A study of nitrogen and carbon dioxide chemisorption on platinum black

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The relationship between sites responsible for nitrogen chemisorption and sites responsible for stronger adsorption of carbon dioxide on platinum black is reported. A 2 to 1 ratio has been found between molecules of more strongly adsorbed carbon dioxide and molecules of nitrogen chemisorbed on individual samples. This relationship has allowed us to deduce the structure of chemisorbed carbon dioxide. Carbon dioxide is relatively weakly chemisorbed on platinum. Reasons for the weakness of this chemisorption are discussed.

Keywords: Chemisorption; nitrogen; carbon dioxide; platinum; water gas shift reaction

Several years ago, we published a detailed study of nitrogen chemisorption on platinum in which we explained our results in terms of selective chemisorption of nitrogen on the stepped planes of platinum [1,2]. We also correlated the presence of these sites with the electrocatalytic activities for propane oxidation [1]. In these studies, we also identified clearly the specific locations at which nitrogen chemisorbs. Shortly before the publication of our second paper, Egerton and Sheppard [3] published a parallel spectroscopic study of the same system. In their analysis of nitrogen adsorption spectra they noted that the spectra of nitrogen adsorbed on nickel, platinum, iron, and other Group VIII metals were very similar and the appearances of the sites responsible for nitrogen adsorption also seemed to follow a similar pattern. Subsequently, Ertl and co-workers [4–6] studied nitrogen chemisorption on iron single crystals and its relation to ammonia synthesis. Nitrogen was shown to chemisorb primarily, if not entirely, on the stepped planes. Similar findings on selective chemisorption of nitrogen have also been reported on nickel and palladium [7]. Thus, it now appears that nitrogen may play the role of a selective absorber or site counter on Group VIII metals.

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Within the same timeframe, Somorjai et al. [8] showed that the stepped planes of platinum were far more reactive for a considerable number of adsorption and dissociation processes.

When the earlier work was published we felt, mistakenly, that there would only be limited interest in a shorter study we had performed on the adsorption of carbon dioxide on platinum. This subject had been investigated by us because it might provide insight into the mechanism of the water gas shift reaction and because Hinshelwood and Prichard showed many years ago that the reduction of carbon dioxide occurs selectively at only certain sites on platinum which are able to chemisorb carbon dioxide at elevated temperatures and pressures [9]. At elevated temperatures, these authors found that carbon dioxide only adsorbs on a small fraction of the platinum surface. Therefore, we also investigated this subject to determine if there was any correlation between the sites where carbon dioxide is more strongly adsorbed and the sites we previously identified as active in nitrogen chemisorption.

The methodology used in this study is identical to that used in the earlier platinum investigation. Specifically, our method is based on the fact that if physical adsorption of nitrogen alone occurs, once correct molecular areas have been chosen, there should be no consistent differences between surface area measurements obtained with either argon or nitrogen. If chemisorption is occurring, however, the obtaining of both nitrogen and argon adsorption isotherm data should reveal the presence of excess nitrogen to variable extents. The amounts of this excess material should be sensitive to sample preparation methods and the excess gas should be more strongly held to the surface than the physically adsorbed species. Once amounts of nitrogen chemisorption were determined, carbon dioxide isotherms were measured to determine amounts of carbon dioxide adsorbed on the same samples. The rationale for the validity of this methodology is discussed in detail in our earlier paper [2].

The apparatus used is described in an earlier paper [2]. The gases used were obtained on one-liter pyrex flasks from Airco. The nitrogen contained 3–10 ppm argon, the hydrogen contained a few ppm nitrogen, the helium contained similar traces of neon, the argon contained 10 ppm nitrogen, and the carbon dioxide contained traces of nitrogen and about 5 ppm carbon monoxide.

Adsorption of carbon dioxide and nitrogen was studied on five platinum black samples whose preparation is outlined in table 1. Determination of nitrogen chemisorption on these samples followed the same procedures outlined in our earlier paper [2]. Specifically, the amount of nitrogen chemisorbed on the five platinum samples was first determined from nitrogen and argon adsorption isotherms obtained at −195°C and application of the BET method to analyze the results obtained [10]. The cross sectional areas used for nitrogen and argon were 16.2 and 15.6 Å^2, respectively, and were derived from the earlier study.

Table 2 shows the results obtained. There, the amounts of chemisorbed nitrogen found are expressed in two manners: as the amount of excess nitrogen

Table 1
Preparation of platinum black samples

Sample No.	Platinum black preparation	Sample pretreatment
1	commercial material (Engelhard)	treated with hydrogen at −80°C, warmed in hydrogen over several hours to 70°C, and then evacuated at that temperature for 16 h
2	prepared by reduction of chloroplatinic acid with formaldehyde using about 1 percent of prenucleated platinum black as a seed material	same as sample 1
3	commercial material	same as sample 1 except 3 h evacuation at 125°C employed
4	same as sample 2	same as sample 1 except 3 h evacuation at 125°C employed
5	commercial material	same as sample 1 except 1 h evacuation at 155°C employed

adsorption, which assumes that chemisorbed nitrogen occupies the same area as the physically absorbed material (i.e. 16.2 Å^2) and based on the assumption that nitrogen only chemisorbs on alternate B5 sites. In the latter case, the area of a pair of B5 sites on platinum is 21.62 Å^2. The nature of these B5 sites has been discussed in earlier publications by ourselves [2] and others [11].

Carbon dioxide isotherms were determined on five platinum black samples at −80°C after these samples had been cleaned and used to study nitrogen chemisorption. The isotherms showed increasing weak physical adsorption above 1 Torr as would be expected. Five minutes evacuation at −80°C left amounts of carbon dioxide adsorbed, as determined from second isotherms, approximately

Table 2
Chemisorption of carbon dioxide and nitrogen on platinum

Sample	Surface area (m^2)	Chemisorbed nitrogen coverages		Number of nitrogen molecules chemisorbed $\times 10^{-18}$	Number of chemisorbed carbon dioxide molecules $\times 10^{-18}$	Ratio CO_2/N_2
		ref. [2]	assuming N_2 chemisorbs on alternate B5 sites			
1	25.31	0.38	0.51	64.8	130.5	2.01
2	19.52	0.25	0.33	30.2	60.1	1.99
3	17.83	0.24	0.32	26.7	55.8	2.09
4	10.96	0.19	0.25	12.9	26.4	2.05
5	7.14	0.06	0.08	2.66	5.40	2.03

equal to 2.5 times the amounts of nitrogen chemisorption observed on the samples. Evacuation at −80°C for 20 min or longer removed about 20% of this material. Room temperature evacuation removed all of the carbon dioxide. Remeasurement of nitrogen adsorption at −195°C on samples exposed to carbon dioxide at −80°C and then evacuated for 20 min at −80°C showed that no nitrogen chemisorption occurs after this exposure. The nitrogen chemisorption coverages on the five samples ranged from 0.06 to 0.38 and the molecular ratio of carbon dioxide adsorbed after 20 min evacuation at −80°C to amounts of nitrogen chemisorption previously observed on the samples was close to 2 to 1 in all cases. These results are also shown in table 2.

What is of interest is the constant 2 to 1 ratio found between chemisorbed carbon dioxide and nitrogen molecules on individual samples and the apparent weak chemisorption of the carbon dioxide. To date, no studies have been reported in the literature of low temperature chemisorption of carbon dioxide on clean platinum surfaces. Ibers [12] recently has reviewed the subject of interaction of liquid carbon dioxide with noble metals and has found that complexes of noble metals with carbon dioxide are unstable. The ease of removal of adsorbed carbon dioxide from platinum at ambient temperatures reported here agrees with this finding.

Stronger adsorption of carbon dioxide on the sites responsible for nitrogen chemisorption is indeed reasonable and to be expected. In our earlier work, we demonstrated that nitrogen chemisorption occurs on the sites most strongly chemisorbing hydrogen on platinum [2]. We also explained that these results were in accord with the findings of Somorjai et al. [8], who found that the stepped planes of platinum were more active than the smooth planes for a number of adsorption and dissociation processes. In general, these authors found stronger adsorption of a variety of species on the stepped planes.

The question then remains as to whether this more strongly held carbon dioxide represents the total of chemisorbed carbon dioxide on platinum. To resolve this question, data characterizing the physical adsorption of carbon dioxide would be needed and it would have to be established that the amounts of more strongly held material were identical to that expected from an analysis of the differences between argon and carbon dioxide isotherms on the same samples. This basically was the method used to establish nitrogen chemisorption in our earlier work [2].

Unfortunately, we had limited time in which to perform these carbon dioxide studies and were unable to complete such an effort. Based on the constant ratio observed, however, it is possible to describe the more strongly adsorbed dioxide. In our earlier work [2], we showed that nitrogen selectively chemisorbs on the less stable crystal planes of platinum. One of these planes, the 110, may be viewed as an alternating series of ridges and valleys. The only way in which carbon dioxide can be chemisorbed on a single B5 symmetry type site and not sterically interfere with adsorption on neighboring sites is for the carbon to be attached to a ridge atom and one of the oxygens to be bonded to a valley atom. The second oxygen will be pointed upwards away from the surface. Such a structure is likely to be highly strained and may easily decompose back into carbon dioxide and platinum at higher temperatures. This may explain why ambient temperature chemisorption of carbon dioxide has not been studied.

The structure of chemisorbed carbon dioxide discussed for platinum is essentially the same as that found at low temperatures for carbon dioxide chemisorbed on nickel 110 prior to its dissociation during reaction with the surface [13]. Platinum is far less chemically reactive than nickel and is not oxidizable by carbon dioxide.

The relationship established between sites adsorbing carbon dioxide more strongly and sites chemisorbing nitrogen indicates that the stepped planes of platinum are the regions capable of chemisorbing carbon dioxide at higher temperatures and pressures. The structure proposed for the adsorbed carbon dioxide lends itself readily to a description of the mechanism of the water gas shift reaction. Strongly bound hydrogen would be present at the valley sites of the stepped planes [2]. Incoming carbon dioxide would chemisorb as we have discussed. The strongly chemisorbed hydrogens would, then, be very close to one of oxygens of the adsorbed carbon dioxide and water would readily form and desorb. The product carbon monoxide so generated would, then, either move from a ridge position to a valley site or desorb.

The constant ratio observed also implies that, due to the low heat of adsorption, only half of the B5 sites actually become populated with chemisorbed nitrogen. This would be explained by nitrogen chemisorption only on alternating B5 sites on platinum. This interpretation is consistent with the infrared spectra of nitrogen chemisorbed on platinum [3] which do not show any band shifts with increasing coverages as would be expected due to nearest neighbor interactions. This allows the relative chemisorption coverages discussed in earlier work [1–3] to be put on an absolute basis as site areas are known.

Since the sites for nitrogen chemisorption have now been clearly defined, this method can be used as a tool in investigating the stereochemistry of reactions on stepped metal surfaces. Relationships between the nitrogen and other adsorbates should help to pinpoint the stereochemistry of these adsorbates and help to determine the exact mechanisms of catalytic reactions.

A B5 site was defined in the earlier literature as one valley atom located between two rows of ridge atoms on the stepped planes [11]. More recent evidence indicates that it is the ridge atoms where the nitrogen is actually chemisorbed. Golze et al. demonstrated adsorption of the nitrogen on alternate ridge sites on nickel 110 [14]. The area occupied by two ridge atoms and two adjacent valley atoms on platinum is 21.62 Å^2.

In our earlier paper, we assigned a second band for chemisorbed nitrogen on platinum to high index plane sites. Golze et al. demonstrated that nitrogen is more strongly chemisorbed on the high index planes on nickel [14]. The only way the more strongly chemisorbed nitrogen could give a band less shifted from the nitrogen–nitrogen stretch of gas phase material would be if one of the back orbitals on the outer nitrogen interacted with the orbitals of other metal atoms. If the nitrogen were located at valley sites, this would not be possible.

On nickel, the heat of adsorption of nitrogen on the 110 plane is 40 kJ/mol, the entropy of adsorption is 97 J/mol, and the activation energy for diffusion is about 15 kJ/mol [14], so that some spillover onto other areas is possible. On platinum, however, the heat of adsorption on the 110 plane is only about 18 kJ/mol [2] and the entropy should be similar to nickel. Since the free energy of adsorption for nitrogen is less than the activation energy for diffusion, no such spillover should occur on platinum.

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