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The Adsorption of Nitric Oxide on Platinum Black

K. OTTO AND M. SHELEF

Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121

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Adsorption isotherms for NO chemisorption on reduced and oxidized platinum black were measured in the range from −78 to 100°C. Monolayer coverage, attained by extrapolation of the Freundlich isotherms, yields a 1:1 correspondence between adsorbed NO molecules and Pt atoms in the surface. The chemisorption characteristics of NO on Pt show a close resemblance to those observed on transition metal oxides.

The selective chemisorption of hydrogen, oxygen, or carbon monoxide is frequently used to determine specific surface areas of catalytically active materials in the presence of inert support substrates, such as Al_2O_3, SiO_2, and MgO (*1*). It has been shown in a series of papers from this laboratory that nitric oxide, too, can be used successfully as a selective adsorbate to measure the surface areas of oxides of chromium (*2*), iron (*3*), nickel (*4*), and copper (*5*) on alumina supports. As the adsorption follows the Freundlich isotherm in these cases, monolayer coverage is explicitly defined. The data of the present investigation show that the NO adsorption method can be expanded to include noble metal adsorbents. At the same time, the results point out limitations inherent in the selective NO chemisorption.

Experimental details concerning the electrobalance, the associated vacuum equipment, gas purification, and the BET measurements have been described before (*2–4*). The adsorbent in the present work is unsupported platinum black, obtained from Engelhard Industries; it was considered as being 100% pure Pt for the purpose of this study. An impurity level of about 300 ppm is possible. A typical impurity composition for Pt black of the same source is given by Vannice, Benson and Boudart (*6*) together with the conclusion that only a small fraction of the surface can be contaminated by foreign atoms, even if all the impurities were accumulated on the surface. Care was taken to prevent shrinkage of the Pt black during the required reduction and oxidation treatment preceding the adsorption measurements. For this purpose the access of the reactive gases was restricted by diffusion through an Ar barrier of 150 Torr with which the balance housing was filled. For reduction or oxidation an adjoining vessel was filled with 155 Torr of H_2 or O_2, respectively, and connected to the balance housing. For the initial reduction, hydrogen was admitted through the argon barrier for 24 hr at room temperature; the temperature was raised slowly to 100°C and held there until a constant weight was established. The gas phase was evacuated, and pure hydrogen was admitted for final reduction. Even with these precautions the first reduction decreased the surface area from 27.2 to 11.0 and 8.6 m^2/g in two separate cases. The average particle size after the first reduction corresponds to about 300 Å. Further shrinkage on subsequent treatments, as evaluated by intermediate BET measurements, was of the order of 0.2 m^2/g only.

Because of the relatively small adsorbent area, care was taken to prevent any spurious weight changes that could be caused by desorption from vessel walls, etc. Evacuation of the sample by the VacIon getter pump before adsorption was therefore continued for 5–10 days at 100–125°C and a residual pressure of 10^{-7} Torr at the pump. Some

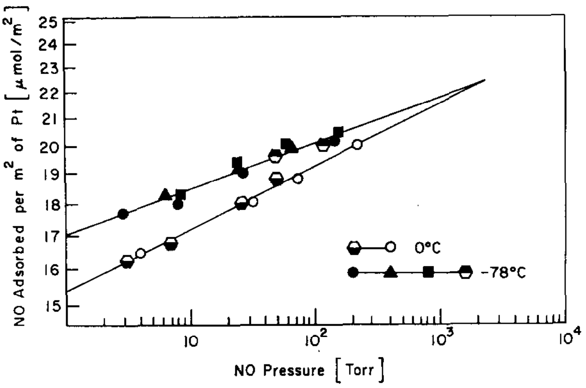

FIG. 1. Adsorption isotherms for NO on reduced platinum black.

hydrogen may remain on the surface even after this rigorous evacuation. According to Vannice, Benson and Boudart (*6*) 30–40% of the surface hydrogen remains on Pt black after short outgassing at 125°C. The possible effect of the residual hydrogen on our results will be discussed below.

At a given pressure the equilibrium amount of NO was adsorbed within 1–2 hr in the temperature range from −78 to 100°C. The isotherms for a reduced and an oxidized surface are shown in Figs. 1 and 2. The ordinate of the graphs is plotted as NO uptake per unit area. The surface area was determined by BET measurements using Ar at the temperature of liquid nitrogen as an adsorbate. The cross section of the adsorbed Ar atom was taken as 16.9 Å^2 (*7*).

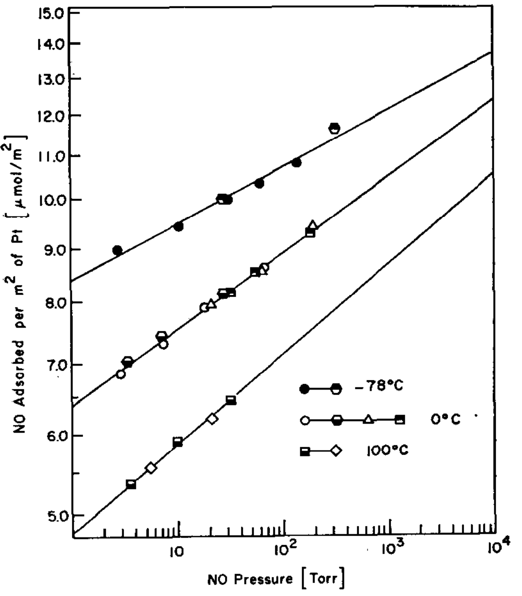

FIG. 2. Adsorption isotherms for NO on oxidized platinum black.

An isotherm at 100°C was also measured in the case of the reduced surface; but these data are not included in Fig. 1, as it must be assumed that a substantial reoxidation of the surface by NO could occur under these conditions, thus rendering the results questionable. Each isotherm was determined by at least two separate runs. Different symbols represent different runs and thus give an indication of the reproducibility. The consistency of the data from one isotherm to another was checked by measuring a few adsorption points at one temperature, cooling the sample to a lower temperature, and continuing the adsorption with increasing pressure. These data are indicated by half-filled symbols in Figs. 1 and 2. Thus the errors introduced by the reestablishment of a clean oxidized or reduced surface are minimized.

The numerical evaluation of the adsorption isotherms was based on a linear least-squares fit through the points of the logarithmic adsorption plots. The numerical coefficients of the Freundlich isotherms ($q = cp^{1/n}$) and the values H_m (heat of adsorption at coverage $\theta = 0.37$) derived therefrom are summarized in Table 1. The use of H_m as a measure for the heat of adsorption derives naturally from the basic relationship between H_m and the slope of the Freundlich isotherm, $H_m = nRT$. Accord-

TABLE 1
COEFFICIENTS OF FREUNDLICH ISOTHERMS

	T (°K)	T (°C)	n	$H_m(=nRT)$ (kcal/mol)	c (μmol/m²)
Reduced surface	195	−78	28.3	11.0	17.0
	273	0	20.5	11.1	15.3
Oxidized surface	195	−78	18.5	7.2	8.36
	273	0	13.9	7.5	6.37
	373	100	11.7	8.7	4.82

ing to the assumptions underlying the Freundlich isotherm the heat of adsorption as a function of coverage is given by $H_\theta = -H_m \ln \theta$. The required reversibility of NO adsorption is warranted on reduced surfaces only at high coverages θ, as we have mentioned before (*2*). This requirement is satisfied in the case of reduced Pt, as the adsorption isotherms refer only to coverages $\theta > 0.7$. Mass spectrometric analysis of the desorption products, which will be discussed below, showed that about 50% of the adsorbed NO can be removed reversibly (cf. Table 2). The numerical values of n and correspondingly $H_m = nRT$ are comparable to those determined for transition metal oxides. For example, the value $H_m = 11$ kcal/mol derived for reduced Pt is almost the same as the corresponding value for Fe_3O_4, which was the largest H_m measured previously (*3*) for a partially reduced metal oxide. Similarly, H_m for oxidized Pt ranks near the upper limits of the H_m values observed for fully oxidized transition metal oxides, which range from 3.5 to 8.6 kcal/mol. As in previous cases the heat of adsorption of a reduced Pt surface is significantly higher than that of an oxidized surface.

The monolayer coverage obtained from the intersection of the isotherms in the case of reduced Pt is 22.3 μmol NO/m² Pt (or 1.34×10^{19} NO molecules/m² Pt). Depending on the method of averaging the three low index planes (1,0,0), (1,1,0), and (1,1,1), the area occupied per Pt surface atom is given as 8.9 (*8*) or 8.4 Å² (*9*), which is equivalent to $(1.12\text{–}1.19) \times 10^{19}$ Pt atoms/m². On this basis the measured monolayer corresponds to a ratio $NO_{ads}/Pt_s = 1.13$ to 1.20. It should be mentioned that according to Van Hardeveld and Van Montfoort (*10*) and Karnaukhov (*11*) the large Pt black crystals are likely to have a cubooctahedral shape with predominantly exposed (1,0,0) and (1,1,1) planes. Electron micrographs of our Pt sample are consistent with these reports; wherever structural details were discernible within the sintered agglomerate, they showed a rounded shape. Averaging of the (1,0,0) and (1,1,1) planes gives an area of 7.15 Å² occupied per Pt atom or 1.40×10^{19} Pt atoms/m², yielding a ratio $NO_{ads}/Pt_s = 0.96$. The lower and upper

TABLE 2
BALANCE OF SITES AND SURFACE SPECIES IN ADSORPTION–DESORPTION EXPERIMENT

	Composition of desorbed gas (μmol/m² Pt)	Equivalent NO removed (μmol/m² Pt)	Oxygen deposited on surface at end of experiment (μg-atom/m² Pt)
NO	6.63	6.63	0
N_2O	3.81	7.62	3.81
N_2	0.09	0.18	0.18
O_2 uptake after desorption at 0°C	—	—	10.10
Total		14.43	14.09

bounds of the ratios calculated from the NO adsorption and the averaging of the surface density of Pt atoms bracket the expected 1:1 ratio of NO monolayer coverage and Pt surface atoms. In fact, the intrinsic uncertainty of a metallic surface, such as Pt black, is considerably less than that of an oxide surface where the possibility of half-populated surfaces (*3*) has to be taken into account.

As observed on fully oxidized Cr_2O_3 (*2*), the NO adsorption on oxidized Pt yields isotherms with little change of slope with temperature. This parallelism requires substantial extrapolation of the isotherms in order to derive monolayer coverage from the point of intersection. These points of intersection as calculated from the extrapolation of the three pairs of isotherms (at −78 and 0, 0 and 100, −78 and 100°C) are 18.9, 28.9, and 21.6 μmol NO/m^2 Pt, respectively. These values are considered as being in agreement with the monolayer coverage on reduced Pt (22.3 μmol NO/m^2 Pt) within the uncertainty introduced by the extrapolation.

The adsorption rates, plotted in terms of the Elovich equation (q vs log t) are given in Fig. 3 for a reduced surface (top curve) and oxidized surface (bottom curve) at 3–4 Torr and 0°C. The adsorption kinetics on both surfaces are described by straight Elovich lines. A break point which has been observed for the NO adsorption on partly reduced transition metal oxides was not detected in case of Pt. Otherwise, a Pt surface behaves similarly to other adsorbents, with the exception of copper oxide (*5*), insofar as NO is chemisorbed more slowly on an oxidized surface than on a reduced surface and with a weaker bond, as evidenced by the lower heat of adsorption.

Since a reduced Pt surface is easily oxidized by oxygen at room temperature, a special effort was made to assess possible surface oxidation by NO. Previous work on a supported Pt catalyst indicated that such a reoxidation is slow at 25°C [Table 7 in Ref. (*12*)], but it seemed important to confirm this finding for Pt black. Gravimetric measurements record total weight changes only and thus cannot distinguish between the uptake of NO molecules and oxygen atoms. The evaluation is further complicated by the fact that NO adsorption is, in part, irreversible, giving N_2O and N_2 besides NO as desorption products (*12*). It was therefore necessary to combine gravimetric measurements of adsorption, desorption, and reoxidation by oxygen, with a mass spectrometric analysis of the gas phase. After the gravimetric measurements had been concluded, the same Pt sample, contained in a small volume (15 cm^3), was connected to the gold leak of a mass spectrometer and adsorption and desorption of NO at 0°C were repeated. At 0°C and 146 Torr of NO a weight gain of 7.09 was registered, corresponding to 20.0 μmol NO/m^2 Pt. The weight loss upon evacuation for 70 hr was 4.36 mg after the sample had been heated slowly to 125°C. Exposure to oxygen caused a weight increase of 1.91 mg at 0°C and a further increase of 0.41 mg at 125°C. From the analysis of the gas phase and the observed weight changes a material

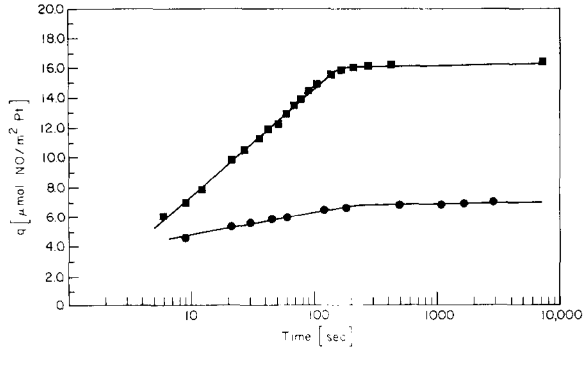

FIG. 3. Elovich plots for NO adsorption on platinum black: (■) reduced surface; (●) oxidized surface.

balance, given in Table 2, is derived. The data are referred to 1 m^2 of Pt area.

The difference between the initially occupied sites (20.0 $\mu mol/m^2$) and those vacated during desorption (14.4 $\mu mol/m^2$) is the NO that could not be desorbed at 125°C (5.6 $\mu mol/m^2$). The total number of available sites, as given by the intersection point in Fig. 1, is 22.3 $\mu mol/m^2$; at the end of the experiment 5.6 are occupied by NO, 14.1 by O atoms, and 2.6 are empty. The ratio between the sites occupied by the oxygen atoms and those available for them is 14.1/16.7 = 0.84. The same ratio was measured when oxygen was adsorbed on a completely reduced surface; it is in good agreement with the recent results of Vannice, Benson and Boudart (*6*). The additional uptake of oxygen at 125°C could occur on the free sites. It is, however, possible that oxygen is chemisorbed at this temperature on sites occupied by NO, forming surface complexes. This conjecture is based on the absence of a temperature dependence of oxygen uptake on a clean Pt surface.

Finally the question of residual hydrogen on Pt black, left during the reduction process, has to be considered. Our mass spectrometric experiment has confirmed the presence of some hydrogen in the surface, as observed by Vannice, Benson and Boudart (*6*). This hydrogen was manifested by a burst of nitrogen which was observed immediately after NO had been admitted to a reduced sample at −78 and 0°C; only 0.5% of the released nitrogen appeared as N_2O. The escape of N_2 was followed by a slow evolution of water, which was speeded up considerably when the sample was warmed up to room temperature. It must be emphasized that this nitrogen did not enter into our desorption products, since the gas phase was removed quickly before the slow desorption was monitored by the mass spectrometer. The nitrogen released during the initial NO uptake amounted to 1.4 $\mu mol/m^2$ Pt. As four H atoms are required to reduce two molecules of NO to one molecule of N_2, it follows that 25% of the surface is covered by H atoms after reduction at 125°C compared to 30–40% given by Vannice, Benson and Boudart (*6*). This result supports the supposition that the initial burst of N_2 is not due to the oxidation of the surface. In this case a lesser coverage by H atoms after reduction would be implied, in disagreement with the findings of Vannice, Benson and Boudart (*6*).

The reaction between residual hydrogen atoms and NO, resulting in H_2O and N_2, causes some uncertainty in the adsorption results. The mass spectrometric analysis shows [in conformity with the observations of Vannice, Benson and Boudart (*6*)] that at 0°C the vapor pressure of water is large enough to allow complete desorption into the large balance volume, and thus does not contribute to the uncertainty of the gravimetric measurements. At −78°C some adsorption sites may remain blocked by water, but at the same time, this water is gravimetrically equivalent to a part of the barred NO molecules. The extreme case is the unlikely situation where all the water produced remains on the surface and in addition NO is adsorbed on the Pt sites covered by water. The water molecules (corresponding to 12.5% of the surface) appear gravimetrically as $(18/30) \times 12.5\% = 7.5\%$ of an NO monolayer. Such a situation will cause a constant increase of all the points of the isotherm at −78°C and correspondingly the calculated monolayer coverage will be increased by the same amount. The effect on the slope of the isotherm is negligible. We do not expect that the most unfavorable situation prevails, as there exists good agreement between adsorption points measured immediately at −78°C (black symbols in Fig. 1) and those measured at the same temperature after an initial adsorption at 0°C (half-filled symbols in Fig. 1). The maximum uncertainty of the gravimetric measurements including both water retention and surface reoxidation, based on the desorption analysis, is estimated to be less than 10%.

It can be concluded that the adsorption characteristics of NO on Pt, such as heats of adsorption, monolayer coverage, and adsorption kinetics are comparable to those observed for transition metal oxides. At monolayer coverage each Pt atom in the surface adsorbs one molecule of NO within the accuracy with which the surface density of Pt atoms is known. Although partial oxidation of a reduced surface by NO may interfere at higher temperatures (around 100°C), it is not important at 0°C. Evaluation of monolayer coverage in case of oxidized Pt requires extensive extrapolation and seriously limits the accuracy of such a determination.

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