JOURNAL OF CATALYSIS 29, 31–39 (1973)

The State of Supported Iridium in a Hydrazine Decomposition Catalyst

J. ESCARD

IRCHA, 91-Vert-le-Petit, France

AND

C. LECLÈRE AND J. P. CONTOUR*

Laboratoire de Cinétique Chimique de l'Université de Paris VI,
E.R.A. au C.N.R.S. No. 24, Paris, France

Received April 28, 1972

Temperature programmed desorption, iridium dissolution in acetylacetone, uv spectroscopy and photoelectron spectroscopy have been used to determine the nature of the adsorption sites and the state of iridium in a hydrazine decomposition catalyst. The catalyst contained 36 wt % iridium impregnated on η-alumina.

The desorption spectrum of hydrogen adsorbed on unsupported iridium shows three peaks (α, β, and γ) from −160 to 600°C. For hydrogen adsorbed on the catalyst, four peaks (α, β_1, β_2 and γ) are observed. The splitting of the β peak reveals adsorption sites peculiar to catalyst surface.

Catalyst attack with acetylacetone allows us to observe a dissolution of supported iridium, giving iridium acetylacetonate which indicates the presence of iridium with a +3 valence. Ultraviolet spectroscopy shows that a part of chloroiridic acid is reduced during the impregnation of alumina giving a chlorinated complex of iridium III and the structure of this iridium III complex is not destroyed by hydrogen reduction.

The chemical shifts measured in photoelectron spectra confirm the presence of complexed iridium and demonstrate an electronic interaction between uncomplexed iridium and alumina.

INTRODUCTION

The catalytic decomposition of hydrazine is an interesting problem because of its many practical applications. The search for a good catalyst has led us to undertake experiments using a supported iridium catalyst.

The influence of the carrier on the activity of such a supported catalyst is a controversial point in the literature (*1–4*). Some experiments which had been undertaken in our laboratory and reported in a previous paper suggest that a support effect can arise with iridium deposited on η-alumina giving new adsorption sites particular to the catalyst surface which are very active for hydrazine decomposition (*5*). The aim of the present study was to confirm the existence of such sites and to show how this support effect may occur.

EXPERIMENTAL METHODS

1. *Materials*

The catalysts were prepared by impregnating porous supports with an aqueous solution of hexachloroiridic acid (H_2IrCl_6—$0 \leqslant pH < 2$). After drying in air at 120°C,

---

[*] To whom all correspondences should be addressed. Now at Laboratoire de Physico-Chimie Instrumentale Université de Paris VII. 2 Place Jussieu 75005 Paris, France.

the samples were reduced by hydrogen at 400°C and contained from 1 to 36% iridium by weight. Physical properties of the metallic oxides used as supports are given in Table 1.

The samples which had been tested in catalytic hydrazine decomposition contained 36% iridium supported on η-alumina; their specific surface area was 125 m^2 g^{-1}, while the metal surface area measured by hydrogen chemisorption was 60 m^2 g^{-1} cat. The chemical analysis of these samples showed that alumina reacts with hexachloroiridic acid during preparation and that the amount of fixed chlorine is about 2% by weight.

In order to study the influence of chlorine, we prepared a catalyst from an olefin derivative of iridium [di-μ-methoxy-bis-(π-cycloocta-1,5-diene) diiridium]. The samples obtained in this way had the same textural characteristics as the ones prepared from hexachloroiridic acid except that they contained no chlorine.

2. Apparatus and Procedure

2.1 Temperature programmed desorption. The experimental setup used in this study was essentially the same as that described by Amenomiya and Cvetanovic (*6–7*), but with a modified design of the reactor in order to obtain a continuous linear programming of the temperature from 80 to 800°K and to record desorption spectra which do not show any discontinuity around room temperature.

TABLE 1

PHYSICAL PROPERTIES OF THE METALLIC OXIDES USED AS CATALYST SUPPORTS

Material	Specific surface area (m^{2}g^{-1})	Pore vol (cm^{3}g^{-1})	Origin
η-Alumina	225	0.75	Pechiney Saint-Gobain pseudoboehmite dehydration
α-Alumina	12	—	Calcination of η-alumina (1350°C, 48 hr, in air)
Silica	150	1.1	Pechiney Saint-Gobain macroporous silica
Silica–alumina	300	0.65	Pechiney Saint-Gobain (13% Al$_2$O$_3$)
Chlorinated alumina	200	0.75	Alumina chlorinated at 200°C by HCl

The following procedure was used for the desorption experiments:

a. Cleaning the surface of the catalyst by heating in hydrogen at 400°C, followed by desorption in argon at 400°C and cooling in argon.

b. Adsorption of hydrogen at room temperature.

c. Cooling of the sample in hydrogen to −196°C.

d. Hydrogen evacuation at −196°C (10^{-5} Torr).

e. Desorption in argon and simultaneous chromatographic analysis of the desorbed products.

2.2 Iridium dissolution in acetylacetone. Dissolution in HCl, HF or acetylacetone has been reported by several authors who studied the state of supported platinum (*8–10*). The ground catalyst was attacked by boiling acetylacetone for 24 hr. The undissolved part was separated from the solution by centrifuging and filtering, and the amount of dissolved iridium was determined with an atomic absorption spectrometer (Perkin-Elmer 305).

2.3 Ultraviolet spectroscopy. Ultraviolet spectra were recorded by means of a Beckman DK2A spectrophotometer. Spectra of the solids were obtained by a diffuse reflectance measurement; the samples were ground, then gently compressed in an aluminum holder and magnesia was used as a reference sample. Liquids were put in a silica cell; the reference cell was filled with water.

2.4 Photoelectron spectroscopy. Photoelectron spectroscopy for chemical analysis (ESCA), as developed by Siegbahn and coworkers (*11*), is based on the study of the energy distribution of electrons which are ejected when samples are bombarded with monochromatic X-radiation. Chemical shifts observed on the spectra give informa-

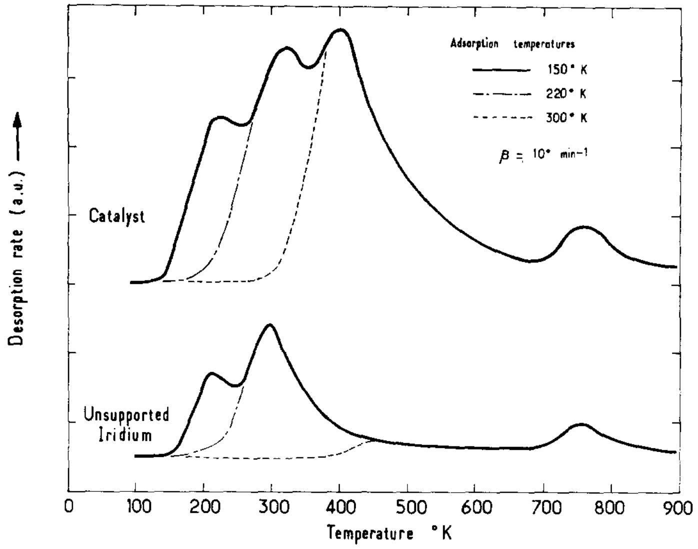

FIG. 1. Desorption spectra of hydrogen adsorbed on a 36% Ir/Al_2O_3 catalyst and on unsupported iridium.

tion on the oxidation state of elements. The results reported by Delgass, Hughes and Fadley (*12*) for various catalysis problems, Wolberg, Ogilvie and Roth (*13*) for copper oxide supported on alumina, and Miller *et al.* (*14*) for Mo/Al_2O_3 systems show that ESCA can be a useful tool for the study of supported catalysts.

The ESCA measurements were made on a Varian Associated Induced Electron Emission Spectrometer using Al $K\alpha$ radiation (E = 1486.6 eV). For every sample the spectrometer was calibrated with the carbon 1s line which has a binding energy of 284.4 eV (*13*).

RESULTS

1. *Temperature Programmed Desorption*

The desorption spectrum recorded after hydrogen adsorption at 25°C and its evacuation at −196°C with unsupported iridium shows three peaks α, β, γ at −66, 25 and 500°C for a heating rate of 10° min^{-1} and the associated activation energies of desorption are 6, 8 and 25 kcal mole^{-1}. For hydrogen adsorbed either on the catalyst (36% Ir) or on the chlorine free samples, four peaks α, β_1, β_2, γ, at −50, 50, 120 and 500°C are observed and the associated activation energies are 6.5, 9, 10.5 and 25 kcal mole^{-1}. The spectra are shown in Fig. 1 and the quantities of hydrogen desorbed from the catalyst and unsupported iridium are given in Table 2. The bad resolution of the desorption peaks reveals a great dependence of activation energy on surface coverage (*15*).

According to the studies carried out on platinum, we have supposed that the α peak may be assigned to molecular adsorption of hydrogen and the β and γ peaks to hydrogen chemisorbed in an atomic form. Two types of atomically adsorbed hydrogen have been observed by different authors (*7, 16–18*) and theoretically explained by Toya (*16*). The weaker one (r-type) has been attributed to hydrogen atoms chemisorbed on the top of platinum atoms and the stronger one (s-type) to hydrogen

TABLE 2

VOLUME OF HYDROGEN DESORBED AS DETERMINED BY TPD (ADSORPTION TEMPERATURE, 150°K)

Sample	Desorbed H_2 (cm^3/g cat)	Desorbed H_2 (cm^3/g Ir)	Metal surface area (m^2/g cat)	Specific surface area (m^2/g)
36% Ir catalyst	12.7	35.4	60	—
Unsupported iridium	0.34	0.34	0.85	0.60

atoms in the interstices between the metal atoms. The β and γ adsorption reported above may be taken to be the weakly and strongly chemisorbed hydrogen atoms as proposed by Toya. The splitting of the β peak recorded for hydrogen chemisorbed on supported iridium may be explained by the existence of a support effect which gives adsorption sites particular to the catalyst surface.

Another theoretical interpretation could be given in terms of hydrogen "spillover" (*4*, *26*), but we consider that, for high metal content catalysts such as the 36% iridium catalysts, the volume of spiltover hydrogen is negligible versus the one chemisorbed on metal. This hypothesis is supported by the good agreement observed between the measurements of iridium dispersion by hydrogen adsorption and electron microscopy (*27*). Moreover, the infrared spectroscopy study of hydrogen adsorption, reported in a previous paper (*5*), suggests that the spiltover hydrogen reacts with the alumina surface and does not desorb as hydrogen molecules but as water molecules (*28*).

2. Iridium Dissolution in Acetylacetone

When the catalyst is attacked by boiling acetylacetone, alumina is completely dissolved while iridium undergoes partial dissolution. The undissolved part is metallic iridium. Evaporation of the solution produces yellow crystals and a brown residue; the yellow crystals have been identified as aluminium triacetylacetonate, the brown residue as a mixture of iridium acetylacetonates. Studies undertaken in our laboratory on iridium chemistry have shown that iridium acetylacetonate can be produced only from iridium III, proving thereby the presence of iridium in the +3 valence on the catalyst surface. Experiments in oxygen free atmosphere have been carried out in order to determine the influence of adsorbed and gaseous oxygen on this reaction. The amount of iridium so dissolved is the same as that measured in the presence of air.

The percentage of dissolved iridium decreases when the iridium content increases, but the weight of dissolved iridium per gram of catalyst does not depend on iridium content if it is higher than 2 wt %, as shown in Fig. 2.

No dissolution was observed either with finely divided unsupported iridium or with chlorine free catalyst under the same conditions. Finally we observed that the amount of dissolved iridium varies with the nature of the carrier and that solubilization increased with the surface acidity of the support in the following manner:

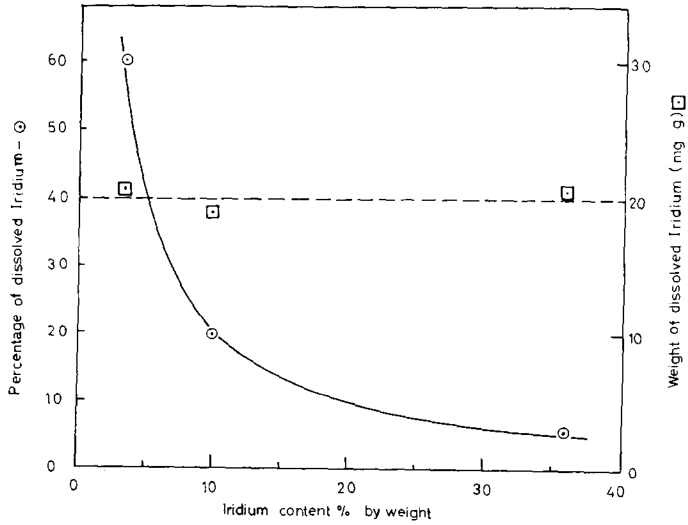

FIG. 2. Amount of iridium dissolved in acetylacetone as a function of the iridium content: (⊙) Percentage of dissolved Ir = (wt of dissolved Ir)/(total wt of Ir); (⊡) weight of dissolved Ir per gram of catalyst.

α-alumina $\ll$ η-alumina $<$ silica-alumina

3. Ultraviolet Spectroscopy

Ultraviolet spectroscopy allows one not only to study the catalyst samples but also to observe the change in the impregnating solution during the catalyst preparation.

The absorption spectrum of $IrCl_6^{2-}$ ion has been given by Jørgensen (*19*), who observed five absorption bands between 700 and 200 nm and found that sodium hydroxide caused a reduction of iridium IV into iridium III chlorocomplex, according to:

$$2\,IrCl_6^{2-} + 2\,Cl^- \rightarrow 2\,IrCl_6^{3-} + Cl_2, \qquad (1)$$

$$Cl_2 + OH^- \rightarrow ClO^- + H^+ + Cl^-. \qquad (2)$$

The ClO^- ion formation was detected by its absorption band at 290 nm.

If the spectrometer cell is filled with a diluted solution of hexachloroiridic acid (0.1 g liter^{-1}) and η-alumina is put in the bottom of the cell, out of the ultraviolet beam, the absorption bands of $IrCl_6^{2-}$ fast disappear and a new band at 290 nm is recorded, proving thereby the formation of ClO^- ions. After drying at 120°C, the impregnated alumina takes on a green color which is peculiar to the +3 valence of iridium (Fig. 3).

The ultraviolet spectrum of the dried sample shows four interesting bands (Fig. 3) which can be compared to those given by Ballhausen (*20*) for iridium III octahedrally coordinated with six chlorine atoms (Table 3). The shift observed for the high energy bands may be due to a partial substitution of chlorine ligands by oxygen or hydroxyl ligands (*19–21*). These data allow us to assume that alumina makes possible the reduction of iridium IV into iridium III chlorocomplex according to the reaction scheme given by Jørgensen.

If the iridium concentration in impregnating solution is increased, a larger amount of metal is deposited. As soon as 2.2% Ir is reached, the color of dried samples becomes greenish-brown and the uv spectrum shows the superposition of absorption bands corresponding to $IrCl_6^{3-}$ and $IrCl_6^{2-}$ ions, indicating that the quantity of iridium which is reduced is the same as the one dissolved in acetylacetone. This reaction is more important with silica–alumina than with η-alumina and does not occur with α-alumina.

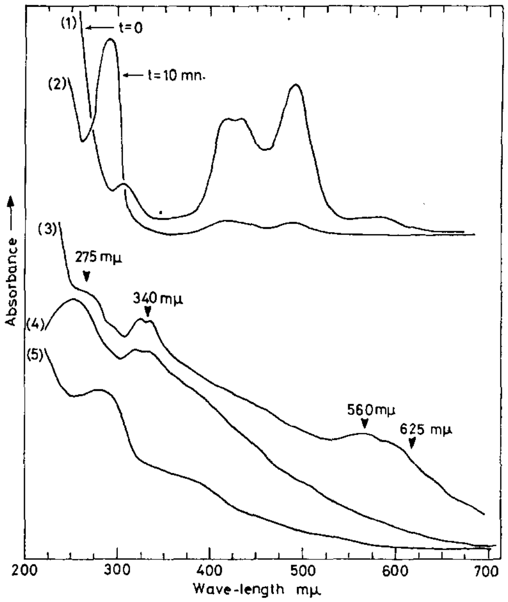

FIG. 3. Ultraviolet spectra recorded during the catalyst preparation: (1) Diluted solution of H_2IrCl_6 with η-alumina (t = 0); (2) 10 min later; (3) 1% Ir/Al_2O_3 unreduced; (4) 3% Ir/Al_2O_3 after reduction by H_2 at 400°C; (5) chlorinated η-alumina.

The ultraviolet spectrum recorded when the catalyst is reduced by hydrogen at 400°C shows that the iridium III complex seems not to be destroyed by this treatment (Fig. 3).

4. Photoelectron Spectroscopy

The Ir ($4f_{5/2}$) and ($4f_{7/2}$) lines from several samples are shown in Fig. 4. Two phenomena appear in the catalyst spectra:

TABLE 3

ABSORPTION BANDS OF IRIDIUM III CHLOROCOMPLEX AND IMPREGNATED ALUMINA

Impregnated alumina		Ballhausen (*20*)	
(nm)	(cm^{-1})	(cm^{-1})	
625	16 000	16 300	${}^1A_{1g} \rightarrow {}^3T_{1g}$
560	17 850	17 900	${}^1A_{1g} \rightarrow {}^3T_{2g}$
340	29 400	28 100	${}^1A_{1g} \rightarrow {}^1T_{2g}$
275	36 400	34 400	${}^1A_{1g} \rightarrow {}^1T_{1g}$

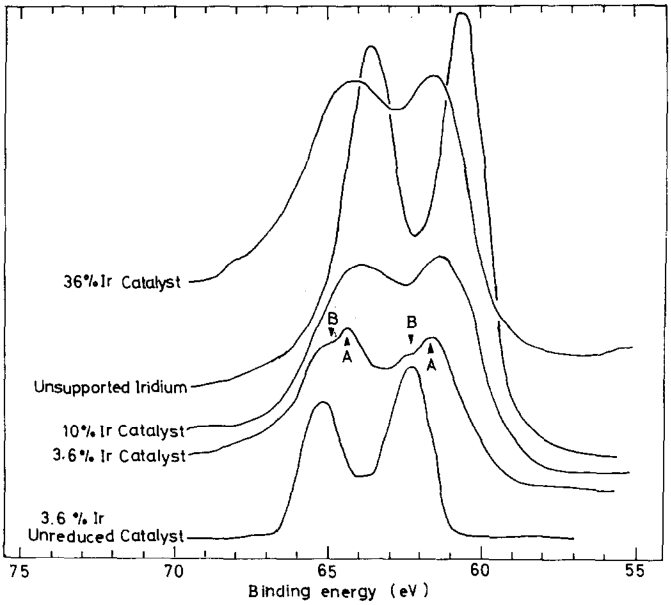

FIG. 4. Photoelectron spectra of various catalyst samples.

first, the iridium doublet is shifted to higher binding energies with respect to that of unsupported iridium and second, the iridium lines have an anomalous breadth which may indicate the presence of more than one type of iridium. When the catalyst contains little metal (3.6 wt %) we can observe that the iridium spectrum is composed of two doublets which are separated by less than 1 eV. The spectrum recorded with unreduced catalyst shows only one doublet and the binding energies associated with the Ir ($4f_{5/2}$) and ($4f_{7/2}$) lines (65.1 and 62.2 eV) are the same as the ones measured for the B doublet in the catalyst spectrum (Fig. 4). Thus, the less shifted doublet (A) is assigned to metallic iridium and the more shifted one (B) to the complexed iridium atoms. Ultraviolet spectroscopy has shown that these atoms are octahedrally coordinated with chlorine, oxygen or hydroxyl ligands, so that iridium atoms have similar surroundings in $(NH_4)_3IrCl_6$ and $(NH_4)_2IrCl_6$. The valence state of complexed iridium may then be determined by comparing the catalyst spectrum with those of $(NH_4)_3IrCl_6$ and $(NH_4)_2IrCl_6$ (Fig. 5). The binding energy associated with the Ir ($4f_{7/2}$) line in the B doublet (62.3 eV) is near the one measured for the $(NH_4)_3IrCl_6$ spectrum showing thereby that the complexed iridium has a +3 valence.

Moreover, the A doublet is shifted to higher binding energies relative to the doublet of unsupported iridium, and we think that this phenomenon may indicate an electronic interaction between uncomplexed iridium and alumina. Such an interaction will depend on the nature of the catalyst support. Photoelectron spectra of supported iridium have therefore been recorded with iridium supported on η-alumina, silica–alumina, α-alumina and silica. The binding energies of the Ir ($4f_{5/2}$) and ($4f_{7/2}$) electrons observed with these samples are given in Table 4; the chemical shifts decrease as a function of the support in the following manner:

silica–alumina > η-alumina > α-alumina > silica.

DISCUSSION

The temperature programmed desorption experiments demonstrate an interaction between supported iridium and alumina in the catalyst investigated, and the results obtained with the other experimental techniques indicate that this effect is both chemical and electronic. Since no complexed iridium is detected on the chlorine-free

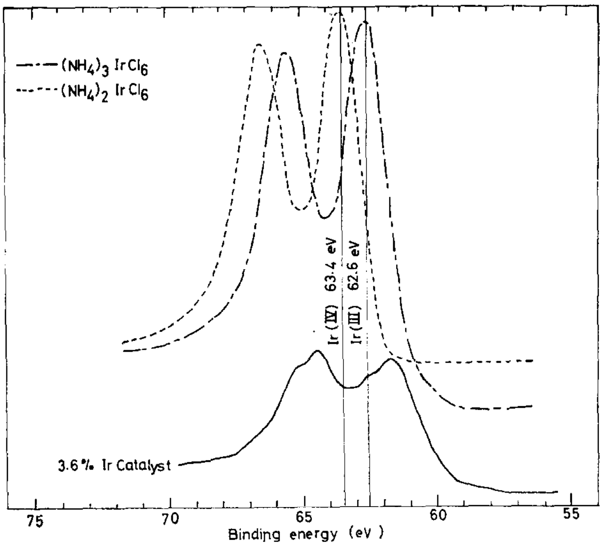

FIG. 5. Dependence of iridium photoelectron spectrum on the oxidation state of iridium.

sample and since the hydrogen desorption spectra for catalyst and chlorine-free samples show no notable difference, we think that the splitting of the β peak observed on the hydrogen desorption spectra is due to the electronic support effect and does not correspond to hydrogen adsorption on the complexed iridium atoms. The two adsorbed species which are revealed by the splitting of this β peak can be identified with the ones that we have previously described in a study of adsorbed hydrogen by infrared spectroscopy (*5*).

Some ions of supported iridium are kept in an unreduced valence state; these ions have a +3 valence state and are octahedrally coordinated with chlorine, oxygen and hydroxyl ligands. The higher the support acidity, the greater is the number of complexed iridium atoms. This iridium is that which is dissolved in acetylacetone and the number of complexed atoms is 0.55×10^{14} atoms cm^{-2} when η-alumina is used as support. Such complexes have been already suggested by McHenry *et al.* (*10*) in order to explain some properties of their dehydrocyclization catalysts and by Goble and Lawrence (*22*) for group VIII isomerization catalysts.

TABLE 4

BINDING ENERGIES OF Ir ($4f_{5/2}$) AND ($4f_{7/2}$) ELECTRONS FOR VARIOUS SUPPORTS

	Silica	α-Alumina	η-Alumina	Silica–alumina
$4f_{5/2}$	64.0	64.0	64.2	65.8
$4f_{7/2}$	61.0	61.1	61.6	62.8

According to our experimental results, we can assume that the complex formation begins with the adsorption of the hexachloroiridate ions on acidic sites of alumina; then the adsorbed $IrCl_6^{2-}$ are reduced into $IrCl_6^{3-}$ ions as proposed in reaction schemes (1) and (2). As soon as the alumina surface is saturated with $IrCl_6^{3-}$ ions, $IrCl_6^{2-}$ ions are deposited without reduction.

During further treatment of the catalyst, the chlorine ligands can be partially exchanged with oxygen or hydroxyl. Finally, the iridium III complex is not destroyed during the H_2IrCl_6 reduction by hydrogen, but the hydrogen chloride produced reacts with alumina and gives stronger acidic sites, as suggested by Goble and Lawrence (*22*) and Basset *et al.* (*23*, *24*).

The chemcial shifts and the line breadths observed in the photoelectron spectra confirm the presence of two types of supported iridium: complexed iridium as described above and metallic iridium. Since the two doublets are shifted to higher energies with respect to the metallic iridium spectrum, and separated by less than 1 eV, we suppose that an electronic interaction occurs between the support acting as an electron acceptor and the uncomplexed iridium acting as an electron donor. This effect is especially strong with supports possessing strong acceptor sites on the surface, such as silica–alumina and chlorinated alumina or alumina chlorinated during the catalyst preparation. A similar interpretation involving an electron donor–acceptor process had already been proposed by Figueras *et al.* (*2*) to explain the variation of supported platinum activity and by Miller *et al.* (*14*) in a study of Mo/Al_2O_3 systems. The concept of these interpretations was based on important findings of the physics of semiconductors, namely, that an electronic interaction develops between two solids with different Fermi levels. According to the Schottky theory of metal–semiconductor contacts (*25*), the Fermi level of the electrons at the interface must be the same at thermodynamic equilibrium. If the work function of the semiconductor is larger than that of the metal, the electrons migrate from the metal into the semiconductor until equilibrium is obtained, the flow of electrons setting up a positive charge on the metal.

Finally, although the data reported in the present study are insufficient to determine the role of chlorine on this support effect, it appears that it acts simultaneously as a chemical effect, making easier the formation of an iridium complex (*22*), and as an electronic one, producing strong oxidizing sites on alumina surface (*23*, *24*).

ACKNOWLEDGMENTS

ESCA experiments have been carried out in the IRCHA Laboratory and the authors express their thanks to Dr. G. Mavel who made possible this cooperation. Financial support of the Centre National de la Recherche Scientifique and the Centre National d'Etudes Spatiales is gratefully acknowledged.

REFERENCES

1. Taylor, W. F., Yates, D. J. C., and Sinfelt, J. H., *J. Phys. Chem.* **68,** 2962 (1964).

2. Figueras, F., Mencier, B., De Mourgues, L., Naccache, C., Trambouze, Y., *J. Catal.* **19,** 315 (1970).

3. Aben, P. C., Platteeuw, J. C., and Stouthamer, B., *Int. Congr. Catal., 4th,* Moscow, prepr. No. 31 (1968).

4. Boudart, M., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 20, p. 153. Academic Press, New York, 1969.

5. Contour, J. P., and Pannetier, G., *J. Catal.* **24,** 434 (1972).

6. Amenomiya, Y., and Cvetanovic, R. J., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 17, p. 103. Academic Press, New York, 1967.

7. Tsuchiya, S., Amenomiya, Y., and Cvetanovic, R. J., *J. Catal.* **19,** 245 (1970).

8. Hermann, R. A., Adler, S. F., Goldstein, M. S., and De Baum, R. H., *J. Phys. Chem.* **65,** 2189 (1961).

9. Figueras, F., Mencier, B., Baucaud, R., and Urbain, H., *C. R. Acad. Sci., Ser. C* **270,** 769 (1970).

10. McHenry, K. W., Bertolacini, R. J., Brennan, H. M., Wilson, J. L., and Seelig, H. S., *Actes Congr. Int. Catal., 2nd, 1960* 2295 (1961).

11. Siegbahn, K., Nordling, C., Fahlman, A., Nordberg, R., Hamrim, K., Hedman, J., Johansson, G., Bergmark, T., Karlsson, S. E., Lindgreen, I., and Lindberg, B., *Ann. Phys.* **3,** 281 (1968).

12. Delgass, W. N., Hughes, T. R., and Fadley, C. S., *Catal. Rev.* **4,** 140 (1971).

13. Wolberg, A., Ogilvie, J. L., and Roth, J. F., *J. Catal.* **19,** 86 (1970).

14. Miller, A. W., Atkinson, W., Barber, M., and Swift, P., *J. Catal.* **22,** 140 (1970).

15. Czanderna, A. W., Biegen, J. R., and Kollen, W., *J. Colloid Interface Sci.* **34,** 406 (1970).

16. Toya, T., *J. Res. Inst. Catal. Hokkaido Univ.* **10,** 236 (1962).

17. Bond, G. C., *Surface Sci.* **18,** 11 (1969).

18. Eischens, R. P., and Pliskin, W. A., *Z. Phys. Chem.* **24,** 11 (1960).

19. Jørgensen, C. K., "Absorption Spectra and Chemical Bonding in Complexes." Pergamon, Elmsford, NY, 1962.

20. Ballhausen, C. J., "Ligand Field Theory." McGraw-Hill, New York, 1962.

21. Johnson, K., *J. Phys. Chem.* **57,** 200 (1963).

22. Goble, A. G., and Lawrence, P. A., *Proc. Int. Congr. Catal., 3rd, 1964* **1,** 320 (1965).

23. Basset, J., Mathieu, M. V., and Prettre, M., *Rev. Chim. Miner.* **5,** 879 (1968).

24. Basset, J., Mathieu, M. V., Naccache, C., and Prettre, M., *J. Chim. Phys.* **66,** 1522 (1969).

25. Solymosi, F., *Catal. Rev.* **1,** 253 (1968).

26. Boudart, M., Benson, J. E., and Kohn, M. W., *J. Catal.* **5,** 307 (1966).

27. Contour, J. P., thesis, Paris, 1970.

28. Weller, S. W., and Montagna, A. A., *J. Catal.* **21,** 303 (1971).