JOURNAL OF CATALYSIS **48**, 209–216 (1977)

Valence State and Interaction of Platinum and Germanium on γ-Al_2O_3 Investigated by X-Ray Photoelectron Spectroscopy

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Received July 1, 1976; revised February 10, 1977

An X-ray photoelectron spectroscopic study of the reducibility of Pt/γ-Al_2O_3, Ge/γ-Al_2O_3, and Pt, Ge/γ-Al_2O_3 systems has shown that: (i) treatment with H_2 at temperatures up to 650°C leads to interaction between Pt and Ge, giving rise to the formation of Pt-Ge alloys; (ii) in the absence of platinum, germanium is difficult to reduce and at 650°C seems to dissolve in the alumina matrix whereas in the presence of platinum, it remains in a exposed state. The results strongly suggest that in both Pt/γ-Al_2O_3 and Pt, Ge/γ-Al_2O_3 "platinum atoms" are present in an electron-deficient state.

INTRODUCTION

A group of well-established catalyst systems that are of practical importance for various hydrocarbon conversions is formed by platinum, either as such or in combination with at least one other element placed in a highly dispersed state on high-surface-area supports, e.g., γ-Al_2O_3. Although catalysts of this type have been used for several decades, relatively little is known about the nature of the platinum and the other component(s), if present, on the support. A major problem with these catalysts is the high degree of dispersion, which makes them "invisible" for electron microscopy and X-ray diffraction.

The advent of new surface-sensitive techniques such as electron spectroscopy (AES,[1] XPS, or ESCA), secondary ion mass spectrometry and ion scattering, has made it possible to study several fundamental aspects of such systems. Some catalytically interesting examples as studied by XPS are the oxidation state of Ir on oxidic supports (*1*), the dispersion of Rh on coal (*2*), and the reducibility of supported tungsten oxides (*3*) and molybdenum oxides (*4*). In the present study we apply XPS to two systems of interest to hydrocarbon conversions, viz, Pt on γ-Al_2O_3 and Pt,Ge on γ-Al_2O_3, with the aim of answering the following two questions: (1) What is the valence state of platinum in its active ("reduced") form? (2) Is there any interaction between Pt and Ge and if so what is its nature?

EXPERIMENTAL METHODS

1. *Preparation of Specimens*

The Pt/γ-Al_2O_3 sample was prepared by impregnating γ-Al_2O_3 containing about 1%wt of chlorine with an aqueous solution of 24.8 mg Pt (as H_2PtCl_6)/ml, drying the mixture at 150°C and calcining it in air at 525°C. The resultant preparation contained about 3.8 g Pt/100 g Al_2O_3.

The Pt,Ge/γ-Al_2O_3 sample was prepared by dissolving elemental germanium in

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[1] AES = Auger electron spectroscopy; XPS = X-ray photoelectron spectroscopy; ESCA = electron spectroscopy for chemical analysis.

ISSN 0021-9517

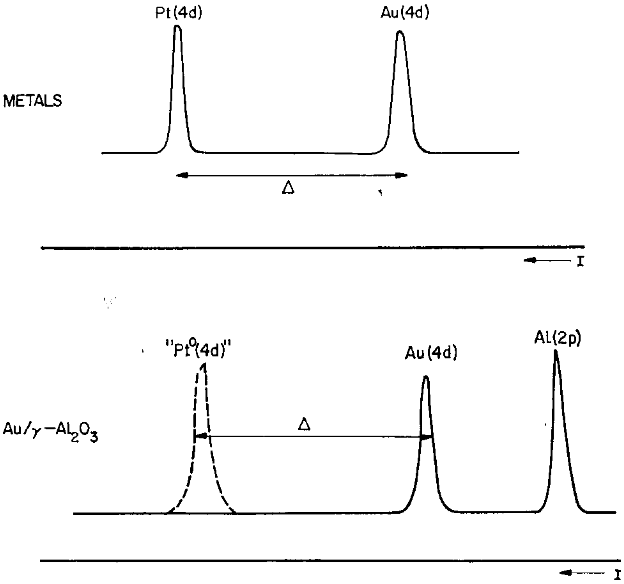

FIG. 1. Schematic view of the determination of the virtual zerovalent plantinum-4d line position on γ-Al_2O_3.

chlorine-saturated water, adding H_2PtCl_6, impregnating the γ-Al_2O_3 with it, drying the system at 150°C and calcining it at 525°C. The product contained 3.8 g Pt and 2.5 g Ge/100 g Al_2O_3.

A system containing 2.5 g Ge/100 g Al_2O_3 was prepared in a similar way.

2. XPS Experiments

The above preparations, in finely divided form, were pressed into the grooves of cylindrical nickel specimen holders adapted to fit the sample introduction system of a Varian IEE-15 spectrometer. The spectrometer was equipped with an Mg$K\alpha$ ($h\nu$ = 1253.6 eV) anode. Spectra of the catalysts were taken after calcination and after reduction at 450, 550, and 650°C for 1 hr at each temperature. Reduction was carried out in flowing hydrogen at a pressure of 1 bar (10^5 N m^{-2}), purified by diffusion through an Ag–Pd thimble. The specimen could be transferred from the treatment site to the analyzer chamber of the spectrometer without exposure to the atmosphere. The vacuum in the analyzer chamber was 5×10^{-7} Torr (1 Torr $= 133.3$ N m^{-2}).

In order to check whether reoxidation of either of the constituents would take place during the measurements, we admitted 2×10^{-4} Torr hydrogen to the sample in the spectrometer in a number of cases. As we found no significant differences be-

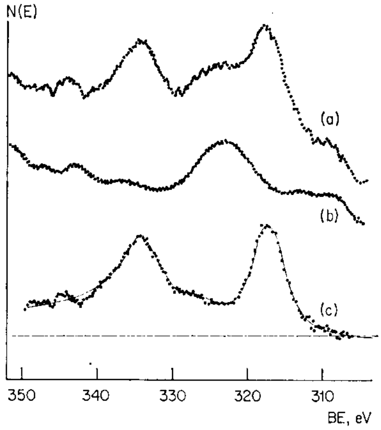

FIG. 2. Pt. 4d doublet of the 3.8%wt Pt/γ-Al_2O_3 catalyst, C 1s set at 284.6 eV. (a) Spectrum of the catalyst calcined at 525°C; (b) spectrum of γ-Al_2O_3 calcined at 525°C; (c) = (a) − (b).

TABLE 1

Line Positions of the Experimental Pt/Al_2O_3, Ge/Al_2O_3 and $Pt,Ge/Al_2O_3$ Catalysts[a]

Temp (°C)	Pt $4d_{5/2}$	Ge $3d$	Cl $2p$	Al $2s$	0 $1s$
3.8% wt Pt/γ-Al_2O_3					
Calcined 525	317.0	—		118.9	531.0
Hydrogen-treated 450	314.8	—		118.8	530.8
550	315.1	—		119.0	530.9
650	314.6	—		118.9	530.9
2.5% wt Ge/γ-Al_2O_3					
Calcined 525	—	32.2	199.7	119.1	531.1
Hydrogen-treated 450	—	32.5	199.6	118.9	530.9
550	—	32.6	199.7	119.1	531.1
650	—	—	199.2	118.9	531.0
3.8% wt Pt + 2.5% wt Ge/γ-Al_2O_3					
Calcined 525	316.7	33.3	200.1	119.2	531.1
Hydrogen-treated 450	315.5	32.6	199.8	119.0	530.9
550	315.6	32.7/31.3	199.7	118.9	531.0
650	315.1	31.4/29.7	199.5	119.0	531.0

[a] C $1s$ = 284.6 eV.

tween the results obtained with and without hydrogen ballast, we believe that the samples remained relatively unaffected in the spectrometer.

The Pt $4d$, Ge $3d$, Al $2s$, O $1s$, and Cl $2p$ photolines were monitored. The strongest photoline of platinum, the Pt $4f$ doublet, could not be monitored because of its overlap with the Al $2p$ photoline from Al_2O_3. Repetitive and sequential scans were made of the five mentioned photolines over scans widths sufficiently large to make the proper background corrections. Contributions of the γ-Al_2O_3 to the spectra were subtracted after measurement of spectra of γ-Al_2O_3 treated in the same way as the experimental catalysts. This procedure was of particular importance for a precise determination of the Pt $4d$ and Ge $3d$ photoline positions and intensities.

A number of reference systems were analyzed to provide the background information necessary for the interpretation of the spectra of the catalysts. Typical reference systems are GeO_2, Ge, PtO_2, Pt, H_2PtCl_6, Na_2PtCl_4, and a bulk PtGe alloy.

A special reference system consisting of γ-Al_2O_3 containing 0.1 monolayer of gold evaporated on top of it, was studied before and after the reduction steps as described above. This experiment served to determine the virtual line position of atomically dispersed platinum in the zerovalent state on the support. The procedure (see Discussion) consisted in measuring the Au $4d_{5/2}$–Al $2p$ line distance of the above system and the Au $4d_{5/2}$–Pt $4d_{5/2}$ line distance from the pure metals in electrical contact with each other (cf. Fig. 1).

RESULTS

The results are given under two subheadings, viz, line positions (binding energies), which provide information on (changes in) the oxidation state of the elements (Pt, Ge), and line intensities, which in principle provide information on agglomeration of the catalytic constituents or dissolution thereof in the carrier.

TABLE 2

Pt $4d_{5/2}$ Line Positions for Some Reference Systems[a]

System	BE (eV)	ΔBE[b]	ΔBE[c]
Metal	314.1	0	
PtO_2	318.0	3.9	
H_2PtCl_6	317.5	3.4	
Na_2PtCl_4	316.7	2.6	
$PtGe_{0.72}$ alloy	315.5	1.4	
"Pt^0"/$\gamma - Al_2O_3$	313.5	−0.6	0
Pt/Al_2O_3			
Calcined, 525°C	317.0	2.9	3.5
Hydrogen-treated, 650°C	314.6	0.5	1.1
Pt, Ge/Al_2O_3			
Calcined, 525°C	316.7	2.6	3.2
Hydrogen-treated, 650°C	315.1	1.0	1.6

[a] C 1s = 284.6 eV.

[b] Reference: platinum metal.

[c] Reference: "Pt^0"/$\gamma - Al_2O_3$, which is obtained by measurement of the $(Au\text{–}Pt)_{bulk}4d_{5/2}$ distance and measurement of the Au $4d_{5/2}$ line position of 0.1 monolayer gold on top of $\gamma - Al_2O_3$.

1. *Line Positions*

Metal line positions were determined by precise subtraction of the γ-Al_2O_3 spectrum from the metal/γ-Al_2O_3 spectrum. An example of this procedure for the Pt 4*d* doublet is given in Fig. 2. All other spectra shown in this paper are smoothed spectra of comparable counting statistics, derived in the same way as the bottom spectrum shown in Fig. 2.

Table 1 gives the line position for the experimental Pt/Al_2O_3, Ge/Al_2O_3, and Pt,Ge/Al_2O_3 preparations. Values of line positions for the various reference systems are given in Tables 2 and 3. Unless stated otherwise, all line positions are referred to C 1*s* = 284.6 eV. The C 1*s* reference is a useful one for these systems, judging from the almost invariant position of the Al 2*s* photolines for the various samples after different treatments (Table 1).

a. Platinum. With Pt/Al_2O_3, the observed chemical shift, ΔBE, for the Pt $4d_{5/2}$ photoline upon hydrogen treatment at 650°C is 2.4 eV against only 1.6 eV with the Pt,Ge/Al_2O_3 system (Tables 2 and 3). Both ΔBE values are lower than those for PtO_2 and H_2PtCl_6 with respect to platinum metal. The Pt $4d_{5/2}$ line position after hydrogen treatment at 650°C is 0.5 eV higher than in platinum metal. A comparison between the Pt $4d_{5/2}$ line positions of the hydrogen-treated Pt/Al_2O_3 system and of platinum in the virtual zerovalent state as it is atomically dispersed on γ-Al_2O_3 ("Pt^0"/γ-Al_2O_3, as determined from the gold experiment) also yields a higher binding energy for the $4d_{5/2}$ electrons of platinum in the Pt/Al_2O_3 catalyst (Table 2).

Platinum in Pt,Ge/Al_2O_3, after hydrogen treatment at 650°C, is characterized by an even higher Pt $4d_{5/2}$ binding energy than platinum in Pt/Al_2O_3 (Table 2). It is noteworthy that the Pt $4d_{5/2}$ photoline of the bulk $PtGe_{0.72}$ alloy also appears at a higher binding energy (Table 2).

b. Germanium. For Ge/Al_2O_3, the Ge 3*d* photoline remains essentially unaffected upon hydrogen treatment up to a temperature of 550°C. It vanishes (or broadens extensively) after treatment at 650°C (Fig. 3).

TABLE 3

Ge 3*d* Line Positions for Some Reference Systems[a]

System	Be (eV)
GeO_2	32.6
Ge	29.7
$PtGe_{0.72}$	
Oxidized	34.1
Hydrogen-treated, 650°C	30.0
Ge/Al_2O_3	
Calcined	32.2
Hydrogen-treated, 650°C	—
Pt, Ge/Al_2O_3	
Calcined	33.3
Hydrogen-treated, 650°C	31.4/29.7

[a] C 1s = 284.6 eV.

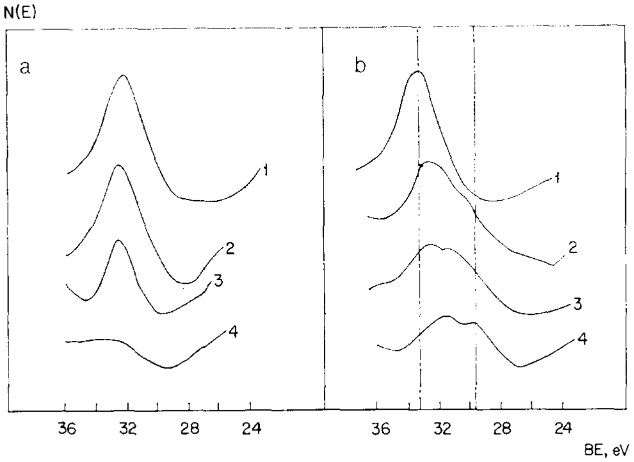

FIG. 3. Line positions of the Ge 3*d* photoline for Ge/Al_2O_3 (a) and $Pt,Ge/Al_2O_3$ (b) (reference: C 1*s* = 284.6 eV). (1) Calcined, 525°C; (2) hydrogen-treated, 450°C; (3) hydrogen-treated, 550°C; (4) hydrogen-treated, 650°C.

The situation is quite different from that for $Pt,Ge/Al_2O_3$. At 550°C, a Ge 3*d* doublet develops, which is shifted by about 1.5 eV to lower binding energy after hydrogen treatment at 650°C.

A comparison with Ge 3*d* reference photoline values (Table 3) would suggest that germanium in the Ge/Al_2O_3 system remains in the tetravalent state.

The situation for $Pt,Ge/Al_2O_3$ is more intricate. Intermediate oxidation states (Ge^{2+}) are probably formed upon treatment with hydrogen.

2. *Line Intensities*

Table 4 lists the relative intensities of the Ge 3*d*, Pt $4d_{(\frac{5}{2}+\frac{3}{2})}$ and Cl 2*p* photolines. Upon hydrogen treatment, the Pt 4*d* and Ge 3*d* lines decrease in intensity. A detailed analysis of the photolines (Fig. 3) would suggest that the large decrease in intensity of the Ge 3*d* line in the Ge/Al_2O_3 system is due to extensive line broadening. This probably reflects the formation of a range of ill-defined germanium compounds. The Pt 4*d* lines, however, remain sharp. Their decrease in intensity is thus to be ascribed either to agglomeration or to diffusion into the carrier.

There is a small decrease in chlorine content upon hydrogen treatment, as follows from the Cl/Al intensity ratio. In each of the treatment stages the chlorine content of the $Pt,Ge/Al_2O_3$ preparation is

TABLE 4

Line Intensity Ratios[a]

System:	Pt/Al_2O_3	Ge/Al_2O_3		$Pt,Ge/Al_2O_3$			
Intensity ratios:	Pt/Al						
Treatment (°C)		Ge/Al	Cl/Al	Pt/Al	Ge/Al	Pt/Ge	Cl/Al
Calcined, 525	0.29	0.048	0.098	0.23	0.050	4.5	0.107
Hydrogen-treated, 450	0.22	0.043	0.087	0.18	0.053	3.3	0.093
550	0.18	0.030	0.079	0.17	0.042	4.0	0.087
650	0.17	—	0.076	0.16	0.030	5.3	0.078

[a] Al = Al 2*s*; Pt = Pt($4d_{\frac{5}{2}} + 4d_{\frac{3}{2}}$); Ge = Ge 3*d*, Cl = Cl 2*p*.

slightly higher than that of the Ge/Al_2O_3 system.

DISCUSSION

The differences between the monometallic Pt/Al_2O_3 and Ge/Al_2O_3 system, on the one hand, and the bimetallic Pt,Ge/Al_2O_3 system, on the other, are remarkable with respect to both intensity and position of the photolines before and after treament.

As regards the germanium photoline intensity (cf. Table 4), the following remarks can be made. In the presence of platinum, we observe only a moderate decrease of the Ge 3*d* signal. In the absence of platinum the signal virtually disappears. The loss in intensity can be explained either by excessive agglomeration into large particles or by compound formation with γ-Al_2O_3. X-Ray diffraction measurements carried out on this system failed to demonstrate the presence of crystalline Ge or Ge oxide species. Thus, we either deal with large amorphous Ge (oxide) lumps or with Ge-γ-Al_2O_3 compounds.

As to the Pt 4*d* photoline intensities, we note that for the Pt/Al_2O_3 system, we observe a decrease of the Pt 4*d* signal intensity of about 40%, as against 30% in the bimetallic system. X-Ray diffraction work proved that no agglomeration takes place under the prevailing conditions, which would, therefore, also point to a migration of (some of) the platinum to less exposed sites of the catalyst. Additional evidence to this effect is presented below.

Before discussing the implications of the observed line positions of platinum and germanium, we should point out that caution is necessary in deriving conclusions about the oxidation state of elements from their line positions, because the elements are present in a highly dispersed state on a foreign matrix (γ-Al_2O_3). When studying binding energies of core electrons of a specific atom, we must bear in mind that it is not only the "oxidation state" of that atom, but also some properties of the surrounding matrix which will affect the measured line position. In this context specific reference is made to the extra-atomic relaxation [polarizability (*5*)] and the local Madelung potential (*6*).

Our experiment with the 0.1 monolayer gold on top of γ-Al_2O_3 (cf. Fig. 1) was designed to circumvent the above complications. The following assumptions underlie our approach:

1. Gold if oxidized, is easily reduced to the metallic state.
2. Isolated gold and platinum atoms on γ-Al_2O_3 are subject to comparable extra-atomic relaxation effects.
3. With gold one measures a surface Madelung potential averaged over different surface sites.

The first assumption is strongly supported by numerous reports on the inertness of gold to the gases prevailing in a high-vacuum system. The second assumption is based on the close fit of the spatial extension of the core hole states of gold and platinum (Au 4*d* compared with Pt 4*d*, etc.).

With regard to the third assumption it can be stated that as a result of the particular deposition method employed (vacuum deposition on a relatively cold substrate) the gold is most probably deposited at random over the available surface sites. In consequence we measure the Madelung surface potential in an averaged way.

It is, however, noteworthy that the fwhm of vacuum-deposited gold on γ-Al_2O_3 is some 0.5 eV higher than that of bulk gold (2.2 and 1.7 eV, respectively). This line broadening could be interpreted as being due to a distribution in surface Madelung potential of γ-Al_2O_3 with a fwhm of about 0.5 eV, and can as such have implications for the interpretation of the "chemical shifts" in platinum.

We therefore expect that the procedure adopted here yields a reasonably approximate value of the Pt $4d_{\frac{5}{2}}$ photoline representative Pt^0/γ-Al_2O_3. Using this standard reference, we observe an apparent Pt $4d_{\frac{5}{2}}$ binding energy value of 313.5 eV, which is 1.1 eV below that of hydrogen-treated Pt/Al_2O_3 and 1.6 eV below that of hydrogen-treated $Pt,Ge/Al_2O_3$. In our opinion these results point to the existence of a "positive," i.e., electron-deficient, form of platinum on γ-Al_2O_3. An alternative explanation, stating that platinum is present on selected sites with an exceptionally high Madelung potential, is not likely because of the relatively small heterogeneity of the surface Madeluug potential on γ-Al_2O_3 as measured with randomly deposited gold. This conclusion, together with the loss of intensity, substantiates the hypothesis that at least a considerable part of the platinum is taken up by the γ-Al_2O_3 matrix.

The situation for the $Pt,Ge/Al_2O_3$ system is even more interesting. Here, we observe two distinct features:

a. Germanium is found in substantial amounts in the Ge^0/Ge^{2+} state after treatment with hydrogen at 650°C.

b. The Pt $4d_{\frac{5}{2}}$ photoline position, after treatment at 650°C, points to an even more electron-deficient state of platinum in comparison with the Pt/Al_2O_3 catalyst.

It is thus evident that the presence of platinum has two effects on germanium in the $Pt,Ge/Al_2O_3$ system:

1. It inhibits germanium from becoming "lost" upon severe hydrogen treatment.
2. It catalyzes the reduction of germanium species (compare Fig. 3a with b).

On the other hand, the presence of germanium gives rise to two effects for platinum:

1. Relatively more platinum is kept in exposed sites.
2. Platinum is more electron deficient than in Pt/Al_2O_3 after severe hydrogen treatment.

Consequently, there must be some interaction between platinum and germanium on γ-Al_2O_3.

The question remains: can we define the "chemical environment" of the metal components? When discussing this, we must bear in mind that platinum, when alloyed with germanium ($PtGe_{0.72}$), is clearly electron deficient (see Table 2). This phenomenon, as yet unexplained, can be used as a clue to the detection of alloys in the supported bimetallic system. A close inspection of Table 2 shows that the photoline positions of Pt in the bulk alloy and in $Pt,Ge/Al_2O_3$ are comparable. Moreover (see Table 3), the chemical shift of the Ge 3*d* line of the $Pt,Ge/Al_2O_3$ system between the oxidized and reduced state ($\Delta BE = -3.6$ eV) is comparable to the shift for Ge in the bulk alloy ($\Delta BE = -4.1$ eV) under similar conditions. These values are larger than the corresponding chemical shift between GeO_2 and Ge metal. These observations all suggest the existence of Pt–Ge alloys on γ-alumina. Part of the germanium that is not bound in the alloy is then present in an intermediate positive form (Ge^{2+}).

CONCLUSIONS

1. Platinum as such on γ-Al_2O_3 is present in an electron-deficient state even after hydrogen treatment at 650°C. Similar studies by Ross *et al.* (*7*) and Escard *et al.* (*1*) suggest a similar electron-deficient state for supported platinum and iridium.
2. The interaction of platinum with a second component may lead to alloy formation on the support. The experimental evidence obtained for the $Pt,Ge/Al_2O_3$ system at least strongly favors this hypothesis.
3. Germanium, in the absence of platinum, is difficult to reduce. At 650°C it probably becomes soluble in the γ-Al_2O_3 matrix. In the presence of platinum, however, the catalyst probably contains Ge^{4+}

and Ge^{2+} species, after hydrogen-treatment at 550°C, while after treatment at 650°C it contains Ge^{2+} and Ge^0 species, the latter being alloyed with platinum.

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