

## An Infrared Study of the Adsorption and Oxidation of Ammonia on Platinum

B. A. MORROW<sup>1</sup> AND I. A. CODY<sup>2</sup>

*Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada*

Received April 9, 1976; revised August 30, 1976

The adsorption of  $\text{NH}_3$  on silica-supported platinum and on oxidized silica-supported platinum has been examined using infrared spectroscopy. Spectra for all H/D mixed isotopic species and for adsorbed  $^{16}\text{NH}_3$  indicate that ammonia only coordinates to the bare Pt surface and is stable up to about 250°C. There was no evidence for dissociative chemisorption. All spectral features disappeared when a large dose of  $\text{O}_2$  was added, but with micromole doses, new spectral features were observed which were tentatively assigned to Pt:NHO as an intermediate in the oxidation. On oxidized Pt, it has been suggested that  $\text{NH}_3$  dissociates to give  $\text{PtONH}_2$  at 20°C which further dissociates near 100°C to form a bridged  $(\text{PtO})_2\text{NH}$  structure.

The oxidation of ammonia by metal catalysts has been the subject of continuous investigation. Although mechanistic details can usually only come from studies of the kinetics of the oxidation, other techniques have to be used in order to determine the mode of chemisorption of  $\text{NH}_3$  and to determine what types of adsorbed intermediates may be formed on the catalyst surface. To the latter end infrared spectroscopy has become a well-established technique for determining the structure of strongly adsorbed species on supported metal and oxide catalysts (1).

There have been several previous infrared studies of  $\text{NH}_3$  adsorbed on metals (2-6) (this work is reviewed in detail in Discussion) and in general the spectra (when shown) have been of poor quality in that broad poorly resolved bands were observed. In spite of this a great diversity of interpretations have been advanced. We

have therefore undertaken a study of the adsorption of ammonia on silica-supported platinum in an attempt to determine the main mode of adsorption. A study of the oxidation of ammonia on bare Pt under mild oxidizing conditions, and of the adsorption of ammonia on pre-oxidized platinum has also been carried out in order to see if any partially oxidized adsorbed intermediates could be detected.

### EXPERIMENTAL METHODS

The techniques used for sample preparation and the reaction cell have been described previously (?). The cell volume was about 300 ml so that a 1 Torr dose of reactant at 20°C corresponds to about 16  $\mu\text{moles}$ . Most Pt/SiO<sub>2</sub> sample discs contained 40 mg cm<sup>-2</sup> of combined material with a Pt loading of 15.8%. Deuterium and nitrogen-15 containing ammonia were obtained from Merck Sharp and Dohme of Montreal, whereas 99.4% <sup>18</sup>O<sub>2</sub> was obtained from the Oak Ridge National Laboratory

<sup>1</sup> To whom correspondence should be addressed.

<sup>2</sup> Present address: Imperial Oil Ltd., Sarnia, Ont. Canada.

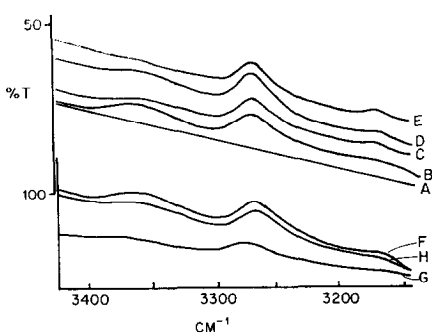


FIG. 1. (A) Background spectrum of reduced Pt/SiO<sub>2</sub>. (B) 10 Torr of NH<sub>3</sub> adsorbed for 5 min, evacuated for 5 min. (C, D) Evacuated for 1 hr at 120 and at 200°C. (E) Evacuated for 16 hr at 200°C. The % *T* scale refers to (A) and (B). (F) Spectrum as for B above. (G) After adding 60 Torr of H<sub>2</sub> to (F), spectrum scanned immediately. (H) Spectrum after evacuation of H<sub>2</sub> for 1 min.

(Union Carbide). Spectra were recorded on a modified Perkin-Elmer Model 13G filter-grating infrared spectrometer. Band positions were calibrated with reference to known band positions of various gaseous molecules. However, in view of the large half widths associated with most of the spectral features observed in this work, most band positions are probably only accurate to about  $\pm 5$  cm<sup>-1</sup>. Isotopic shift data for <sup>18</sup>O and <sup>15</sup>N are probably accurate to within  $\pm 2$  cm<sup>-1</sup>. Force constant refinement calculations were carried out using the standard programs developed by Schachtschneider (8). All spectra were recorded at room temperature, about 20°C.

## RESULTS AND DISCUSSION

### a. Adsorption of NH<sub>3</sub> on Pt

As previously reported by others (4-6), NH<sub>3</sub> did not chemisorb at 20°C onto the silica support but bands near 3400, 3320 and 1625 cm<sup>-1</sup> due to hydrogen bonded NH<sub>3</sub> and a broad band near 3000 cm<sup>-1</sup> due to perturbed surface silanol groups (SiOH--H<sub>3</sub>N) were observed when 10 Torr of NH<sub>3</sub> was left in contact with a 40 mg cm<sup>-2</sup> silica disc. All bands dis-

appeared following 1 min evacuation at 20°C.

The spectrum observed after 10 Torr of NH<sub>3</sub> had been allowed to react on a 40 mg cm<sup>-2</sup> Pt/SiO<sub>2</sub> sample is shown in Fig. 1B. The cell had been evacuated for 5 min so as to remove hydrogen bonded NH<sub>3</sub> and three broad bands at 3372, 3268 and 3155 cm<sup>-1</sup> and an extremely weak broad feature near 1600 cm<sup>-1</sup> (see Fig. 4A) did not alter with respect to intensity or peak position following prolonged evacuation at 20°C. However, the peak height of the 3372 cm<sup>-1</sup> band decreased if the sample was evacuated at 100°C, whereas that of the two low wavenumber bands apparently increased slightly while the band width narrowed. Little change resulted if the degassing temperature was raised to 200°C (Fig. 1D, E) but all bands disappeared at 300°C. The series could be repeated if NH<sub>3</sub> was added again. The generation of the initial spectrum did not depend on the adsorption time prior to evacuation (1 min to 5 hr), or on the initial pressure (>1 Torr) of NH<sub>3</sub>.

The spectrum shown in Fig. 1B did not change if the saturation vapor pressure of H<sub>2</sub>O at 20°C was admitted to the cell but all bands disappeared when 30 Torr of CO was added and a spectrum of PtCO was observed. When NH<sub>3</sub> was added to partially covered PtCO surface a similar but weaker spectrum of adsorbed NH<sub>3</sub> was observed and the PtCO band shifted by about 25 cm<sup>-1</sup> to lower wavenumber, as has been found by Primet *et al.* (3).

When a small dose of H<sub>2</sub> (10 μmole) was added to a sample which contained adsorbed NH<sub>3</sub> no spectral changes resulted but if 60 Torr of H<sub>2</sub> was added all of the ν(NH) bands diminished in intensity, the 3268 and 3372 cm<sup>-1</sup> bands shifted by about 10 cm<sup>-1</sup> to higher wavenumber and a band at 2120 cm<sup>-1</sup> due to PtH was observed (Fig. 1F and G). Evacuation of the H<sub>2</sub> restored the intensity to within about 80% of that before the addition of H<sub>2</sub> (Fig. 1H). This sequence could be repeated, and each

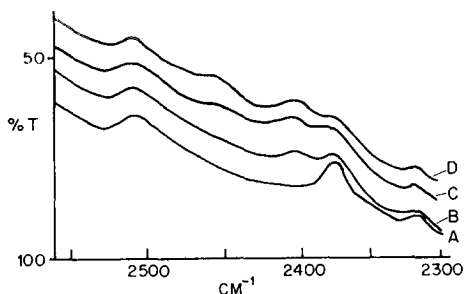


FIG. 2. (A) Spectrum after the adsorption of ND<sub>3</sub> on a deuterated Pt/SiO<sub>2</sub>. (B-D) Spectra after the successive additions of about 10 μmole of H<sub>2</sub>, in each case the H<sub>2</sub> was left in the cell for 1 min and evacuated for 1 min. The % *T* scale refers to (A).

time the spectrum was restored to about 80% of the intensity before addition of H<sub>2</sub>. The scan time used above was about 5 min. However, if 60 Torr of H<sub>2</sub> was left in the cell for several hours, then following evacuation no bands due to adsorbed ammonia were detected. The above spectral changes were also observed if H<sub>2</sub> was added to a Pt/NH<sub>3</sub> sample which had been degassed at 200°C prior to adding H<sub>2</sub> (as in Fig. 1E). The intensity at 3372 cm<sup>-1</sup> remained near zero during the sequence and no new spectral features were observed.

The spectrum observed when ND<sub>3</sub> was used (with a predeuterated silica) is shown in Fig. 2A; prominent bands are at 2315, 2375 and 2515 cm<sup>-1</sup>. Following the addition of about 10 μmole of H<sub>2</sub>, an additional band appeared at 2410 cm<sup>-1</sup> (Fig. 2B) and with additional doses of H<sub>2</sub> another band appeared at 2460 cm<sup>-1</sup> (Fig. 2C and D). At the same time, a broad band initially appeared near 3320 cm<sup>-1</sup> and eventually bands were observed at 3372 and 3268 cm<sup>-1</sup>. When a 1:1 NH<sub>3</sub>/ND<sub>3</sub> mixture was used, the spectrum was virtually identical to that shown in Fig. 2D. When a Pt/ND<sub>3</sub> sample had been degassed at 200°C, as with NH<sub>3</sub>, the band at 2515 cm<sup>-1</sup> had near zero intensity. None the less, when micromole doses of H<sub>2</sub> were added, again a band at 2410 cm<sup>-1</sup> appeared initially, followed by the 2460 cm<sup>-1</sup> band. Finally, when ND<sub>3</sub>

was adsorbed onto a 10 mg cm<sup>-2</sup> Pt/SiO<sub>2</sub> sample a weak band at 883 cm<sup>-1</sup> was observed [such thin samples are partially transmitting from 1000–850 cm<sup>-1</sup> (11)], whereas this spectral region showed no new features with NH<sub>3</sub>. All resolvable band positions for the stretching modes of adsorbed <sup>14</sup>NH<sub>3</sub>, <sup>14</sup>ND<sub>3</sub> and <sup>15</sup>NH<sub>3</sub> are listed in Table 1.

### b. Identity of the Adsorbed Species

The unusual changes in relative intensity of the bands due to adsorbed ammonia discussed above is usually indicative of the presence of more than one adsorbed species. Thus it is not surprising that there have been varying views as to the number and nature of the adsorbed species when NH<sub>3</sub> is adsorbed on various metallic catalysts (2–6). None the less, the results obtained here indicate that only coordinately bound NH<sub>3</sub> is formed.

The isotopic data for the partially deuterated species clearly shows that the adsorbed species has at least 3 NH bonds since there are two partially labeled species. Thus, the first infrared band to appear when a micromole dose of H<sub>2</sub> was added

TABLE 1

Observed and Calculated Stretching Frequencies (cm<sup>-1</sup>) for Adsorbed Ammonia

		NH <sub>3</sub>	NH <sub>2</sub> D	NHD <sub>2</sub>	ND <sub>3</sub>	<sup>15</sup> NH <sub>3</sub>
Obsd	ν <sub>1</sub>	3372 <sup>a</sup>	— <sup>b</sup>	— <sup>c</sup>	2515 <sup>a</sup>	3365
	ν <sub>2</sub>	— <sup>d</sup>	— <sup>c</sup>	— <sup>e</sup>	— <sup>d</sup>	— <sup>d</sup>
	ν <sub>3</sub>	3268 <sup>a</sup>	2460	2410	2375 <sup>a</sup>	3265
Calcd <sup>f</sup>	ν <sub>1</sub>	3372	3372	3342	2515	3362
	ν <sub>2</sub>	— <sup>d</sup>	3308	2515	— <sup>d</sup>	— <sup>d</sup>
	ν <sub>3</sub>	3271	2462	2413	2367	3265

<sup>a</sup> These frequencies were used in the force constant refinement calculation.

<sup>b</sup> Presumed to be at 3372 cm<sup>-1</sup>.

<sup>c</sup> Not resolved.

<sup>d</sup> Degenerate with ν<sub>1</sub>.

<sup>e</sup> Presumed to be at 2515 cm<sup>-1</sup>.

<sup>f</sup> Force constants: *F*<sub>NH</sub> = 6.173 mdyn/A. Interaction constant *f* = 0.014 mdyn/A.

to adsorbed  $\text{ND}_3$  appeared at  $2410\text{ cm}^{-1}$  and can be assigned to the symmetric  $\nu(\text{ND})$  mode of  $\text{NHD}_2$ , whereas with increasing H substitution a second band appeared at  $2460\text{ cm}^{-1}$  which can be assigned to the single  $\nu(\text{ND})$  mode of  $\text{NH}_2\text{D}$ . A simple force constant calculation treating the high frequency  $\nu(\text{NH})$  modes as being independent of the low frequency modes [see Ref. (9) for a discussion of the procedure] confirms these assignments and, as with the  $\nu(\text{CH})$  modes of  $\text{SiOCH}_3$  (9), predicts that  $\nu_1(\text{ND}_3)$  and  $\nu_2(\text{NHD}_2)$  will be coincident, and explains our failure to detect the latter as a distinct band (Table 1). Due to the smaller spread between  $\nu_a$  and  $\nu_s$  of  $\text{NH}_3$ , we were unable to resolve the distinct  $\nu(\text{NH})$  bands for  $\text{NH}_2\text{D}$  and  $\text{NHD}_2$ . The extremely weak band at  $1600\text{ cm}^{-1}$  can be assigned to the antisymmetric deformation mode of coordinated  $\text{NH}_3$  (this band was so weak that our failure to detect the corresponding bands for the partially deuterated species was not unexpected). The "umbrella" mode of gaseous  $\text{NH}_3$  ( $932/965\text{ cm}^{-1}$ ) shifts to  $1150\text{--}1250\text{ cm}^{-1}$  when  $\text{NH}_3$  coordinates and is termed the symmetric deformation mode,  $\delta_s(\text{NH}_3)$ . In coordinated  $\text{ND}_3$  this shifts to about  $900\text{ cm}^{-1}$  and we can assign the observed  $883\text{ cm}^{-1}$  band to this mode (10). [A band also occurs in this region for coordinated  $\text{ND}_3$  on Ni (2).] It is to be stressed that no other distinct  $\nu(\text{ND})$  bands were observed on partial deuteration and if the  $2515/2375\text{ cm}^{-1}$  bands were also due to a coadsorbed  $\text{PtND}_2$  species, a band midway between these at  $2445\text{ cm}^{-1}$  due to  $\text{PtNHD}$  would have been expected. [In the case of  $\text{SiND}_2$ ,  $\nu_a = 2634\text{ cm}^{-1}$ ,  $\nu_s = 2529\text{ cm}^{-1}$  and the  $\nu(\text{ND})$  mode of  $\text{SiNHD}$  is at  $2578\text{ cm}^{-1}$  (11).] The weak bands at  $3155\text{ cm}^{-1}$  ( $\text{NH}_3$ ) and  $2315\text{ cm}^{-1}$  ( $\text{ND}_3$ ) are presumed to be overtones of the antisymmetric deformation mode, enhanced in intensity by Fermi resonance interaction with the corresponding symmetric stretching mode. Finally, in spite of the unusual changes in relative

intensity after degassing at  $200^\circ\text{C}$ , the same bands due to mixed H/D isotopic species were observed. We conclude that the spectroscopic results are entirely consistent with the idea that a single adsorbed species is present, this being coordinately bonded  $\text{NH}_3$ .

### c. Intensity Effects

The bands at  $3372$  and  $3268\text{ cm}^{-1}$  have been assigned to the symmetric and antisymmetric  $\text{NH}$  stretching modes of  $\text{Pt:NH}_3$ , respectively. In most isolated molecules containing  $\text{AH}_2$  or  $\text{AH}_3$  functional groups (A is any other atom) the infrared band due to the antisymmetric mode ( $\nu_a$ ) is more intense than that of the symmetric mode ( $\nu_s$ ), whereas the reverse is true in the present case for  $\text{PtNH}_3$ , as has been found previously for  $\text{PtCH}_2$  (12). These effects are probably due to a combination of optical effects due to reflection and dipole imaging effects. For the  $\nu_a$  mode the dipole moment change lies parallel to the surface, whereas it lies perpendicular to the surface for  $\nu_s$ . Greenler has shown (13) that when infrared radiation is reflected from a flat metal surface only symmetric modes are capable of absorbing energy from the oscillating electric field. Whether this treatment is valid when considering transmission through a heterogeneous supported metal sample is open to question. On the other hand a dipole imaging theory produces a similar qualitative result. The surface image or induced dipole moment change lies in the same direction for  $\nu_s$ , whereas the image is antiparallel for  $\nu_a$ . Thus one would expect intensity enhancement for the  $\nu_s$  modes and a relative decrease in intensity for the  $\nu_a$  modes. This is experimentally observed for  $\text{Pt:NH}_3$  and a similar effect has been recently reported by Prentice *et al.* (14) for ethylene adsorbed on palladium and platinum.

This argument may also explain why the intensity of the antisymmetric deformation mode ( $1600\text{ cm}^{-1}$ ) was so low. In  $\text{NH}_3$

coordination compounds (10) this is usually one of the strongest bands, as it is for coordinated NH<sub>3</sub> on alumina (1, 15). Thus it is not surprising that this band for Pt:NH<sub>3</sub> (3) or Ir:NH<sub>3</sub> (15) was not observed in isolation in previous studies where Al<sub>2</sub>O<sub>3</sub> was the support. In other work where Pt/SiO<sub>2</sub> was used Griffiths *et al.* (4) only studied the region from 4000–1900 cm<sup>-1</sup> whereas Pozdhyakov and Filimonov (5) reported a deformation band at 1630 cm<sup>-1</sup> but did not show the spectrum or comment on the intensity. Blyholder and Sheets (2) also reported a band of medium intensity near 1600 cm<sup>-1</sup> (no spectra) for NH<sub>3</sub> coordinated on evaporated Ni, Pd, Fe and V.

The unusual intensity changes which occurred during evacuation at 100–200°C, viz, the apparent intensification of the 3268 and 3155 cm<sup>-1</sup> bands while the 3372 cm<sup>-1</sup> band decreased in intensity, would suggest that more than one adsorbed species is present, possibly a PtNH<sub>2</sub> or Pt<sub>2</sub>NH species. However, all band areas did appear to decrease during this treatment; whereas the peak intensity at 3268 increased slightly, the half band width narrowed considerably. Bearing in mind that no new bands were observed when small amounts of H<sub>2</sub> were added (whereas exchange with D<sub>2</sub> occurred readily) and that all peak intensities more or less reversibly decreased when higher pressures of H<sub>2</sub> were added (the latter are discussed further below), then we would have to conclude that if small amounts of dissociatively adsorbed ammonia are present, these are not hydrogenated in the presence of excess H<sub>2</sub>. This seems unlikely and we have to assume that the unusual intensity changes on degassing might be due to dipole-dipole interaction effects between neighboring adsorbed molecules. At high surface coverages the dipole moment changes associated with  $\nu_s$  would tend to cancel each other (i.e., the induced dipole moment change in a neighboring molecule would be of opposite sign), whereas for  $\nu_a$  they would be enhanced by

an inductive effect. Hence  $\nu_a$  would be anomalously intense and  $\nu_s$  would be anomalously weak at high coverage. During heating, which may lead to desorption, or, if patches of Pt:NH<sub>3</sub> molecules were formed on the outer skin of the Pt/SiO<sub>2</sub> disc these might redistribute themselves by diffusing into the bulk of the disc [as has been reported for PtCO during heating (16)] neighboring interactions diminish and, for an equal number of oscillators, we expect an apparent intensification of  $\nu_s$  and a corresponding decrease in the intensity of  $\nu_a$ . Such effects are observed in the experimental spectra.

The usual changes in intensity which were observed after H<sub>2</sub> was added are difficult to account for on chemical grounds. With chemisorbed hydrocarbons (12, 17) one frequently observes a decrease in the intensity of  $\nu(\text{CH})$  modes upon evacuation and a subsequent increase in intensity upon adding H<sub>2</sub> again (presumed to correspond to a dehydrogenation-hydrogenation sequence), whereas the opposite spectral changes were observed in the case of adsorbed ammonia. A possible explanation may be drawn from an idea proposed by Blyholder and Sheets (2).

They observed a more intense spectrum due to coordinated NH<sub>3</sub> on Ni or Pd when NH<sub>3</sub> and CO were coadsorbed than in the absence of CO. They suggested that back donation of negative charge to the CO ligand (accompanied by an observed shift of  $\nu(\text{CO})$  to lower wavenumber) effectively drained charge from the surface and hence facilitated the coordination of NH<sub>3</sub>. Primet *et al.* (3) also observed a shift of  $\nu(\text{CO})$  to lower wavenumber when CO preadsorbed ( $\theta = 0.1$ ) on an alumina-supported Pt surface was subsequently exposed to NH<sub>3</sub>. The same effects have been noted in this work, indicating the acceptance of charge by the CO ligand.

In the case of H<sub>2</sub> adsorption, if H donates charge to the surface as has been reported in studies of H and CO coadsorption (18)

then the PtN bond would be weakened. As a result, the dipole moment and the change in dipole moment during vibration would be expected to decrease. Such effects are also known in metal coordination compounds of  $\text{NH}_3$  where the infrared bands due to  $\nu(\text{NH})$  modes both decrease in intensity and shift to higher frequency as the degree of negative charge on the metal atom increases (19, 20). Since this effect is observed we must conclude that when hydrogen is coadsorbed with  $\text{NH}_3$  on platinum, the platinum hydrogen bond should have some partial ionic character,  $\delta^- \delta^+$  Pt—H. We do not believe that the observed effects are simply due to a weakening of the Pt—N bond such that  $\text{NH}_3$  becomes hydrogen-bonded to the support because of the total absence of a band near  $3400 \text{ cm}^{-1}$  which is characteristic of the latter.

The only previous infrared studies of the adsorption of ammonia on Pt have been carried out by Primet *et al.* (3), by Griffiths *et al.* (4) and by Pozdhyakov and Filimonov (5) and it does not seem fruitful to compare the results of this work with results obtained using say iron and nickel where considerable differences could be expected. [Indeed with iron, spectra which are quite different from those reported here have been obtained and three different interpretations have been advanced (2, 5, 6).] Primet *et al.* (3) reported no spectral bands which they attribute to  $\text{NH}_3$  on Pt (mainly because of interfering bands due to  $\text{NH}_3$  on  $\text{Al}_2\text{O}_3$ ) but they did conclude that  $\text{NH}_3$  did not dissociate on Pt, but it did coordinate. Griffiths *et al.* (4) using a low resolution spectrometer for a study of the adsorption on Pt/ $\text{SiO}_2$  came to the same conclusion but their spectra were extremely weak (they only used  $10 \text{ mg cm}^{-2}$  samples and did not state the percentage of Pt) and usually strongly overlapped by bands due to H-bonded  $\text{NH}_3$ . Their study was mainly concerned with the oxidation of  $\text{NH}_3/\text{O}_2$  mixtures over Pt and no attempt was made

to prove whether the above conclusion was correct. Pozdhyakov and Filimonov (5) also used Pt/ $\text{SiO}_2$  ( $28\text{--}51 \text{ mg cm}^{-2}$ , 10% Pt) and obtained spectra after adsorption at  $20^\circ\text{C}$  which resembled ours except that the high wavenumber band was initially more intense but after evacuation at  $200^\circ\text{C}$  their spectra resembled ours, i.e., the same relative intensity changes were observed. On adding  $\text{H}_2$ , the  $3268 \text{ cm}^{-1}$  band did not change, whereas the high wavenumber band intensified. They assumed that both coordinated and dissociatively adsorbed ammonia were present but their spectra might equally well be attributed to a mixture of coordinated  $\text{NH}_3$  plus traces of H-bonded  $\text{NH}_3$ . Their study was relatively incomplete and their conclusions must be suspect in the absence of further isotopic data.

#### d. Addition of $\text{O}_2$

Griffiths *et al.* (4) investigated the reaction of adsorbed Pt: $\text{NH}_3$  with  $\text{O}_2$  and found that infrared bands which they attributed to physically adsorbed  $\text{N}_2\text{O}$  grew as the bands due to coordinated  $\text{NH}_3$  decreased. They always used a large excess of  $\text{O}_2$  and frequently the reaction was carried out at elevated temperatures (up to  $150^\circ\text{C}$ ) which might account for their failure to detect chemisorbed intermediates.

In the present work we have used micromole quantities of  $\text{O}_2$  in order to minimize the chance of rapid and complete oxidation. A series of spectra showing the effect of adding a micromole dose of  $\text{O}_2$  to pre-adsorbed ammonia are shown in Figs. 3 and 4. For  $^{14}\text{NH}_3$ , the major changes were the growth of new bands at  $3544 \text{ cm}^{-1}$  and  $1605 \text{ cm}^{-1}$ , and the disappearance of the  $3372$  and  $3155 \text{ cm}^{-1}$  bands due to Pt: $\text{NH}_3$  leaving only a broad weak band centered near  $3265 \text{ cm}^{-1}$ . The strong band at  $1605 \text{ cm}^{-1}$  shifted slightly to higher wavenumber and eventually decreased in intensity if the number of doses of  $\text{O}_2$  was increased (Fig. 4C–E). If about 10 Torr of  $\text{O}_2$  was added

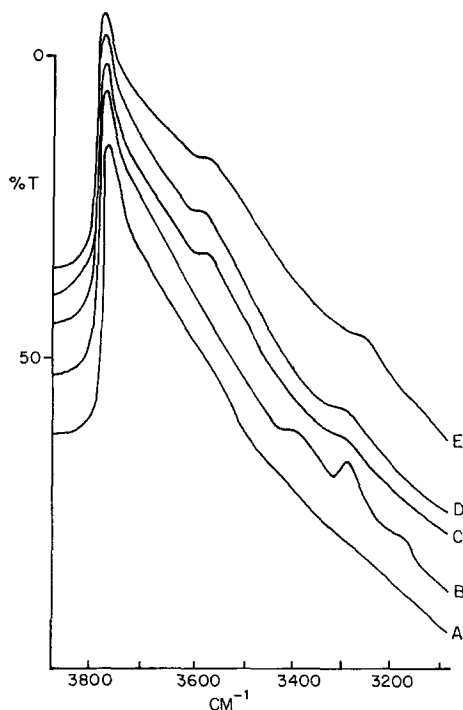


FIG. 3. (A) Background spectrum (4000–3100  $\text{cm}^{-1}$ ) of Pt/SiO<sub>2</sub>. (B) After adsorption of NH<sub>3</sub>. After the addition of about 5  $\mu\text{mole}$  of <sup>16</sup>O<sub>2</sub> with no evacuation. (D) As for C using <sup>18</sup>O<sub>2</sub>. (E) As for C using <sup>16</sup>O<sub>2</sub> to adsorbed <sup>15</sup>NH<sub>3</sub>. The % *T* scale refers to (A).

all bands disappeared except that at 3544  $\text{cm}^{-1}$  which broadened and shifted to about 3520  $\text{cm}^{-1}$ . Although the 3265  $\text{cm}^{-1}$  band was extremely weak, it did disappear in excess O<sub>2</sub> in unison with the 1605  $\text{cm}^{-1}$  band. The corresponding band positions for various nitrogen-15, oxygen-18 and deuterium containing combinations are listed in Table 2.

TABLE 2

New Infrared Bands Observed for the Oxidation of Adsorbed Ammonia ( $\text{cm}^{-1}$ )

<sup>14</sup> NH <sub>3</sub>	<sup>15</sup> NH <sub>3</sub>	<sup>14</sup> ND <sub>3</sub>	<sup>14</sup> NH <sub>3</sub> <sup>a</sup>	Assignment
3544	3544	2609	3533	PtOH (II) <sup>b</sup>
3265	3265	2397	3265	Pt:NHO
1605	1580	1605	1574	Pt:NHO

<sup>a</sup> Oxygen-18 used.

<sup>b</sup> See Ref. (7).

It would appear that the new strong band at 1605  $\text{cm}^{-1}$  can be assigned to a partially oxidized adsorbed intermediate, a species which is probably converted to a gaseous nitrogen oxide in excess O<sub>2</sub>. The 3265  $\text{cm}^{-1}$  band could have been assigned to unoxidized NH<sub>3</sub>, but in view of its shift to the unique position of 2397  $\text{cm}^{-1}$  (where bands due to Pt:ND<sub>3</sub> do not interfere) we can infer that this is also attributable to the same intermediate. Further, when a 1:1 NH<sub>3</sub>/ND<sub>3</sub> mixture was used, these were the only new bands detected during the oxidation which suggests that the intermediate only contains one hydrogen atom. Finally, the band at 3544  $\text{cm}^{-1}$  coincides in position, <sup>18</sup>O shift and D shift with a band which has previously been assigned to a type II PtOH species (7).

The <sup>15</sup>N and <sup>18</sup>O shift of the 1605  $\text{cm}^{-1}$  band would lead us to believe that this band can be assigned to an N=O stretching mode. Nitric oxide adsorbed on Pt has a pair of high frequency  $\nu(\text{NO})$  bands at about 1800 and 1600  $\text{cm}^{-1}$ , and the lower wavenumber band always has about one quarter of the intensity of the 1800  $\text{cm}^{-1}$  band (21). The origin of these bands has not yet been fully established but the 1600  $\text{cm}^{-1}$  band has

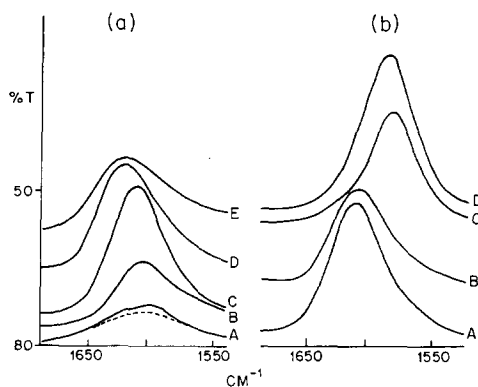


FIG. 4a. (A) (---) Background spectrum of Pt/SiO<sub>2</sub>; (—) after adsorption of NH<sub>3</sub>. (B–E) After successive additions of about 2  $\mu\text{mole}$  of O<sub>2</sub>. (b). Spectra as in (a) C for various isotopic species. (A) <sup>16</sup>O<sub>2</sub>, <sup>14</sup>NH<sub>3</sub>; (B) <sup>16</sup>O<sub>2</sub>, <sup>14</sup>ND<sub>3</sub>; (C) <sup>16</sup>O<sub>2</sub>, <sup>14</sup>NH<sub>3</sub>; (D) <sup>16</sup>O<sub>2</sub>, <sup>15</sup>NH<sub>3</sub>.

never been observed in isolation. Primet *et al.* (22) have also observed these two bands for NO adsorbed on Pt/Al<sub>2</sub>O<sub>3</sub> but contend that the weak 1600 cm<sup>-1</sup> band was removed after a brief evacuation. Therefore, we do not believe that the 1605 cm<sup>-1</sup> band in the present work can be assigned to a simple PtNO surface species but we cannot conclusively rule this idea out. Further work on the Pt-NO problem is under way, but we do note that, whereas the 1605 cm<sup>-1</sup> band in the present work disappeared when a very slight excess of O<sub>2</sub> was added, this does not happen when O<sub>2</sub> is added to adsorbed NO (21).

In view of the preceding, the most likely

candidate is adsorbed Pt:  $\begin{array}{c} \text{O} \\ \diagup \\ \text{Pt:N} \\ \diagdown \\ \text{H} \end{array}$  where we

have to assume that the 3265 cm<sup>-1</sup> band is the  $\nu(\text{NH})$  mode (2397 cm<sup>-1</sup> for D). Such a species would almost certainly be very readily oxidized in excess O<sub>2</sub>. The molecule HNO itself is not stable, it is usually produced by photochemical means and its spectrum has been studied in the gas phase in flash photolysis experiments (23), or as a solid trapped in inert matrices at low temperatures (24-28). The  $\nu(\text{NH})$  mode is weak and early work (24-27) suggested a range of values from 3300 to 3600 cm<sup>-1</sup>, whereas a recent study has tentatively placed it as low as 2717 cm<sup>-1</sup> where the N-H bond is presumed to be unusually long and, therefore, weak (28). All studies place the  $\nu(\text{N=O})$  mode near 1565 cm<sup>-1</sup>, the most accurate value being 1563 cm<sup>-1</sup> (28). The <sup>15</sup>N shift was 14 cm<sup>-1</sup> (25 cm<sup>-1</sup> this work) and the <sup>18</sup>O shift was 31 cm<sup>-1</sup> (31 cm<sup>-1</sup> this work). Assuming that the structure of a coordinated Pt:NHO species could be quite different from that of the free molecule, we feel that the isotopic shift data lends some support to this as being the postulated intermediate,

It is not possible to say anything definitive about the mechanism of formation of Pt:NHO. The type II PtOH species is normally only produced (?) when gaseous H<sub>2</sub>O is added to a partially oxidized Pt surface and no dissociation occurs when H<sub>2</sub>O is added to a Pt sample which had been pretreated in O<sub>2</sub> at 20°C (see the next section for a further discussion). However, it can also be produced when micro-mole quantities of O<sub>2</sub> are added to a hydrogen covered Pt. Since hydrogen must be liberated if Pt:NHO is produced, the formation of type II PtOH may just be a secondary process and it is not fruitful to start postulating a reaction mechanism since many possibilities exist.

#### e. Adsorption of NH<sub>3</sub> on Oxidized Pt

We have recently shown that two types of surface PtOH species can be generated on silica-supported Pt (?). It was suggested that type I PtOH [ $\nu(\text{OH}) = 3497 \text{ cm}^{-1}$ ] was only formed when the Pt surface was highly oxidized, whereas the type II PtOH [ $\nu(\text{OH}) = 3544 \text{ cm}^{-1}$ ] was formed on a partially oxidized surface.

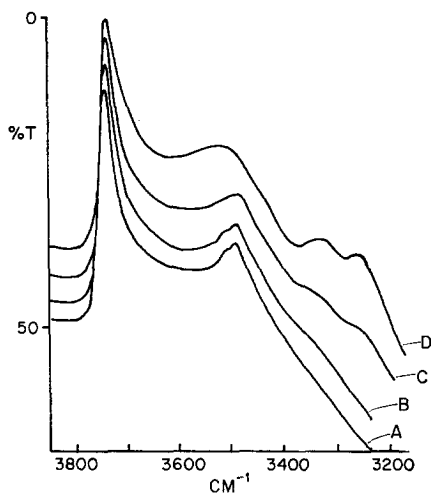


FIG. 5. (A) Background spectrum of oxidized Pt/SiO<sub>2</sub> containing type I PtOH band at 3497 cm<sup>-1</sup>. (B, C) After successive additions of 5  $\mu\text{mole}$  of NH<sub>3</sub>. (D) After addition of 16  $\mu\text{mole}$  of NH<sub>3</sub> for 1 min then evacuated for 1 hr. The % T scale refers to (A).



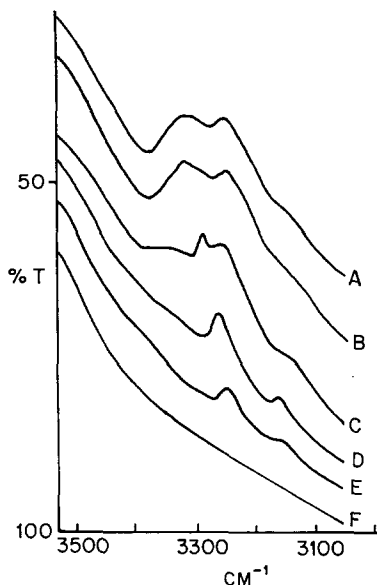


FIG. 6. (A) Spectrum after adsorption of 10 Torr of NH<sub>3</sub> on oxidized Pt/SiO<sub>2</sub>. Spectra observed after degassing at the following: (B) 16 hr at 20°C; (C) 1 hr at 100°C; (D) 1 hr at 200°C; (E) 16 hr at 200°C; (F) 1 hr at 300°C. The % *T* scale refers to (F).

When NH<sub>3</sub> reacted with a sample which contained type II PtOH a normal spectrum of coordinated NH<sub>3</sub> was observed. However, the spectra shown in Fig. 5 were

obtained when successive doses of NH<sub>3</sub> had been added to a surface which was prepared so as to contain only type I PtOH. Bands initially appeared at 3345, 3265 and 1495 cm<sup>-1</sup> (the latter not shown) and the 3497 cm<sup>-1</sup> band gradually broadened and shifted to about 3520 cm<sup>-1</sup>. The same final spectrum was also observed if NH<sub>3</sub> reacted with an oxidized Pt surface not containing the PtOH (I) species which was prepared by adding O<sub>2</sub> to a hydrogen free Pt/SiO<sub>2</sub> sample.

The spectrum shown in Fig. 5D did not change following prolonged evacuation at 20°C, but upon degassing at 100°C new bands grew together at 3308 and 1425 cm<sup>-1</sup> as the 3345 and 1495 cm<sup>-1</sup> bands disappeared. At higher temperatures (200°C) the 3308 and 1425 cm<sup>-1</sup> bands disappeared leaving bands at 3372, 3268 and 3155 cm<sup>-1</sup> characteristic of coordinated NH<sub>3</sub>. Spectra showing these changes in the ν(NH) region are in Fig. 6.

The initial assessment was that two new adsorbed species were formed, species (I) with bands at 3345, 3265 and 1495 cm<sup>-1</sup> which upon degassing is converted to species (II) with bands at 3308 and 1425

TABLE 3

Observed Infrared Bands for Ammonia Adsorbed on Oxidized Platinum (cm<sup>-1</sup>)

	<sup>14</sup> NH <sub>3</sub>	<sup>14</sup> ND <sub>3</sub>	<sup>16</sup> NH <sub>3</sub>	<sup>14</sup> NH <sub>3</sub> <sup>a</sup>	<sup>14</sup> NH <sub>3</sub> / <sup>14</sup> ND <sub>3</sub> <sup>b</sup>	Assignment
Initial ads'n.	3345		3338	3338	— <sup>c</sup>	ν <sub>a</sub> (ONH <sub>2</sub> )
	3265		3265	3263	— <sup>c</sup>	ν <sub>s</sub> (ONH <sub>2</sub> )
		2487			2487	ν <sub>a</sub> (OND <sub>2</sub> )
		2375			2440	(ONHD)
	1495	—	1495	1495	2375	ν <sub>s</sub> (OND <sub>2</sub> )
New bands after degassing at 100°C	3308		3305	3305	—	δ(OH <sub>2</sub> )
		2420			3305	ν(NH) <sup>d</sup>
	1425	—	1425	1425	2420	ν(ND)
					1425	δ <sub>a</sub> (ONH)

<sup>a</sup> Oxygen-18.

<sup>b</sup> 1:1 mixture of <sup>14</sup>NH<sub>3</sub> and <sup>14</sup>ND<sub>3</sub>.

<sup>c</sup> Only a broad band was observed from 3345–3265 cm<sup>-1</sup>.

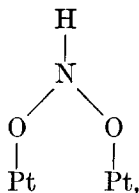
<sup>d</sup> NH stretching mode of (PtO)<sub>2</sub>NH<sub>2</sub>.

$\text{cm}^{-1}$ . In addition, a small amount of Pt:  $\text{NH}_3$  was probably always present.

The band positions for various isotopic combinations are listed in Table 3. Species I has two  $\nu(\text{NH})$  bands and a single new  $\nu(\text{ND})$  band is observed upon partial deuteration which suggests an  $\text{NH}_2$  containing species. There was a small shift in the  $3345 \text{ cm}^{-1}$  band both for  $^{15}\text{N}$  and  $^{18}\text{O}$  substitution, not at all for the  $1495 \text{ cm}^{-1}$  band, whereas the latter disappeared upon partial or complete deuteration. The data are consistent with species I being  $\text{PtONH}_2$  where the  $1495 \text{ cm}^{-1}$  band can be assigned to the  $\text{NH}_2$  deformation mode. No shift of this mode is expected for  $^{15}\text{N}$  substitution [as for  $\text{SiNH}_2$  (11)] or  $^{18}\text{O}$  substitution, and partial deuteration (NHD) would be expected to result in a shift to at least  $1350 \text{ cm}^{-1}$ , a region where the sample is totally absorbing in the infrared.

The only closely related "compound" to  $\text{PtONH}_2$  is hydroxylamine (10),  $\text{NH}_2\text{OH}$ . Here the  $\nu(\text{NH})$  modes absorb at  $3302$  and  $3245 \text{ cm}^{-1}$  while the  $\delta(\text{HNH})$  mode is unusually low,  $1515 \text{ cm}^{-1}$ . To the authors knowledge, no  $^{15}\text{N}$  or  $^{18}\text{O}$  data are available.

Species II is generated from  $\text{PtONH}_2$  and the  $\nu(\text{NH})$  data suggest that it contains only one hydrogen atom. The band at  $1425 \text{ cm}^{-1}$  is too low to be an antisymmetric deformation mode of a  $\text{NH}_2$  or  $\text{NH}_3$  unit; none the less it must have shifted by at least  $75 \text{ cm}^{-1}$  upon deuteration since it was not detected. Therefore, the most reasonable structure for species II would be,

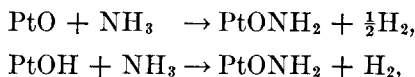


where the  $1425 \text{ cm}^{-1}$  band would be assigned to the antisymmetric  $\delta(\text{ONH})$  mode. Very small shifts would be expected for  $^{15}\text{N}$  or  $^{18}\text{O}$  substitution but, by analogy

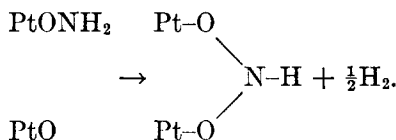
with structurally similar compounds this mode could shift by about  $300 \text{ cm}^{-1}$  upon deuteration. Some examples are  $\text{F}_2\text{NH}$  (29) [ $1425$ – $1042 \text{ cm}^{-1}$ ],  $\text{HBF}_2$  (30) [ $1402$ – $1195 \text{ cm}^{-1}$ ] and  $\text{NaHCO}_2$  (31) [ $1380$ – $1028 \text{ cm}^{-1}$ ].

We note that the identity of species I and II has not been conclusively established by the above spectroscopic arguments. For example  $\text{PtNH}_2$  or  $\text{Pt}_2\text{NH}$  would be expected to exhibit identical spectral features although the antisymmetric deformation mode of the latter would probably not be as high as  $1425 \text{ cm}^{-1}$ . However, if these were the correct structures we might have anticipated that they could also be formed during adsorption on bare Pt at some temperature within the range  $20$ – $200^\circ\text{C}$  or even when  $\text{O}_2$  was added to Pt:  $\text{NH}_3$ . Therefore, since species I and II are exclusively associated with a platinum oxide surface we feel that the structures involving PtON bonds are more reasonable.

The broad band near  $3520 \text{ cm}^{-1}$  may be due to traces of adsorbed water or to perturbed PtOH groups and it is not possible to distinguish between these. It is therefore not possible to formulate a detailed mechanistic picture except to suggest that the primary process is almost certainly one of the following;



where the  $\text{H}_2$  presumably reacts further with PtO to form water. During heating we assume that a mobile surface oxygen reacts as follows;



The liberated  $\text{H}_2$  above might reduce some  $\text{PtONH}_2$  back to Pt:  $\text{NH}_3$  since, with higher degassing temperatures (Fig. 6E) only the spectrum of the latter remained.

Finally, we note the unusual thermal stability of species II [(PtO)<sub>2</sub>NH]. Ostermaier *et al.* (32) have recently studied the effect of crystallite size on the rate of NH<sub>3</sub> oxidation at low temperatures (120–200°C) and have noted that the catalyst was deactivated during the first 6 hr of operation in a differential, fixed bed, flow reactor. This deactivation was not due to the individual reactants alone, but was due to a product of the reaction and they attributed this to a change in the concentration of "active" oxygen on the catalyst. Part of this deactivation may also be due to the unusual stability of partially oxidized intermediates as described above.

#### CONCLUSIONS

Infrared spectroscopic evidence derived from partial deuteration and from H/D exchange studies of adsorbed ammonia on silica supported platinum suggests that ammonia does not dissociately chemisorb on Pt in the temperature range 20–200°C but that it does form a strong coordinate bond, presumably with a surface Pt atom. When micromole doses of O<sub>2</sub> are added a transient intermediate is formed which might be Pt:NO, or more probably Pt:NHO. The transient is rapidly oxidized in excess O<sub>2</sub> and no infrared bands attributable to an adsorbed species are observed.

When ammonia adsorbs on a Pt/SiO<sub>2</sub> sample which had been pretreated in O<sub>2</sub>, a PtONH<sub>2</sub> species is probably formed. This is stable at 20°C, but at about 100°C it reverts to a new adsorbed species which has been tentatively identified as a bridged (PtO)<sub>2</sub>NH species. The latter is stable up to about 200°C.

#### ACKNOWLEDGMENT

We are grateful for financial support from the National Research Council of Canada. B. A. M. also acknowledges the help provided by Dr. G. Somorjai and the staff at the University of California,

Berkeley, where this manuscript was written while he was on sabbatical.

#### REFERENCES

1. Kiselev, A. V., and Lygin, V. I., "Infrared Spectra of Surface Compounds," Wiley, New York, 1975.
2. Blyholder, G., and Sheets, R. W., *J. Catal.* **27**, 301 (1972).
3. Primet, M., Basset, J. M., Mathieu, M. V., and Prettre, M., *J. Catal.* **29**, 213 (1973).
4. Griffiths, D. W. L., Hallam, H. E., and Thomas, W. J., *Trans. Faraday Soc.* **64**, 3361 (1968).
5. Pozdhyakov, D. V., and Filimonov, V. N., *Kinet. Katal.* **13**, II, 475 (1972).
6. Nakata, T., and Matsushita, S., *J. Phys. Chem.* **72**, 458 (1968).
7. Morrow, B. A., and Ramamurthy, P., *J. Phys. Chem.* **77**, 3052 (1973).
8. Schachtschneider, J. H., Tech. Rep. No. 231-64 and 57-65, Shell Development Co., Emeryville, Calif.
9. Morrow, B. A., *J. Chem. Soc. Faraday Trans. I* **70**, 1527 (1974).
10. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds," Wiley (Interscience), New York, 1970.
11. Morrow, B. A., Cody, I. A., and Lee, L. S. M., *J. Phys. Chem.* **79**, 2405 (1975).
12. Morrow, B. A., and Sheppard, N., *Proc. Roy. Soc., Ser. A* **311**, 391, 415 (1969).
13. Greenler, R. G., *J. Chem. Phys.* **44**, 310 (1966); **50**, 1963 (1969).
14. Prentice, J. D., Lesiunas, A., and Sheppard, N., *J. Chem. Soc. Chem. Commun.* **76**, (1976).
15. Contour, J. P., and Pannetier, G., *J. Catal.* **24**, 434 (1972).
16. Hammaker, R. M., Francis, S. A., and Eischens, R. P., *Spectrochim. Acta* **21**, 1295 (1965).
17. Avery, N. R., *J. Catal.* **19**, 15 (1970).
18. Pliskin, W. A., and Eischens, R. P., *Z. Phys. Chem* **24**, 11 (1960).
19. Babaeva, A. V., and Evstaf'eva, O. N., *Russ. J. Inorg. Chem.* **6**, 29 (1961).
20. Svatos, G. F., Curran, C., and Quagliano, J. V., *J. Amer. Chem. Soc.* **77**, 6159 (1955).
21. Morrow, B. A., and Moran, L., unpublished data.
22. Primet, M., Basset, J. M., Garbowski, E., and Mathieu, M. V., *J. Amer. Chem. Soc.* **97**, 3655 (1975).
23. Bancroft, J. L., Hollas, J. M., and Ramsay, D. A., *Canad. J. Phys.* **40**, 322 (1962).
24. Ogilvie, J. F., *Spectrochim. Acta* **23A**, 737 (1967).

25. Harvey, K. B., and Brown, H. W., *J. Chim. Phys.* **56**, 745 (1959).
26. Brown, H. W., and Pimentel, G. C., *J. Chem. Phys.* **29**, 883 (1958).
27. Miligan, D. E., Jacox, M. E., Charles, S. W., and Pimentel, G. C., *J. Chem. Phys.* **37**, 2302 (1962).
28. Jacox, M. E., and Milligan, D. E., *J. Mol. Spectrosc.* **48**, 536 (1973).
29. Comeford, J. J., Mann, D. E., Schoen, L. J., and Lide, D. R., *J. Chem. Phys.* **38**, 461 (1963).
30. Lynds, L., *J. Chem. Phys.* **42**, 1124 (1965).
31. Harvey, K. B., Morrow, B. A., and Shurvell, H. F., *Canad. J. Chem.* **41**, 1181 (1963).
32. Ostermaier, J. J., Katzer, J. R., and Manogue, W. H., *J. Catal.* **33**, 457 (1974); **41**, 277 (1976).