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Hydrazine Decomposition over a Supported Iridium Catalyst

J. P. CONTOUR AND G. PANNETIER

Laboratoire de Cinétique Chimique de la Faculté des Sciences, 1 rue Guy de la Brosse - 75 Paris 5ᵉ, Equipe de Recherche associée au CNRS No. 24

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Adsorption and desorption of hydrazine and its decomposition products (H_2, N_2, NH_3) on an iridium alumina catalyst have been studied by temperature programmed desorption and ir spectroscopy in order to determine the mechanism of the decomposition and the nature of the active centers.

Hydrogen is chemisorbed on two types of adsorption sites. Activation energies of desorption have been calculated for these sites and they are 10.5 and 25 kcal mole^{-1}. Sites of lower energy are attributed to the existence of an Ir–alumina complex and these of higher energy to bulk iridium. Nitrogen is not adsorbed from the gaseous phase between 25 and 700°C. Ammonia is adsorbed on metal and alumina at room temperature, its decomposition begins at 200°C.

Desorption spectra, recorded after adsorbing and decomposing hydrazine, show a new desorption peak, which is attributed to nitrogen remaining adsorbed on iridium. It corresponds to a desorption activation energy of 14 kcal mole^{-1}, and it confirms that the first step of decomposition is the formation of a bond between the nitrogen atoms of the hydrazine molecule and the unfilled *d* orbitals of the metal. Apparently, at 300°K, the decomposition is carried out according to the reaction $3N_2H_4 \rightarrow 4NH_3 + N_2$.

The ir spectra of ammonia and hydrazine adsorbed on the catalyst exhibit a band at 1220 cm^{-1}, besides the adsorption bands characteristic of ammonia adsorbed on alumina; this band could be attributable to ammonia chemisorbed on iridium.

INTRODUCTION

The catalytic decomposition of hydrazine is an interesting problem because of its many practical applications: gas generators, fuel cells, and microrockets for artificial satellites are but a few examples. The search for a good catalyst has led us to undertake experiments using a supported iridium catalyst.

The decomposition of hydrazine has already been investigated both in the gas phase and the liquid phase (*1–5*). Two major hypotheses have been put forward on the decomposition mechanism:

I. The superposition of reactions (1) and (2):

$$(1)\quad N_2H_4 \rightarrow N_2 + 2H_2,$$
$$(2)\quad 3N_2H_4 \rightarrow N_2 + 4NH_3.$$

II. The existence of a hydrogenolysis reaction in which the hydrogen produced by reaction (1) is consumed by (3):

$$(1)\quad N_2H_4 \rightarrow N_2 + 2H_2,$$
$$(3)\quad N_2H_4 + H_2 \rightarrow 2NH_3.$$

In this study, we use the temperature programmed desorption (TPD) technique and ir spectroscopy to examine the adsorption and desorption of hydrazine and its decomposition products (H_2, N_2, NH_3) on an iridium catalyst supported one γ-alumina, in order to determine the mechanism of the reaction and the nature of the active centers.

EXPERIMENTAL METHODS

Apparatus and Procedure

1. *Temperature Programmed Desorption*

The temperature programmed desorption technique, which was developed by Amenomiya and Cvetanovic (*6*), has made it possible to study irreversible adsorption (*7, 8*). The desorption spectrum is obtained by recording the rate of desorption in relation to temperature, and analysis of the spectrum provides the following informations:

- —number of phases adsorbed,
- —number of adsorption sites,
- —order of reaction,
- —activation energy and desorption rate constant.

The experimental apparatus is essentially the same as that described by Amenomiya and Cvetanovic (*6*). The carrier gas, argon, is dehydrated as it passes over a two-meter column packed with 5 Å molecular sieves. Stability of flow is maintained by an initial capillary loss. Regulation of the pressure on the upstream side makes it possible to vary the flow. The desorbed gases may be analyzed by gas chromatography. The following procedure was used for the temperature programmed desorption experiments:

(a) Cleaning the surface of the catalyst by heating it in hydrogen at 500°C, followed by desorption in argon at the same temperature. Cooling of the sample in argon.
(b) Adsorption.
(c) Desorption in argon for different heating rates. Simultaneous chromatographic analysis of the desorbed products.

The heating rates vary between 4 and 35°C min^{-1}.

Hydrogen and Ammonia adsorption were carried out by the dynamic method which consists in consecutive injections of a known volume of gas. Hydrazine was fed into the carrier gas by means of a Hamilton syringe through a septum and vaporized at 120°C. The injected volume was 30 μl, for each experiment. Desorption spectra were recorded following the removal of all reversibly adsorbed species.

2. *Infrared Spectroscopy*

The ir cell was an all-glass system into which the windows (CaF_2) were not waxed but sealed with Viton O rings. The reason for this is that despite their low vapor pressure, many of the adhesives used to attach the windows to the ir cell body may contaminate the sample. Preliminary experiments performed over a one-week period confirmed that there was no contamination of the samples by vacuum grease (Apiezon). The spectrophotometer was the Perkin Elmer 521 and the spectra were recorded at room temperature (*9*).

Materials

1. *Catalysts Studied*

The catalysts studied were prepared by the cogelation of boehmite and chloroiridic acid on the one hand and, on the other, by the impregnation of a porous support with a solution of chloroiridic acid. The samples contained between 20 and 40% iridium by weight.

The specific surface area of the samples was between 100 and 150 m^2/g while the metal surface area measured by hydrogen chemisorption was between 40 and 90 m^2/g (*21*).

An electron microscope study of these catalysts revealed the existence of two populations of iridium particles. The first was a population of small particles corresponding to an agglomeration of a few elementary celles smaller than 30 Å. The second, an irregular population, takes the form to particles up to several microns in size. These particles correspond either to microcrystals or to aggregates of crystallites.

The chemical analysis of these catalysts shows that the alumina surface reacts with the chloroiridic acid during the preparation of the catalyst, the quantity of fixed chlorine varying between 1 and 4% by weight.

2. *Samples Used in Infrared Spectroscopy*

The support, Degussa c alumina, was impregnated with a solution of hexachloroiridic acid in order to titrate 10% iridium by weight. The mixture was next placed in the drying oven where it was dried at 150°C. It was then ground, sifted to 80 μ and finally compressed at 5 t/cm^2. The pellet obtained was treated at a pressure of 45 Torr of oxygen at 400°C and then degassed at the same temperature. Reduction followed, by heating the sample at 350°C at a pressure of 300 Torr of hydrogen, and finally desorption took place at 400°C and 10^{-5} Torr. Each of these treatments lasted 2 hr. The specific surface area of the samples was 97 m^2/g while the metal surface area measured by hydrogen chemisorption was 37 m^2/g of catalyst.

Treatment in oxygen proved indispensable in order to eliminate the impurities adsorbed on the support (*9*). Without this treatment, the formation of an adsorption band around 2,030 cm^{-1} was observed, which indicates the presence of adsorbed carbon monoxide (*10*). This carbon monoxide must be due to the catalytic oxidation of hydrocarbons adsorbed on the support through contact with the metal.

RESULTS

1. *Hydrogen Adsorption*

1.1. Temperature programmed desorption. Cleaning the surface of the catalyst with hydrogen proved indispensable for eliminating the oxygen which is adsorbed by the catalyst when kept in contact with air.

In fact, if the only cleaning of the catalyst in the reactor is by heating it in argon at 500°C, and if it then undergoes an initial adsorption–desorption cycle, the recorded spectrum corresponds to curve (1) in Fig. 1. A chromatographic analysis of the de-

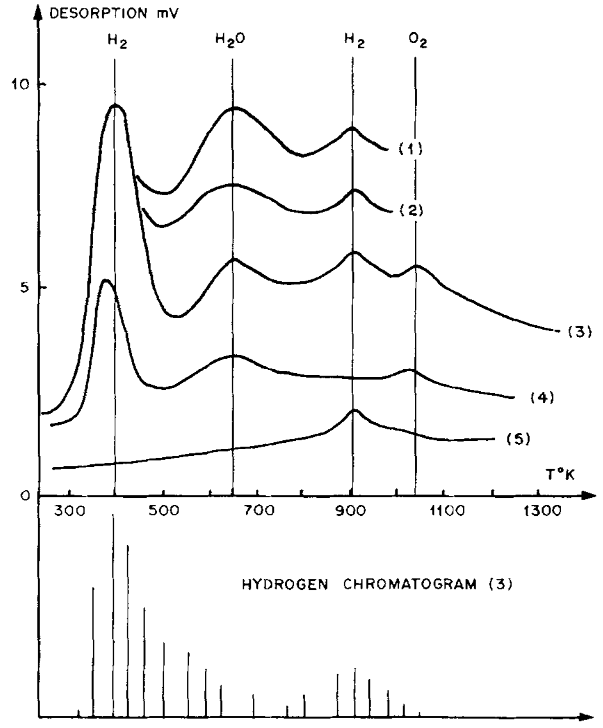


FIG. 1. Desorption spectra of hydrogen: (1) 36% iridium catalyst—first adsorption desorption cycle; (2) 36% iridium catalyst—second adsorption desorption cycle; (3) 36% iridium catalyst—third adsorption desorption cycle; (4) Catalyst used in spectroscopy; (5) Metallic iridium.

sorbed products for the intermediate peak reveals the presence of water and traces of hydrogen.

During a second adsorption–desorption cycle on the sample, the intermediate peak is smaller (curve 2, Fig. 1). It is even smaller in the following cycle, then levels out, but never disappears completely (curve 3, Fig. 1). At the same time, there is an increase in the intensity of the desorption peak corresponding to the hydrogen adsorbed on the weaker energy sites, since hydrogen is no longer being used for the reduction of surface oxide. If the catalyst is pretreated in hydrogen, however, spectrum (*3*) of Fig. 1 is observed immediately.

The adsorption of hydrogen, thus, has the effect of reducing the surface-oxidized iridium. The water produced is adsorbed by the alumina; its desorption between 150 and 400°C corresponds to the intermediate peak observed in the spectra.

The hydrogen desorption spectrum revealed by the chromatographic analysis has two peaks, the first appearing between 100 and 200°C and the second between 500 and 650°C (Fig. 1). These peaks are symmetrical in shape, which shows that desorption has a second-order reaction.

Hydrogen is, therefore, adsorbed in an atomic form on both types of sites. If the adsorption temperature exceeds 200°C, only the second desorption peak is recorded.

Neither adsorption nor desorption of hydrogen is observed on γ-alumina. In the case of unsupported bulk iridium, the first peak disappears whereas the desorption spectrum recorded for the samples used in ir spectroscopy have just one peak between 100 and 200°C. Such results reveal the existence of two types of irreversible-adsorption sites, the first corresponding to a weakly bound hydrogen atom (site I) the second to a more strongly bound atom (site II).

The activation energies and preexponential factor of the desorption rate constant were calculated for the sites I and II, based on the formulae established earlier.

$$\text{Ed (I)} = 10.5 \pm 0.5 \text{ kcal mole}^{-1},$$
$$\text{Ed (II)} = 25 \pm 3 \text{ kcal mole}^{-1},$$
$$A_1 = 10^4 \text{ sec}^{-1}.$$

1.2. Infrared spectroscopy of the adsorbed hydrogen. In the case of platinum catalysts supported on alumina or silica, Pliskin and Eischens were the first to study the adsorption of hydrogen by ir spectroscopy (*10*); they revealed two types of adsorption on platinum. Eley, Moran, and Rochester (*11*) took up this study and provide a different interpretation of the bonding of hydrogen, by introducing alumina hydroxyl groups at the surface.

The fundamental vibration frequency of a diatomic molecule of hydride X–H may be calculated using the formula below:

$$\bar{\nu} = (1/2\pi c)\sqrt{k/\mu},$$

where $\bar{\nu}$ is the wave number of the vibration in cm^{-1}, c is the speed of light, k the constant of the bond strength (in dynes cm^{-1}), and μ the reduces mass of the molecule. The constant k is established using the proportionality relationship which links it to the square of the ionization potential of the X element (*24*).

In the case of the Ir–H system, the application of these two equations gives a wave number of 2138 cm^{-1} and the frequency observed in the organic complexes of iridium is not very different from this theoretical value: between 2250 and 2010 cm^{-1} according to the compounds (*25*).

After the sample has been treated at 200°C at a hydrogen pressure of 400 Torr for 1 hr, the ir spectrum recorded with the gas phase shows two types of adsorption bands:

—Bands due to water adsorbed physically (deformation band near 1620 cm^{-1}) and to bound hydroxyls (wide valency band around 3500 cm^{-1}).

—Two bands at 2120 and 2050 cm^{-1} which may be attributed to the hydrogen adsorbed on the iridium.

The influence of the hydrogen pressure on these two bands is different (Fig. 2). When the pressure is lowered in successive steps of 400 to 10^{-4} Torr, the band at 2120 cm^{-1} is the first to disappear, as soon as 10^{-2} Torr is reached. The band at 2050 cm^{-1} is only eliminated after a 15-min treatment at 10^{-5} Torr. At the same time, we see a diminution of the deformation band of the

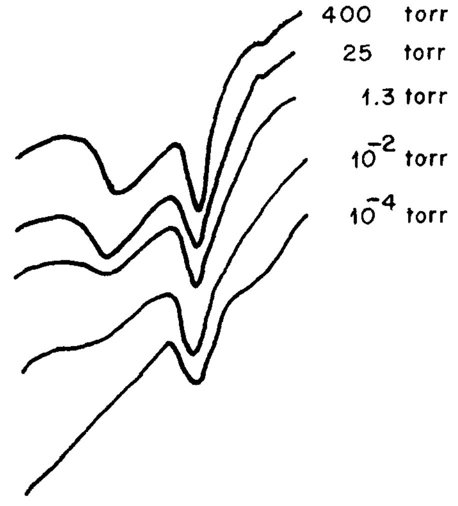


FIG. 2. Influence of pressure on ir spectra of chemisorbed hydrogen.

physically adsorbed water. These two bands have, therefore, been attributed, respectively, to hydrogen weakly and strongly adsorbed on the iridium. Identical results were obtained after hydrogen adsorption at 25°C and 400 Torr. Particularly noticeable here is the appearance of physically adsorbed water, a phenomenon which is not seen on alumina below 400°C. The formation of water is due either to the reduction of surface oxydized iridium or to the reaction of surface alumina hydroxyls with the hydrogen that is activated in contact with the metal.

The chemisorption of deuterium at 200°C in the same conditions on a sample reduced by deuterium, allows us to observe the formation of D_2O and the deuteration of the alumina hydroxyl groups at the surface, on the one hand, and on the other, the appearance of a wide band with two indistinct extremes at 1520 and 1490 cm^{-1}. These two bands are due to the deuterium weakly and strongly adsorbed by the iridium and correspond to a deuteration ratio of 1:39, the theoretical ratio ($\bar{\nu}$Ir–H)/($\bar{\nu}$Ir–D) being 1:41.

From these results we can conclude that hydrogen is adsorbed in two distinct forms having different bond strengths with respect to the surface. In such conditions, the more weakly adsorbed portion (band at 2120 cm^{-1}) could be identified with the moelcular ion H_2^+. If this assumption were checked, deuterium hydride adsorption should cause quantities of HD^+ to form, and consequently, an adsorption band to appear around 1730 cm^{-1}. In the course of our experiments at 200°C with hydrogen–deuterium, however, we saw no bands in this range. It seems, therefore, that the two kinds of bands observed are caused by dissociative adsorption.

2. *Nitrogen Adsorption*

Iridium is generally classed as a metal which does not chemisorb nitrogen. In fact, in our experiments with the iridium catalyst, no nitrogen chemisorption was detected by the dynamic method from room temperature to 700°C, and it was therefore impossible to record desorption spectra in this temperature range.

3. *Ammonia Adsorption*

Ammonia adsorption has often been used for evaluating solid surface acidity and was, thus, the method we used to compare the acidity of γ-alumina with that of the catalyst. Temperature programmed desorption and ir spectroscopy also provide information about the nature of adsorption sites and about the adsorption bond between ammonia and either alumina or iridium.

3.1. Adsorption and temperature programmed desorption. Adsorption isobars obtained by the dynamic method for alumina and the catalyst have shown that the amount of ammonia adsorbed decreases when the temperature is increased (Fig. 3). From 400°C for alumina and 250°C for the catalyst, gas-phase chromatography shows that ammonia is decomposed into hydrogen and nitrogen.

3.1.1. Activation energies of desorption. The desorption spectrum obtained for γ-alumina consists of only one peak at about 100°C. This would indicate kinetics of a first order desorption and a corresponding activation energy of desorption of 7.1 kcal $mole^{-1}$. The pre-exponential factor is 1.44×10^3 mn^{-1}. These results are in

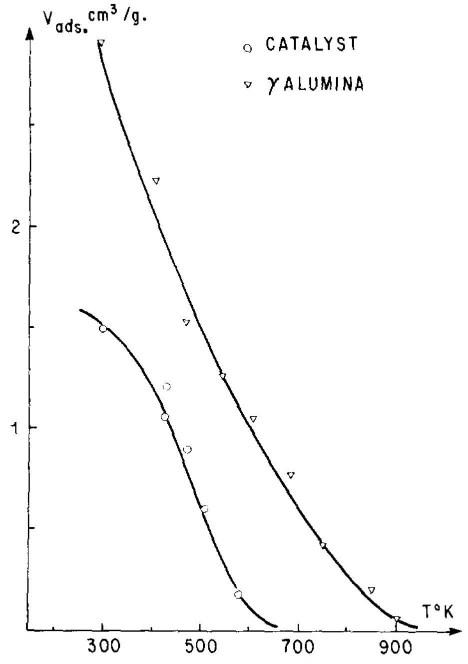


FIG. 3. Adsorption isobars for ammonia.

agreement with the findings of Amenomiya and Cvetanovic (*6*).

In the case of the iridium catalyst, two distinct desorption peaks are recorded, one at about 100°C, the other at 250°C. The first one corresponds to the desorption of ammonia from the support, and we have supposed that the second one could be attributed to the ammonia adsorbed by the iridium, the activation energy of desorption is 10.7 kcal mole^{-1}. Analysis by gas chromatography reveals the presence of ammonia with a small amount of nitrogen and hydrogen, proving that ammonia is partially decomposed into nitrogen and hydrogen, during desorption (Fig. 4).

We undertook two kinds of experiments with bulk iridium and catalyst in order to determine the nature of ammonia adsorption sites and obtained the following results:

(a) With bulk iridium powder, no ammonia adsorption has been detected from room temperature to 200°C and it was, therefore, impossible to record a desorption spectrum.

(b) When hydrogen is adsorbed on catalyst after ammonia preadsorption, the adsorption spectrum has a much lower desorption peak for hydrogen chemisorbed on sites I, but the peak attributed to the sites II appears as normal.

From these two experiments, we were led to believe that ammonia and hydrogen are competitively adsorbed on sites I.

3.1.2. Variation of activation energies with surface coverage. This phenomenon was studied for both γ-alumina and the iridium catalyst. Figure 4 shows the variation of the spectra with initial surface coverage for alumina. The temperature corresponding to the maximum rate of desorption increases when the rate of coverage decreases; ammonia is, thus, removed from sites that have higher and higher energies of adsorption. It was noted that the desorption spectrum recorded following surface saturation is given by the superposition of all spectra obtained for different coverages.

The desorption spectra of ammonia adsorbed by the catalyst also depend on sur-

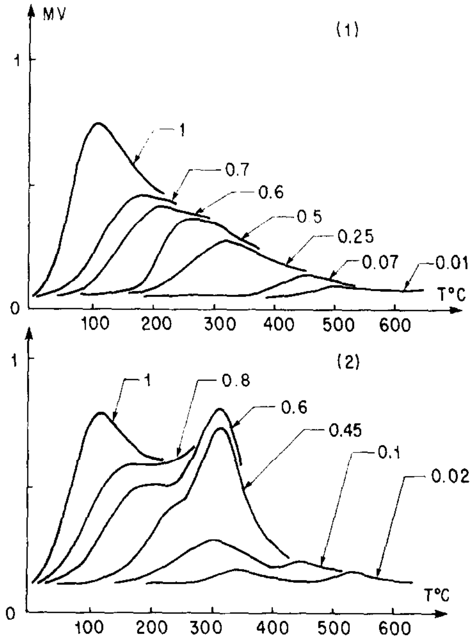


FIG. 4. Desorption spectra of ammonia for different initial coverages: (1)—γ-alumina; (2)—catalyst.

face coverage. The first peak varies as in the case of alumina; the second one, however, is independent of coverage.

The energy distribution curves are given in Fig. 5 and corroborate results obtained by others *(6, 12, 13)*.

3.2. Infrared spectroscopy of adsorbed ammonia. Many research projects have shown interest in the use of ir spectroscopy for studying the mode of adsorption of ammonia on silica, alumina, and silica–alumina catalysts among others *(13, 14, 15)*.

Four vibratory modes may be observed. The different vibration frequencies of ammonia molecules are given in Table 1. In a previous paper, we noted that the surface of alumina reacted with hydrochloric acid during preparation of the catalyst. This led us to investigate ammonia adsorption not only on an iridium catalyst and on Degussa *c* alumina, but also on chlorinated alumina (a reaction of hydrochloric acid or carbon tetrachloride).

3.2.1. Infrared spectra of adsorbed ammonia. Since catalyst samples have very poor transmission for frequencies over 2000 cm^{-1}, we chose to observe ν_2 and ν_4 bending vibrations of ammonia.

Figure 6 gives the spectra of adsorbed ammonia. The first spectrum, recorded before evacuating the cell, shows three absorption bands at 1615, 1460, and 1250 cm^{-1}. These frequencies correspond to ν_4 (NH_3 and NH_4^+) and ν_2 (NH_3) bending vibrations.

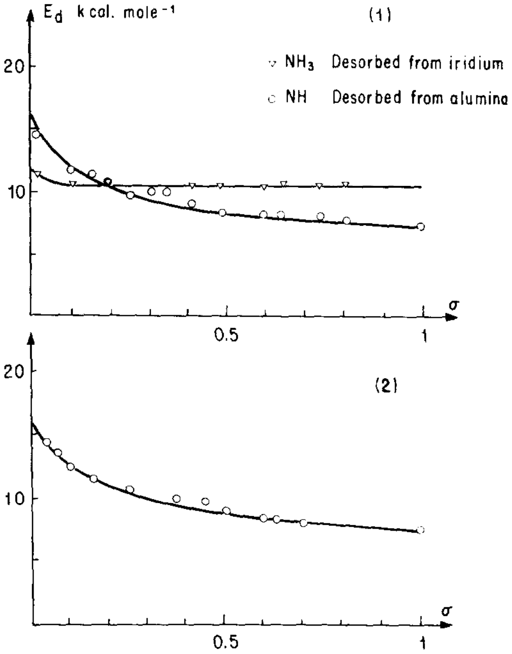


FIG. 5. Variation of activation energy of desorption with surface coverage: (1)—catalyst; (2)—γ-alumina.

After desorption of ammonia at room temperature for 1 hr, a shoulder appears

TABLE 1
VIBRATION FREQUENCIES OF AMMONIA AND AMMONIUM ION

Species	Vibratory mode	Gas	Adsorbed on alumina[a]	Adosrbed on alumina[b]	Adsorbed on alumina[c]	Adsorbed on silica–alumina catalyst[a]
NH_3	ν_3	3443.9 3443.6	3350	3415	3400	3350
	ν_1	3337.2 3336.2	3265	3370	3355	3280
	ν_4	1627.4 1626.1	1615	1625	1620	1615
	ν_2	968.3 932.5	1270	1260		
NH_4^+	ν_3	3100 3322				3280
	ν_4	1390 1484				1445

[a] After P. Pichat *et al.* *(14)*.
[b] After H. Dunken *et al.* *(15)*.
[c] After J. B. Peri *(13)*.

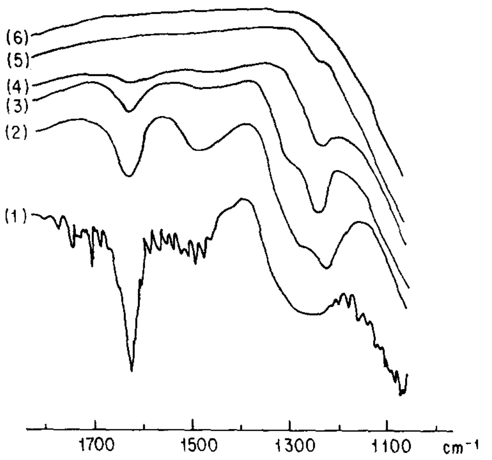


FIG. 6. Infrared spectra of ammonia adosrbed on catalyst: (1) 60 Torr NH_3; (2) 1 hr 10^{-5} Torr—room temperature; (3) 1 hr 10^{-5} Torr—180°C; (4) 1 hr 10^{-5} Torr—250°C; (5) 1 hr 10^{-5} Torr—350°C; (6) 2 hr 10^{-5} Torr—450°C.

between 1260 and 1270 cm^{-1} and the main band shifts to 1220 cm^{-1}. If the temperature of desorption is increased to 180°C, the absorption band at 1460 cm^{-1} disappears. At 250°C the other bands are weakened and the shoulder disappears, but at 350°C all that remains is a very weak band at 1215 cm^{-1}.

The spectra of ammonia adsorbed on alumina or on chlorinated alumina (illustrated in Fig. 7) are somewhat different, for they show no splitting of the band corresponding to vibration ν_2. This band is recorded at 1250 cm^{-1} for alumina and at 1260 cm^{-1} for chlorinated alumina. The ir spectra vary with the temperature of desorption as observed in the case of the catalyst.

3.2.2. Identification of 1615, 1460, 1265, and 1220 cm⁻¹ bands. The 1615 cm^{-1} band is attributed to the ammonia either physisorbed or chemisorbed on Lewis acid sites. It disappears at 350°C when all the ammonia is desorbed. The absorption maximum at 1460 cm^{-1} indicates the formation of ammonium ions. This band is stronger in the case of the catalyst, than for alumina, because samples cannot be dehydrated over 400°C; it disappears at 180°C.

For alumina and chlorinated alumina, the 1260 cm^{-1} band indicates that ammonia

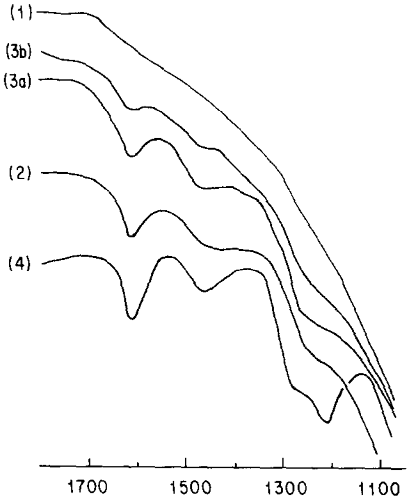


FIG. 7. Infrared spectra of ammonia adsorbed on alumina and catalyst: (1) back ground of alumina; (2) NH_3 on alumina after 1 hr at room temperature under 10^{-5} Torr; (3)—*a*—chlorinated alumina same conditions as (2), *b*—chlorinated alumina, after 1 hr at 180°C under 10^{-5} Torr; (4) NH_3 catalyst same conditions as 2.

is strongly adsorbed by coordination bonds on acid sites. For the catalyst, this band is composed of two bands: the first one at 1260 cm^{-1} is attributed to ammonia coordinated with aluminum on Lewis acid sites, the second one at 1220 cm^{-1} to ammonia coordinated with iridium on sites I.

4. *Hydrazine Adsorption*

4.1. Temperature programmed desorption. A chromatographic analysis of products eluted after hydrazine has been introduced reveals only nitrogen, ammonia, water, and a small amount of hydrogen. This shows that the hydrazine is entirely decomposed in contact with the iridium catalyst.

Following the elimination of all reversibly adsorbed entities, the desorption spectrum is recorded in the same conditions as for ammonia with alumina and iridium catalysts.

No hydrazine desorption is detected after adsorption on alumina. Once the ammonia and water have been removed from the surface, the adsorbed hydrazine is decomposed between 250 and 300°C. The presence

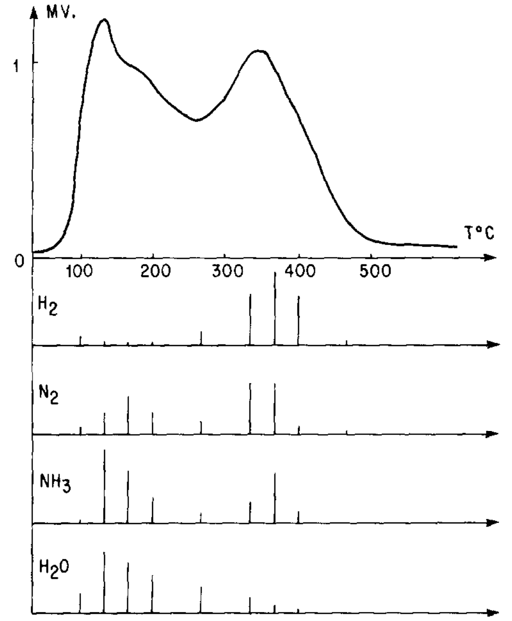


FIG. 8. Desorption spectrum recorded after hydrazine adsorption on catalyst and simultaneous chromatographic analysis.

of hydrogen, nitrogen, and ammonia may also be detected by gas-phase chromatography analysis (Fig. 8).

For catalysts, the desorption of water and ammonia is the same as described above. On the other hand, the hydrogen desorption spectrum differs from that previously observed: The desorption peak corresponding to the hydrogen chemisorbed on type I sites disappears, but a new hydrogen peak is recorded at 320°C, caused by decomposition either of the ammonia adsorbed on the iridium or the hydrazine adsorbed on the alumina. The peak corresponding to the strongest adsorption of hydrogen on iridium on sites II normally occurs around 600°C (Fig. 9).

Finally, this experiment allows us to observe nitrogen desorption, since the nitrogen atoms remains chemisorbed on the metal after decomposition of the hydrazine molecule. The spectrum has only one symmetrical peak between 200 and 250°C, showing that desorption occurs with a second-order kinetics and that nitrogen is adsorbed in an atomic form.

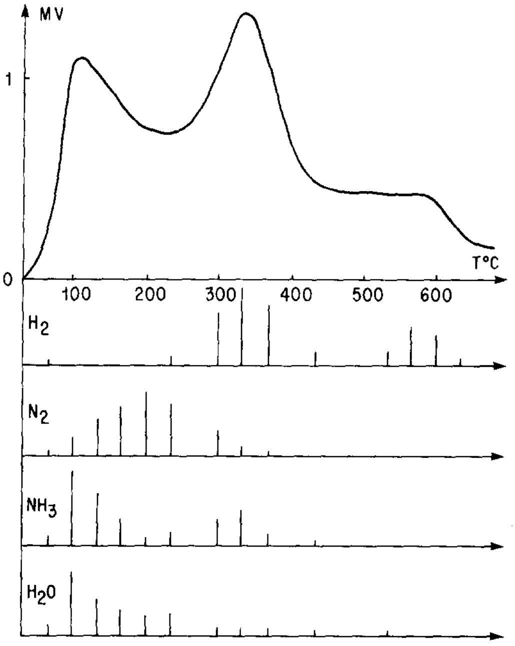


FIG. 9. Desorption spectrum recorded after hydrazine adsorption on alumina and simultaneous chromatographic analysis.

4.2. Infrared spectroscopy of adsorbed hydrazine. Several papers have been published on the ir spectroscopy of hydrazine in the vapor phase (*16, 17*). Maximum absorption frequencies corresponding to the different vibratory modes of hydrazine molecules have been listed by Guigere and Liu (*17*). In our study of adsorbed hydrazine, we concentrated particularly on the ir spectra between 2000 and 1000 cm^{-1}.

When hydrazine is adsorbed under a pressure of 10 Torr at room temperature, four absorption bands are observed at 1665, 1620, 1460, and 1270 cm^{-1}. The intensity of each band decreases after the cell is evacuated at the same temperature. The spectrum recorded after desorption at 180°C for 1 hr is the same as that obtained for ammonia in earlier experiments (Fig. 10).

The 1665 cm^{-1} band is attributed to the ν_{10} vibration of hydrazine adsorbed on alumina. The adsorption maximum at 1460 cm^{-1} is due to ammonium ions which are produced by the reaction of ammonia (produced when the hydrazine is decomposed) with water (3% in hydrazine). The

FIG. 10. Infrared spectra of hydrazine adsorbed on catalyst: (1) 10 Torr N_2H_4 at room temperature; (2) after 1 hr under 10^{-5} Torr; (3) after 1 hr under 10^{-5} Torr at 180°C.

1270 cm^{-1} band is attributed to the superposition of the spectra corresponding to vibrations ν_2 of ammonia and ν_{11} of hydrazine.

DISCUSSION OF RESULTS

The study of hydrogen adsorbed by the catalyst reveals the existence of two types of adsorption sites (I and II). An investigation into the different desorption spectra let us assume that the existence of sites I is linked to an electronic interaction between iridium and alumina. Such complexes have already been proposed by different authors for the case of supported platinum catalysts (*18*, *19*). It also appears that hydrogen chemisorbed on sites II is removed only at high temperature and that iridium corresponding to these sites is bulk iridium.

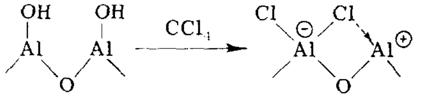
The bands at 2120 and 2050 cm^{-1} observed by ir spectroscopy cannot be attributed to hydrogen adsorbed on the sites I and II, since the band at 2120 cm^{-1} disappears as soon as hydrogen pressure reaches 10^{-2} Torr, this band would correspond to hydrogen reversibly adsorbed which is not possible to study in our experiments of temperature programmed desorption. However, hydrogen adsorbed on sites I may be identified as the entity corresponding to the band at 2050 cm^{-1}.

For the catalyst samples used in ir spectroscopy the number of sites II is so low that an absorption band or a desorption peak corresponding to hydrogen atoms adsorbed on these sites cannot be recorded.

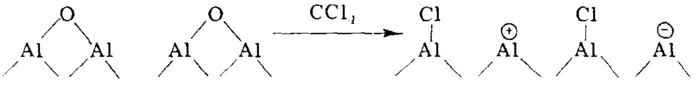
The simultaneous desorption of ammonia and its decomposition products implies that ammonia is partially decomposed into hydrogen and nitrogen during desorption but that the hydrogen thus produced is not adsorbed on iridium. The ammonia adsorption sites are sites I which might be due to the existence of an Ir–alumina complex. Besides, ir spectroscopy gives us to believe that ammonia is strongly adsorbed on iridium by a coordination bond. Similar results have been obtained by Griffiths *et al.* for silica supported platinum catalysts (*20*).

Assuming that 80% ammonia is adsorbed on alumina and 20% on iridium, the surface concentration of Lewis acid sites may be calculated from the energy distribution curves: for γ-alumina there are 4.6×10^{12} sites per cm^2, and for the catalyst alumina, 6.2×10^{12} sites per cm^2.

The catalyst alumina surface adsorbs more ammonia than pure γ-alumina. This increase in acidity is probably caused by the surface chlorination of alumina during preparation of the catalyst. Goble and Lawrence have shown that this reaction, which gives a more acidic alumina, is caused by a stabilization of Lewis acid sites by chlorine (*21*).



Basset *et al.* have suggested the existence of bicoordinated aluminum atoms which form very strong Lewis acid centers (*22*).



After adsorption and decomposition of hydrazine at 300°K, temperature programmed desorption reveals that nitrogen is adsorbed in an atomic form on iridium and, with ir spectroscopy shows that hydrogen is chemisorbed only on sites II, which correspond to strong irreversible adsorption. From these results, we can assume that the first step in catalytic decomposition is the formation of a coordination bond between the nitrogen atoms of hydrazine molecule and the iridium atoms of the sites I.

The absence of a desorption peak for hydrogen adsorbed on sites I is in good agreement with the results of Sayer (*22*) and Ken-Ichi Aika *et al.* (*5*) who have found that the products of the hydrazine decomposition over iridium are essentially nitrogen and ammonia. Ken-Ichi Aika *et al.* (*5*) think that a reaction takes place in the form of a hydrogenolysis of hydrazine which consumes the hydrogen produced by direct decomposition.

$$N_2H_4 \rightarrow N_2 + 2H_2,$$

$$2N_2H_4 + 2H_2 \rightarrow 4NH_3.$$

Similar conclusions have been obtained by Volter and Lietz using chromium, manganese, iron, tungsten, rhenium, and osmium catalysts (*4*).

The schemes of the reaction mechanisms would be as follows:

(1) *Adsorption*	$N_2H_4 \rightarrow 2NH_2\,(a)_I$
(2) *Direct decomposition*	$2NH_2\,(a)_I \rightarrow 2NH\,(a)_I + 2H\,(a)_{I \text{ or } II}$ $2NH\,(a)_I \rightarrow 2N\,(a)_I + 2H\,(a)_{I \text{ or } II}$ $2N\,(a)_I \rightarrow N_2\,(g)$ $2H\,(a)_I \rightarrow H_2\,(g)$
(3) *Hydrogenolysis*	$N_2H_4 \rightarrow 2NH_2\,(a)_I$ $NH_2\,(a)_I + H\,(a)_I \rightarrow NH_3\,(a)_I$
(4) *Desorption*	$NH_3\,(a) \rightarrow NH_3\,(g)$

The hydrogen which is produced by catalytic decomposition is adsorbed on sites I and II, but only the hydrogen chemisorbed on site I is active in the hydrogenolysis of hydrazine.

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REFERENCES

1. Askey, P. J., *Amer. Chem. Soc.* **52,** 910 (1930).
2. Audrieth, L. F., and Ogg, B. A., "The Chemistry of Hydrazine," Wiley, New York, 1951.
3. Frolov, V. M., *Kinet. Katal.* **6,** 149 (1965).
4. Volter, V. J., and Lietz, G. W., *Z. Anorg. Allg. Chem.* **366,** 191 (1969).
5. Aika, K. I., Ohhata, T., and Ozaki, A., *J. Catal.* **19,** 140 (1970).
6. Amenomiya, Y., and Cvetanovic, R. J., *Advan. Catal. Relat. Subj.* **17,** 103 (1967).
7. Contour, J. P., and Prud'homme, R., *Bull. Soc. Chim. Fr.* **8,** 2693 (1969).
8. Contour, J. P., Thèse, Paris, 1970.
9. Bozon-Verduraz, F., *J. Catal.* **18,** 12 (1970).
10. Eischens, R. P., and Pliskin, W. A., *Z. Phys. Chem.* **24,** 11 (1960).
11. Eley, D. D., Moran, D. M., and Rochester, C. H., *Trans. Faraday Soc.* **64** (8), 2168 (1968).
12. Stone, F. S., and Whalley, L., *J. Catal.* **8,** 173 (1967).
13. Peri, J. B., *J. Phys. Chem.* **69,** 231 (1965).
14. Pichat, P., Mathieu, M. V., and Imelik, B., *J. Chim. Phys.* **66,** 865 (1969).
15. Dunken, H., and Fink, P., *Z. Chem.* **5,** 432 (1965).
16. John, W. J., and Bardhan, S., *J. Sci. Technol.* 3 (4), 234 (1965).
17. Giguere, P. A., and Liu, I. D., *J. Chem. Phys.* **20,** 136 (1952).
18. Figueras, F., Mencier, B., De Mourgues, L., Naccache, C., and Trambouze, Y., *J. Catal.* **19,** 315 (1970).
19. Mc Henry, K. W., Bertolacini, R. J., Brennan, H. M., Wilson, J. L., and Seelig, H. S., *Actes Congr. Int. Catal., 2nd.* **1960, 2295.**
20. Griffiths, D. W. L., Hallam, H. E., and

THOMAS, W. J., *Trans. Faraday Soc.* **64** (12), 3361 (1968).

21. GOBLE, A. G., AND LAWRENCE, P. A., 3rd International Congress on Catalysis I, 320, Amsterdam 1964.
22. BASSET, J., MATHIEU, M. V., AND PRETTRE, M., *J. Chim. Phys.* **66** (4), 611 (1969).
23. SAYER, C. F., *U. S. Gov. Res. Develop. Rep.* **69** (19), 53 (1969).
24. HERZBERG, G., "Molecules spectra and molecules structure," Vol. I p. 501, 1950. D. Van Nostrand Company Inc., New York 1950.
25. VASKA, L., AND CATONE, D. L., *J. Amer. Chem. Soc.* **88** (22), 5324 (1966).