could be detected.

Volumetric determination of the extent of adsorption was done by means of a Pyrex high vacuum and gas supply system. A catalyst sample of 0.6 to 0.8 g was used for the experiments. The system had been equipped with a quadrupole mass spectrometer (Leybold Heraeus, QM 200). Two types of experiments with the mass spectrometer were done to study the reaction of NO with the catalysts. In experiments at constant temperature an amount of NO (2.34 ml (STP)) was dosed to the catalyst followed by establishment of a small leak to the sensing head of the spectrometer, which allowed a continuous monitoring of the gas phase. Temperature-programmed desorption (TPD) experiments were carried out after dosing of NO and evacuating the sample at room temperature. Heating the sample at a rate of about 6°C/min was accompanied by continuous evacuation and analysis of the gas phase with the mass spectrometer.

The pretreatment of the samples used in the infrared and volumetric experiments was similar. The samples were reduced in a flow of 10% H₂ and 90% Ar at 400°C overnight, followed by outgassing at that temperature for 2 h. Oxidation of the catalysts was done by keeping them overnight in a flow of 1 atm O₂ at 400°C. Prior to the experiments described in this paper, the catalysts had been subjected to repeated oxidation–reduction treatments to remove all impurities and to obtain a reproducible chemisorption behaviour [17].

3. Results

3.1. Infrared spectroscopy

NO was dosed to the reduced 6wt% Pt/SiO₂ catalyst at room temperature. The spectra were recorded at room temperature both in the presence of gaseous NO and after evacuation at a series of increasing temperatures (fig. 1). In the presence of gaseous NO an intense absorption band with its maximum at 1780 cm⁻¹ was observed, together with much weaker bands at 1600 and 1935 cm⁻¹. Evacuation at temperatures up to 150°C shifted the main peak to slightly higher frequencies (1815 cm⁻¹), whilst its integrated intensity dropped. The band at 1600 cm⁻¹, however, showed a remarkable growth. Evacuation at 250°C removed the infrared-active species for the greater part. At this point we cannot decide whether desorption or dissociation of the adsorbed NO molecules is responsible for the phenomena observed.

In fig. 2 the spectra for NO adsorbed on the reduced Pt and PtAg catalysts are compared. Catalyst F6 (containing 31 at% Ag) exhibited the main absorption band at 1795 cm⁻¹. Comparison with Pt/SiO₂ showed the low-frequency side of the band to have dropped markedly. Moreover, the band at 1600 cm⁻¹ had disappeared almost completely. The higher silver content of catalyst F2 led to a further drop of the intensity, while the band maximum was now observed

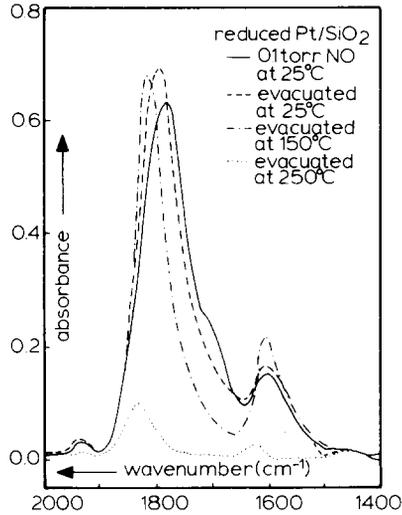


Fig. 1. Infrared spectra of NO adsorbed at room temperature on the 6 wt% Pt/SiO₂ catalyst which had been previously reduced and outgassed at 400°C.

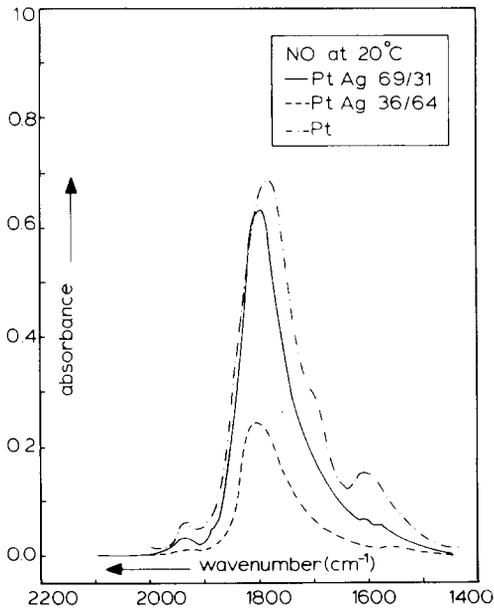


Fig. 2. Infrared spectra of NO adsorbed at room temperature on Pt/SiO₂ (·-·-·) and PtAg/SiO₂ catalysts F6 (—) and F2 (---).

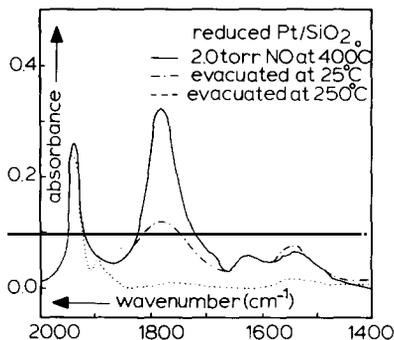


Fig. 3. Infrared spectra measured after exposure of Pt/SiO₂ to NO at 400°C and subsequent cooling down to room temperature.

at 1805 cm⁻¹. As reported before [17], the integrated intensity of the bands plotted against the alloy composition showed a straight line. It was concluded that the bulk and surface compositions of the PtAg particles are similar and that NO is a suitable adsorbate to estimate the number of Pt atoms in the alloy surface.

Dosing of 2.0 Torr NO to the reduced platinum catalyst at 400°C and cooling down to room temperature led to the spectra of fig. 3. The appearance of an intense band at 1935 cm⁻¹, which was very stable against evacuation, is most remarkable. In the presence of gaseous NO a band at 1780 cm⁻¹ was observed. The low stability of this band against evacuation showed it to be due to an adsorbed species quite different from that present after exposure to NO at room temperature (fig. 1). Besides the bands at 1935 and 1780 cm⁻¹, weak bands were observed in the frequency range of 1400–1700 cm⁻¹.

Comparison of Pt/SiO₂ and PtAg/SiO₂ catalyst F2 after dosing of NO at 400°C, showed that the band at 1935 cm⁻¹ had decreased with the bimetallic catalyst (fig. 4). Moreover, the main absorption band had shifted to 1820 cm⁻¹

Table 1

Adsorbed amounts of NO and H₂ in ml(STP)/g catalyst both for reduced and oxidized catalysts; the oxidation was performed at 400°C in 1 atm O₂

Catalyst	Reduced		Oxidized NO
	H ₂	NO	
Pt/SiO ₂	3.35	2.67 (3.38 ^{a)})	1.45
PtAg/SiO ₂ - F6	2.65	2.19	1.31
PtAg/SiO ₂ - F2	0.90	0.71	0.37

^{a)} Value determined from an isotherm.

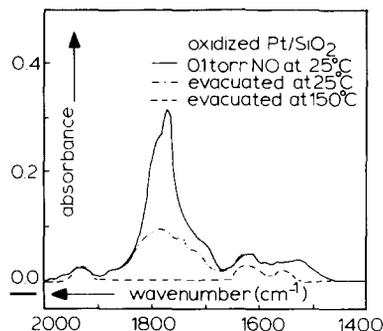
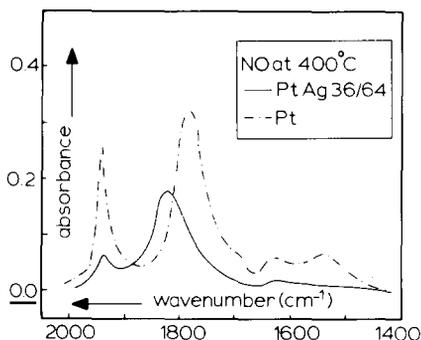


Fig. 4. Infrared spectra measured after exposure of Pt/SiO₂ and PtAg/SiO₂ (catalyst F2) to NO at 400°C and subsequent cooling down to room temperature.

Fig. 5. Infrared spectra of NO adsorbed on Pt/SiO₂ previously oxidized at 400°C in 10 Torr O₂.

and the structureless bands at low frequencies had disappeared.

An extensive study was also made with previously oxidized catalysts. The interaction with NO was investigated after oxidation with 10 Torr O₂ both at 25 and 400°C. Although the oxidation procedure caused some minor differences of the infrared spectra, we will restrict ourselves to the adsorption of 0.1 Torr NO at room temperature on Pt/SiO₂ after oxidation at 400°C (fig. 5). The main absorption band was found at similar frequencies as before, viz. 1770 cm⁻¹. The band at 1935 cm⁻¹ was very weak and some weak absorptions at 1450–1700 cm⁻¹ were observed. Evacuation at room temperature brought about a strong decrease of the main peak.

3.2. Volumetric and mass spectrometric results

The extent of adsorption of NO at room temperature has been determined with reduced and oxidized samples. The uptake of NO was measured by dosing of 2.34 ml (STP) to the sample and recording the pressure as a function of time for at least 1 h. The values tabulated were found by extrapolation of the slowly declining part of the curve to zero time. The data of NO adsorption collected in table 1 have been extended with H₂ chemisorption measurements. The H₂ volumes were determined from the isotherms (0–10 Torr) by extrapolation to the zero-pressure axis. With the reduced Pt/SiO₂ catalyst the adsorption of NO was also measured from an isotherm; the value obtained is added to table 1. With the mass spectrometer it was observed that exposure of NO to the reduced samples at room temperature led to an amount of N₂ in the gas phase of at most 5%. Apparently, NO only dissociates to a small extent at ambient temperatures. With the oxidized sample, room temperature adsorption

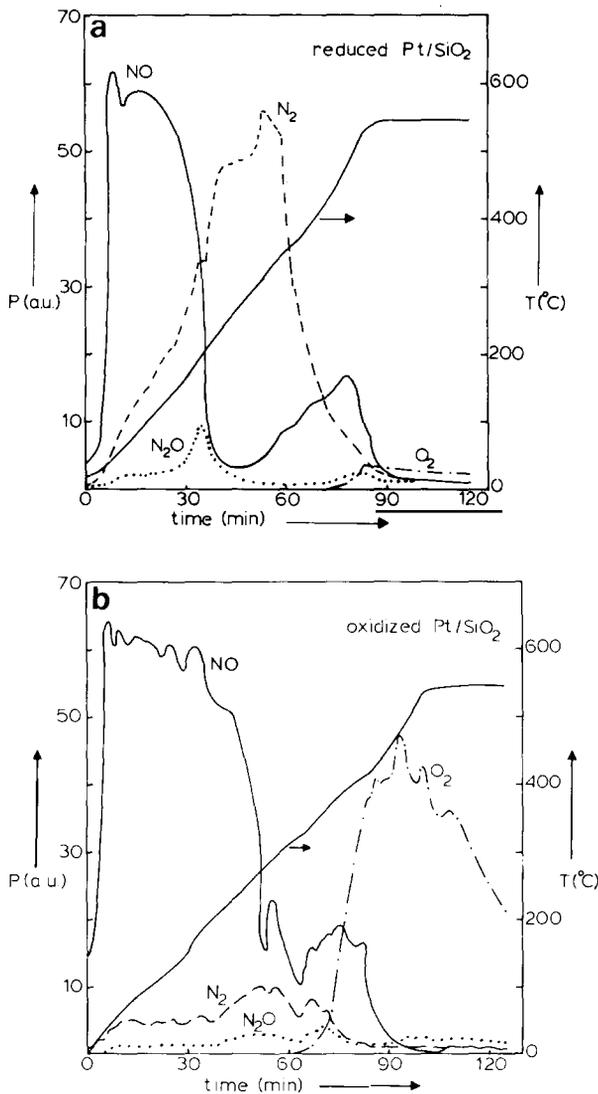


Fig. 6. TPD experiments after adsorption of NO and evacuation, both at room temperature. The Pt/SiO₂ catalyst had been previously reduced (a) and oxidized in 1 atm O₂ at 400°C (b).

did not produce N₂ in the gas atmosphere.

TPD experiments provided further information concerning the surface reactions of adsorbed NO. An experiment with the reduced Pt/SiO₂ catalyst has been represented in fig. 6a. Just above room temperature both NO and N₂ started to desorb. The peak in the TPD spectrum appeared at around 100°C

for NO and at 300°C for N₂. At 450°C a second desorption peak for NO was found. The desorption of N₂O and O₂ was very limited. This experiment shows that NO species on reduced Pt/SiO₂ either desorb molecularly or dissociate to produce gaseous N₂ and adsorbed oxygen atoms. The dissociation of NO, although starting at around room temperature, becomes significant at elevated temperatures. With the reduced alloy catalysts it was observed that with increasing silver content the desorption of N₂ was suppressed, while that of NO became predominant.

The TPD spectrum for oxidized Pt/SiO₂ is shown in fig. 6b. A most important feature of the spectrum was the large peak of NO right on from ambient temperature. At 350°C O₂ started to desorb. The production of N₂ was observed to be limited. The results show oxidized platinum particles to be little active for NO dissociation. Similar results were obtained with the alloy catalysts after oxidation; even a further decline of the N₂ production was noted.

To distinguish between the reaction of NO adsorbed at low temperature and subsequently heated on the one hand, and the reaction of NO dosed at high temperatures on the other hand, we performed the following experiments: NO was dosed at several temperatures whilst the gas phase was analyzed continuously. We will now concentrate on the results recorded at a catalyst temperature of 400°C. Dosing of 2.34 ml (STP) NO at 400°C to a freshly reduced Pt/SiO₂ sample led to a fast drop of the NO signal and a simultaneous increase of the N₂ signal. Thirty minutes after dosing, NO was no longer detected in the gas phase. Furthermore, we did not observe O₂ to be produced. After evacuation at that temperature for 1 h and repeated dosing of NO, N₂ was formed to a small extent only. The results demonstrate a reduced platinum surface to be active for NO dissociation by reaction from the gas phase at elevated temperatures, but the adsorbed oxygen thus produced inhibits further dissociation of NO. The latter conclusion was confirmed by the low activity of the oxidized Pt/SiO₂ catalyst for NO decomposition at 400°C. With the alloy catalysts the dissociation of NO was found to proceed to a smaller extent than with the platinum catalyst.

4. Discussion

4.1. Infrared spectra

Studying the infrared spectra of adsorbed NO on reduced platinum catalysts, several authors report an intense absorption band with its maximum in the range of 1760 to 1865 cm⁻¹ [9–13,18]. The assignment of this band, which is observed at 1780 cm⁻¹ in this work, to the stretching vibration of linearly adsorbed NO bound via its nitrogen atom to the platinum surface is beyond

doubt. The variation of the frequencies reported can be connected with the surface structure of the platinum metal.

A complete set of data for the low-index planes of platinum has become available recently. At high NO coverages, vibrational frequencies of 1710 cm⁻¹ for the (111) face [4,7], 1760 cm⁻¹ for the (110) face [5] and 1790 cm⁻¹ for the (100) face [19] have been established by EELS. Assuming an increasing fraction of (111) planes with increasing particle size, these data predict a shift to lower frequencies with larger particles. This shift has been observed by Primet et al. [10]. It can be concluded, moreover, that the Pt particles studied in this work mainly expose the atomically more rough faces.

Adsorption of NO on the Pt particles oxidized by either molecular oxygen or NO decomposition, causes again a band around 1780 cm⁻¹, now of moderate intensity (see figs. 5 and 4, respectively). Although the frequencies for the reduced and oxidized platinum surfaces are the same, the stability of the bands against evacuation shows NO to be more weakly adsorbed with the oxidized samples. Apparently, the mode of NO adsorption is not characterized unequivocally by the vibrational frequency observed: Weak adsorption on an oxidized surface brings about the same frequency as does strong adsorption on a reduced surface. Similar observations were reported by Ghorbel and Primet [11].

Dunken and Hobert [9] and Ghorbel and Primet [11] found absorptions around 1600 cm⁻¹ in their infrared study of NO on Pt catalysts. The latter authors ascribe the absorptions to oxidized forms of NO, because of the occurrence with both reduced and oxidized samples. Concerning NO adsorption on an oxidized platinum surface we agree on this assignment. The quite different behaviour of the 1600 cm⁻¹ band against evacuation (cf. figs. 1 and 5) calls, however, for another interpretation with the reduced surface. With single crystals low coverages of NO led to vibrational frequencies of 1470, 1610 and 1690 cm⁻¹ for the (111), (110) and (100) planes, respectively [6]. Although there is some discussion in the literature about the explanation, recent results suggest these frequencies to originate from bridged or multiply bound NO species [5]. We propose the same assignment for the 1600 cm⁻¹ band found with reduced Pt/SiO₂. The spectra of the PtAg/SiO₂ catalysts strongly support this proposal: Dilution of the Pt surface with Ag atoms leads to a more rapid decline of the 1600 cm⁻¹ band than of the 1780 cm⁻¹ band (fig. 2). Multiply bound NO is scarce with the alloy surface because of the low probability for larger ensembles of Pt atoms.

Having attributed the frequencies at 1780 and 1600 cm⁻¹ to terminally and bridged bound NO, respectively, the behaviour of adsorbed NO on Pt/SiO₂ upon evacuation can be understood in more detail (fig. 1). Evacuation at 150°C obviously leads to more bridge-bonded species, whereas the number of terminally bound species diminishes. The TPD spectra show at 150°C desorption of molecular NO to be predominant over dissociation (fig. 6a). The

resulting lower coverage of NO molecules may enhance the number of (more strongly held) species bound to several Pt atoms.

The resolved band at 1935 cm⁻¹ observed in this work was not reported before with platinum. With other noble metals, however, the high-frequency band has been observed several times. A concise survey of the literature will lead to the conclusion that the 1935 cm⁻¹ band is due to molecular adsorption of NO on a partly oxidized platinum surface. Studying the interaction of NO with a 5 wt% Ir/Al₂O₃ catalyst, Solymosi and Raskó [20] found a band at 1950 cm⁻¹ in case of high NO pressures and elevated adsorption temperatures. With the oxidized catalyst the 1950 cm⁻¹ band even dominated the spectrum. The 1950 cm⁻¹ band was ascribed to NO adsorption on oxidized Ir sites. Arai and Taminaga [21] reported an infrared band at 1910 cm⁻¹ with a Rh/Al₂O₃ catalyst and attributed it to Rh-NO⁺ complexes. According to Brown and Gonzalez [22] NO adsorption on Ru sites in the neighbourhood of (ad)sorbed oxygen brings about absorptions at 1860–1880 cm⁻¹. The present investigations show a strong high-frequency band to appear after exposure of the reduced Pt/SiO₂ catalyst to NO at 400°C and subsequent cooling down to room temperature (fig. 3). It is remarkable that the 1935 cm⁻¹ band is almost absent with the Pt catalyst oxidized by O₂ (fig. 5). From the mass spectrometric results we can be sure that NO dosed at 400°C brings about oxidation of the previously reduced Pt particles. Subsequent molecular adsorption of NO on the thus oxidized Pt surface gives rise to the 1935 cm⁻¹ band. Apparently, oxidation of platinum using NO leads to a surface condition which differs from that using O₂. We think that O₂ oxidizes the Pt particles to a larger extent than does NO. Adsorption of NO on a platinum (surface) oxide produces absorptions below 1850 cm⁻¹ (fig. 5), whereas a partly oxidized platinum surface exhibits the 1935 cm⁻¹ band as well (fig. 3). The absence of this band with a PtAg/SiO₂ catalyst (fig. 4) may be due to the lower activity for NO decomposition. Another explanation is surface segregation of silver induced by adsorbed oxygen [17]. Finally we remark that in line with a small production of N₂ after dosing of NO to reduced Pt/SiO₂ at room temperature, a weak band at 1935 cm⁻¹ is observed in fig. 1.

In the case of an oxidized Pt surface, weak bands between 1400 and 1650 cm⁻¹ were invariably detected (figs. 4 and 5). In accordance with Ghorbel and Primet [11], we think these absorptions to be due to oxidized forms of NO, e.g. nitrates.

4.2. Adsorption and reactivity of NO on platinum

The initial degree of coverage of NO influences the product distribution during thermal desorption. Working with a stepped Pt single crystal plane, Gland [8] observed the production of N₂ to drop from 100 to 30% when the initial coverage increased from 10% of the maximum coverage to maximum

coverage. It appears that NO species are more strongly held at low coverages which has been put together with repulsive interactions at high coverages [6]. At this point it is tempting to correlate the bridge-bonded NO molecules with the strongly held species at low coverage which dissociate upon heating. At high coverages linearly bound species may predominate and desorb molecularly at elevated temperatures. This proposition is supported by our results in two ways. First of all the dissociation activity of the PtAg particles is low compared to Pt, which can be connected with the absence of bridge-bonded NO on the alloy. Secondly, the TPD spectrum of fig. 6a shows that molecular desorption of NO proceeds to a large extent before N₂ production becomes significant. Obviously, the high coverage of NO hampers dissociation because of a large majority of linearly bonded species. The latter idea can be extended by considering again the infrared spectra of fig. 1: Evacuation at 150°C enlarges the number of bridge-bonded species. The enhanced production of N₂ above 150°C during the TPD experiment nicely agrees with this observation.

Finally, we discuss the influence of the degree of oxidation of the platinum surface on the bonding of NO. The general conclusion from work with single crystals is that adsorbed atomic oxygen does not inhibit NO adsorption but suppresses the decomposition reaction [6,8]. This finding is confirmed by our TPD spectrum of NO adsorbed on oxidized Pt/SiO₂ (fig. 6b): NO desorbs molecularly for the greater part. On the other hand, we found the oxidized Pt surface to bind NO more weakly if compared to the reduced surface. This is apparent from a smaller saturation coverage (table 1) and a low stability of the infrared absorption bands against evacuation (fig. 5). The low dissociation activity of the Pt/SiO₂ catalyst after oxidation can thus be attributed to weak adsorption of NO which favours molecular desorption. An interesting situation occurs when studying NO adsorption on Pt/SiO₂ after mild oxidation with NO at 400°C. This situation can be inferred from the infrared spectra of fig. 3 and the mass spectrometric results. Exposure of NO to reduced Pt/SiO₂ at 400°C led to a fast production of N₂, whereas O₂ was not observed in the gas phase. Repeated dosing of NO did not lead to an extensive dissociation which shows adsorbed oxygen to inhibit further decomposition of NO. After cooling down to room temperature, infrared spectroscopy showed the surface in this condition to bring forth the noteworthy band at 1935 cm⁻¹. Whereas the NO species absorbing at 1780 cm⁻¹ are weakly held, the high-frequency NO is very strongly bound, but does not seem to be active for dissociation. A platinum surface which has been oxidized heavily (1 atm O₂, 400°C) starts to release O₂ at 350°C (fig. 6b). On the other hand, the decomposition of NO at 400°C stops before desorption of O₂ occurs. Therefore, no steady-state activity for NO decomposition will be displayed by platinum surfaces at moderate temperatures. This conclusion is in accordance with the literature [23,24].

References

- [1] H.P. Bonzel and G. Pirug, *Surface Sci.* 62 (1977) 45.
- [2] H.P. Bonzel, G. Brodén and G. Pirug, *J. Catalysis* 53 (1978) 96.
- [3] C.M. Comrie, W.H. Weinberg and R.M. Lambert, *Surface Sci.* 57 (1976) 619.
- [4] J.L. Gland and B.A. Sexton, *Surface Sci.* 94 (1980) 355.
- [5] R.J. Gorte and J.L. Gland, *Surface Sci.* 102 (1981) 348.
- [6] R.J. Gorte, L.D. Schmidt and J.L. Gland, *Surface Sci.* 109 (1981) 367.
- [7] H. Ibach and S. Lehwald, *Surface Sci.* 76 (1978) 1.
- [8] J.L. Gland, *Surface Sci.* 71 (1978) 327.
- [9] H. Dunken and H. Hobert, *Z. Chem.* 3 (1963) 398.
- [10] M. Primet, J.M. Basset, E. Garbowski and M.V. Matthieu, *J. Am. Chem. Soc.* 97 (1975) 3655.
- [11] A. Ghorbel and M. Primet, *J. Chim. Phys.* 73 (1976) 89.
- [12] M.F. Brown and R.D. Gonzalez, *J. Catalysis* 44 (1976) 477.
- [13] F. Solymosi, J. Sárkány and A.J. Schauer, *J. Catalysis* 46 (1977) 297.
- [14] W.M.H. Sachtler and R.A. van Santen, *Advan. Catalysis* 26 (1977) 69.
- [15] K.P. de Jong and J.W. Geus, in: *Proc. 3rd Intern. Symp. on Scientific Bases for the Preparation of Heterogeneous Catalysts*, Louvain-la-Neuve, 1982, preprint A9.
- [16] K.P. de Jong, J.W. Geus and J. Joziassse, *Appl. Surface Sci.* 6 (1980) 273.
- [17] K.P. de Jong, PhD Thesis, Utrecht (1982), ch. 6.
- [18] J.B. Peri, *J. Catalysis* 52 (1978) 144.
- [19] G. Pirug, H.P. Bonzel, H. Hopster and H. Ibach, *J. Chem. Phys.* 71 (1979) 593.
- [20] F. Solymosi and J. Raskó, *J. Catalysis* 62 (1980) 253.
- [21] H. Arai and H. Taminaga, *J. Catalysis* 43 (1976) 131.
- [22] M.F. Brown and R.D. Gonzalez, *J. Catalysis* 47 (1977) 333.
- [23] A. Amirnazmi, J.E. Benson and M. Boudart, *J. Catalysis* 30 (1973) 55.
- [24] A. Amirnazmi and M. Boudart, *J. Catalysis* 39 (1975) 383.