JOURNAL OF CATALYSIS **100**, 75–85 (1986)

A Study of the Platinum–Germanium Catalytic System

JOSE GOLDWASSER,[1] BERNARDO ARENAS, CARMELO BOLIVAR, GERMAN CASTRO,*
ARGENIS RODRIGUEZ, ALFREDO FLEITAS, AND JESUS GIRON

*Escuela de Química and *Escuela de Física, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela*

Received April 24, 1985; revised October 20, 1985

Two series of platinum–germanium over alumina catalysts were prepared. Both series were calcined at 673 K after the addition of both components, while series B was calcined prior to the addition of platinum at 873 K. Temperature-programmed reduction and hydrogen consumption under reactions conditions showed complete reduction of Pt(IV) to Pt(0) for all catalysts and partial reduction of the germanium(IV) precursor in the case of the high loading germanium catalysts of Series A. Series B showed no signs of germanium reduction. Benzene hydrogenation and *n*-butane hydrogenolysis were used as test reactions. For both series the specific activity decreased when the amount of germanium was increased. The selectivity ratios in the hydrogenolysis reaction remained constant for Series B while there was a variation in Series A with the percentage germanium on the catalyst. The results are discussed in terms of the current literature.

INTRODUCTION

The research on bimetallic catalysts in which platinum is one of the components has given rise to many studies in recent years (*1–3*). The main advantages of bimetallic supported catalysts over the monometallic system are the higher selectivity to aromatic products and the lower rate of deactivation.

Two schools of thought have tried to explain the modification of the catalytic properties of these systems. The geometric explanation (*4, 7, 9*) states that the atoms of the second metal divide up the platinum surface into small ensembles which are unable to catalyze undesirable reactions such as hydrogenolysis or the formation of carbonaceous residues.

The electronic reasoning supported by the work of Davis *et al.* (*5*), Burch and co-workers (*6*), and Figueras and co-workers (*7*) suggest that the electronic properties of the platinum are modified by the presence of the second metal, e.g., in the case of platinum–tin bimetallic catalysts the changes in selectivity are attributed to the modification of the Pt–C bond strength induced by the changes of electronic density at platinum atoms (*7*).

Among the bimetallic catalysts studied the Pt-IVA metal systems have been the subject of many detailed investigations (*8–10*). In the case of platinum–tin catalysts Bacaud *et al.* (*8*) suggested from Mössbauer spectroscopic measurements the formation of alloys at various Pt/Sn compositions. Poisoning by tin of the strong acidic sites of the alumina support responsible for cracking was invoked to explain the catalytic behavior observed.

Dautzenberg *et al.* (*9*) measured the oxygen consumed in the reoxidation of previously reduced tin oxide on alumina. The results were interpreted in terms of a total reduction of the tin to the zero-valent state. Burch (*10*), who studied the platinum–tin system by TPR, disagreed with the results of Dautzenberg *et al.* (*9*) since he found that tin is stabilized in the Sn(II) state by

---

[1] To whom all correspondence should be addressed: Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Apartado 47102, Los Chaguaramos, Caracas, Venezuela.

0021-9517/86 $3.00

interaction with the support, and no proper Pt–Sn alloy was formed. A recent work by Coq and Figueras (*7*) on the conversion of methylcyclopentane over Pt–Sn/Al_2O_3 shows a stabilizing effect on the catalytic activity and a decrease of the hydrogenolysis reaction as well as an increase in the aromatization activity as the amount of tin is increased on the catalyst. Dilution and electronic effects were invoked to explain the results.

Palazov and co-workers (*11*) studied the Pt–Pb on alumina catalyst. They followed the adsorption of CO by infrared spectroscopy and the catalytic conversion of cyclohexane. The results show a decrease of the CO stretching vibration frequency and a strong suppression of fragmentation and deactivation in the C_6H_{12} conversion as the amount of lead was increased. Ligand as well as ensemble effects were suggested to explain the mentioned results.

In the related Pt–Ge/Al_2O_3 catalyst Bouwman and Biloen (*12*) showed by XPS that the catalyst contained Ge^{2+} and Ge^{4+} after reduction at 823 K while after reduction at 923 K it contained Ge^{2+} and Ge^0 species; the latter was found to be alloyed with platinum.

Romero *et al.* (*13*) studied the hydrogenolysis of *n*-butane and the hydrogenation of benzene over fluorided platinum–germanium catalysts and concluded that germanium enhanced considerably the selectivity toward isomerization to isobutane for the hydrogenolysis transformation, while the hydrogenation of benzene went through a maximum at about 0.3% Ge. Electronic effects were invoked to explain the results. In more recent work of the same group (*14*) fluorided Pt–Ge/Al_2O_3 catalysts were characterized using infrared spectroscopy, electron microscopy, H_2–O_2 cycles and catalytic measurements for test reactions such as hydrogenolysis of *n*-butane and hydrogenation of benzene. A marked decrease in the dispersion of the platinum was found as well as an increase in the CO stretching frequency when germanium was added to the catalyst. Electron microscopy showed a bimodal distribution of particle size for the bimetallic catalyst while the catalytic activity pattern was basically the same as before (*13*). The authors suggested that the drop in the dispersion of the catalyst as the amount of germanium was increased was related to a weaker exchange of the $PtCl_6^{2-}$ ions (precursors of the metallic platinum) with the surface hydroxyl groups of the alumina due to the presence of GeF_6^{2-} ions which could compete for the same sites of the alumina surface.

The present work was undertaken to shed some light on the catalytic behavior of the cholorided Pt–Ge/Al_2O_3 system. In order to do so H_2–O_2 cycles, reduction studies, hydrogenation of benzene, and hydrogenolysis of *n*-butane were used as tools for characterization of the catalysts.

EXPERIMENTAL

I. Catalysts

Commercial γ-alumina (Ketjen CK-300), surface area 180 m^2/g, was used as support. Two series of catalysts were prepared, in both series the incipient wetness technique was employed for impregnation. The platinum was introduced as H_2PtCl_6 (BDH reagent grade) and the germanium as a hydrochloric solution of Ge(IV) (BDH analytical standards). The procedure for Series A was as follows: a known amount of preconditioned alumina (*14*) was impregnated with a known volume of the germanium solution in order to obtain a certain concentration of the metal, this concentration varied from 0 to 1% in weight of germanium. Different amounts of diluted hydrochloric acid(IV) were added at this stage to try to keep the chlorided level reasonably constant (for each catalyst of the series). After drying the solid at 383 K for 12 h a certain amount of platinum was introduced (as H_2PtCl_6) in order to obtain a series of catalysts with 1% in weight of platinum. The solid was then dried for 12 h and calcined in air at 673 K for 12 h.

The Series B was prepared in a similar fashion, the only difference was the calcination of the catalyst at 873 K for 12 h preceding the addition of the H_2PtCl_6.

Atomic absorption was used to analize the metal concentration of the catalysts. Chloride concentration was obtained using the X-ray fluorescence by neutronic activation technique. Table 1 summarizes all the analytical information concerning the composition of the two series of catalysts. Each catalyst is named according to the percentage of germanium present and the series were it belongs.

II. Methods

1. Dispersion measurements. A vacuum Sartorius microbalance was employed. Two hundred and fifty grams of the catalyst was used. The hydrogen pressure used for reduction of the catalyst was 100 Torr (1 Torr = 133.3 N · m^{-2}) and the heating rate 10°C/min. The final reduction temperature which was 773 K was kept constant for 2 h after which the system was evacuated overnight at the same temperature to a pressure of less than 1×10^{-5} Torr.

After the reduction, the H_2–O_2 cycles were performed in the following way: 100 Torr of either H_2 or O_2 (as the case would be) were introduced at room temperature and left until a constant weight was obtained (15–20 min), this was followed by vacuum ($<10^{-5}$ Torr) for 30 min and the sequence was repeated with the other gas.

TABLE 1

Catalyst Composition

Catalyst	% Ge	% Pt	% Cl
0.0A	0.00	1.00	2.70
0.1A	0.10	0.99	2.53
0.2A	0.18	0.98	—
0.3A	0.33	1.11	2.36
0.5A	0.45	1.08	1.93
0.6A	0.62	0.97	1.73
0.9A	0.85	1.03	1.66
1.0A	0.96	0.99	1.66
0.0B	0.00	0.99	2.74
0.1B	0.10	1.00	2.47
0.2B	0.18	1.03	—
0.3B	0.33	0.99	2.00
0.5B	0.45	1.07	1.77
0.6B	0.62	1.00	1.74
0.9B	0.85	0.97	1.61
1.0B	0.96	0.99	1.59

The percentage dispersion was calculated from these data assuming a 1 : 1 surface stoichiometry (H : Pt) according to Ref. (*14*).

2. Temperature-programmed reduction (low pressure). A low-pressure (0.9 Torr) volumetric system similar to the one described in Ref. (*15*) was used, the only difference was the weight of catalyst (300 mg). From the TPR studies it was possible to obtain the curve of hydrogen consumption as a function of temperature as well as the temperature of maximum hydrogen uptake which was calculated according to Ref. (*16*).

3. Reduction in hydrogen at atmospheric pressure. To check whether a more profound reduction could occur under normal experimental conditions, both series of catalysts were reduced at atmospheric pressure, for 1 h at 773 K in a calibrated conventional recirculation system similar to that used in Ref. (*17*). The sample (500 mg) was evacuated at room temperature for 1 h and then exposed to hydrogen (760 Torr). The temperature was increased (10°C/min) up to 773 K and the hydrogen consumption was measured after 1 h (at 773 K) from the pressure drop due to the reduction process. Care was taken to trap the H_2O and HCl (reduction subproducts) at 78 K. Pressures were measured using a MKS pressure transducer.

4. Catalytic activity measurements. A conventional flow system at atmospheric pressure was used for the hydrogenolysis of *n*-butane as well as for the hydrogenation of benzene. For the former the *n*-butane partial pressure was 60 Torr. The total (H_2 + *n*-C_4H_{10}) flow rate was 60 cm^3(STP)/min. A sample of 200 mg of catalyst was reduced for 1 h with H_2 at 773 K and 1 atm preceding the reaction. The effluent gases were analyzed by on-line gas chromatography using a 8-m × $\frac{1}{8}$-in. column packed with squalane on Chromosorb W (12%).

For the hydrogenation of benzene, the partial pressure of the hydrocarbon was kept constant at 40 Torr by means of a cold-water bath (281 K) that surrounded a saturator where hydrogen became saturated with the corresponding vapor pressure of benzene. The total flow was 60 cm^3(STP)/min, while the catalyst weight was 60 mg. A 1-h reduction with H_2 at 773 K and 1 atm preceeded the reaction. The gases were analyzed by gas chromatography using a 5% Carbowax 1540 over Chromosorb GAW column.

III. Reactants

Hydrogen was purified passing it through a molecular sieve and commerical Deoxo traps to remove water and oxygen traces. *n*-Butane was Matheson 99.9% and showed no chromatographic imputities. Benzene was BDH reagent grade and was distilled prior to the reaction, gas chromatography showed no impurities.

IV. Data Treatment for the Catalytic Conversions

For the hydrogenation of benzene the catalytic activity was obtained by extrapolation at zero conversion and is given in moles of benzene converted per hour per gram of surface platinum. The activation energies were calculated using these catalytic activities and the corresponding Arrhenius plots.

For the hydrogenolisis of *n*-butane the total catalytic activity was defined as the sum of the activities for the different reactions observed: hydrogenolysis (production of $CH_4 + C_2H_6 + C_3H_8$), isomerization (production of isobutane), and dehydrogenation (production of *cis*- and *trans*-2-butene). For every possible reaction the amount of each product was expressed in terms of the amount of converted reactant. The different catalytic activities were obtained by extrapolation at zero conversion and are given in moles of *n*-butane converted per hour per gram of surface platinum. For both test reactions the measured conversions were always less than 5%.

RESULTS

A. Dispersion

Table 2 shows the results for the platinum dispersion for both series of catalysts.

In Series A there is a mild drop of the platinum dispersion when the amount of germanium is increased, while in Series B the dispersion remains basically constant throughout the addition of germanium.

B. TPR

Figures 1 and 2 show the TPR profiles (hydrogen consumption vs. *T*) for the 0.0A, 0.3A and 1.0A catalysts. The curve for the 0.0A catalyst shows that at 550 K the

TABLE 2

Platinum Percentage Dispersion

Catalyst	Percentage dispersion (% *D*)
0.0A	70
0.1A	67
0.3A	69
0.5A	60
0.6A	59
1.0A	56
0.0B	65
0.1B	68
0.3B	70
0.5B	70
0.6B	66
1.0B	67

Note. The percentage dispersion (% *D*) is defined as $\% D = \frac{\text{surface Pt atoms}}{\text{total Pt atoms}} \times 100$. It was calculated assuming a 1 : 1 surface stoichiometry (Pt : H). For experimental details see text, for calculation details see Ref. (*14*).

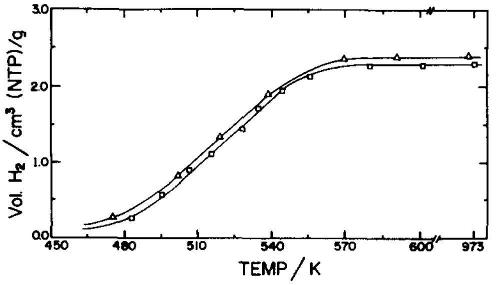

FIG. 1. TPR profile of the 0.0A (□) and 0.3 (△) catalysts.

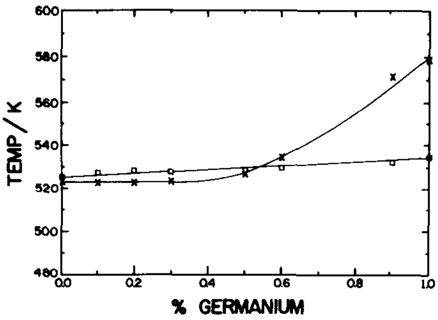

FIG. 3. Temperature of maximum hydrogen uptake vs percentage Ge; Series A (×), Series B (△).

platinum(IV) is totally reduced to Pt(0) since the volume of hydrogen consumed is almost the same as the expected theoretical value (2.30 cm^3(NTP)/g catalyst for a 1% Pt/Al_2O_3 catalyst). The temperature of maximum hydrogen uptake which is shown in Fig. 3 for this catalyst is 523 K. The curve for the 0.3A catalyst is identical (within experimental error) to the 0.0A catalyst. There is no sign of germanium(IV) reduction since the total hydrogen uptake, which is shown in Table 3, corresponds to the reduction of Pt(IV) to Pt(0). The temperature of maximum hydrogen uptake (Fig. 3) is basically the same as the 0.0A catalyst.

The 1.0A curve shows several distinct features compared to the above-mentioned catalysts. Two well-defined temperature regions are present, 298–623 and 740–973 K. The first one corresponds to a hydrogen uptake of 2.36 cm^3(NTP)/g (Table 3) which corresponds to the reduction of Pt(IV) to Pt(0), while the second region corresponds to an uptake of hydrogen of 2.20 cm^3(NTP)/g. If the reduction of germanium is assumed to take place by the following equation: $GeO_2 + 2H_2 \rightarrow Ge + 2H_2O$ the amount of hydrogen consumed will correspond to a 38% of the total needed for complete reduction. The temperature of maximum hydrogen uptake (for the first region) is 580 K which is significantly higher that the value obtained for the 0.0A catalyst (523 K).

The 0.5A and 0.9A catalysts behave in a similar fashion as the 1.0A catalyst since they show two temperature regions (Table 3) and the percentage germanium reduced is similar to the 1.0A catalyst. The temperature of maximum hydrogen uptake (for the first region) which is shown in Fig. 3 increases after the 0.3A catalyst with the percentage germanium.

For Series B the results are different. Figure 4 and Table 3 show no reduction of germanium for the catalysts of this series up to 973 K. The temperature of maximum hydrogen uptake increases mildly with the germanium content (Fig. 3).

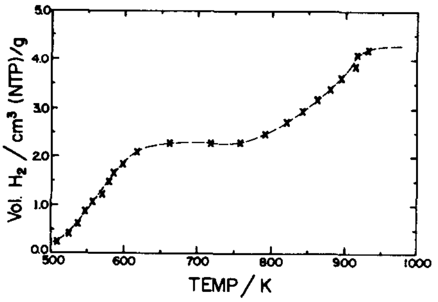

FIG. 2. TPR profile of the 1.0A catalyst.

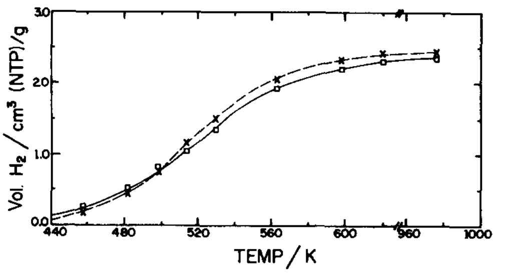

FIG. 4. TPR Profile of the 0.0B (□) and 1.0B (×) catalysts.

TABLE 3

Volume of H_2 Consumed at the Equilibrium H_2 Pressure of 0.9 Torr[a]

Catalyst	V_{H_2} (cm^3(NTP)/g catalyst)[b] 298–623 K	V_{H_2} (cm^3(NTP)/g catalyst)[b] 740–973 K	Percentage germanium reduced[c]
0.0A	2.28	0	0
0.1A	2.28	0	0
0.2A	2.27	0	0
0.3A	2.39	0	0
0.5A	2.35	1.15	40
0.6A	2.33	1.52	39
0.9A	2.38	1.88	38
1.0A	2.36	2.22	38
0.0B	2.35	0	0
0.1B	2.29	0	0
0.2B	2.30	0	0
0.3B	2.39	0	0
0.5B	2.35	0	1
0.6B	2.38	0	1
0.9B	2.31	0	0
1.0B	2.32	0	0

[a] See experimental details in text.

[b] The hydrogen consumption is presented in two temperature regions, 298–623 and 740–973 K. The calculated hydrogen volume for the Pt(IV) → Pt(0) conversion is 2.30 cm^3(NTP)/g for a 1% in weight of platinum catalyst.

[c] Percentage germanium reduced calculated as the difference between the hydrogen consumed in reducing Pt–Ge catalysts and the hydrogen consumed in reducing the Pt/Al_2O_3 catalyst divided by the total amount of hydrogen needed for the stoichiometric reaction $GeO_2 + 2H_2 \rightarrow Ge + 2H_2O$.

C. Reduction at Atmospheric Pressure

The reduction conditions used in the TPR experiments (P = 0.9 Torr) do not reproduce the experimental conditions used in the pretreatment of a catalyst prior to a reaction. In order to check whether a more complete reduction could occur during the pretreatment, some experiments were performed using 760 Torr of hydrogen at 773 K. Table 4 summarizes the results. For the 0.0A, 0.2A, and 0.3A catalysts the volume of hydrogen consumed at 773 K is almost constant and basically the one needed for complete reduction of Pt(IV) to Pt(0). For the catalysts of Series A with higher content of germanium the situation is different since the volume of hydrogen consumed is in each case larger than the expected for total reduction of platinum. As in the TPR experiments the percentage germanium reduced (assuming the same stoichiometric reaction) is almost constant for the mentioned catalysts. For Series B the results are different; there is no reduction of germanium observed (Table 4).

D. Catalytic Activity Measurements

The test reactions employed were the hydrogenation of benzene and the hydrogenolysis of *n*-butane. Checking experiments were performed with the alumina support as well as with a 1% germanium/alumina system. No catalytic activity (for either re-

TABLE 4

Volume of H_2 Consumed at 760 Torr and 773 K[a]

Catalyst	V_{H_2} (cm^3(NTP)/g catalyst)[b]	Percentage germanium reduced[c]
0.0A	2.40	0
0.2A	2.42	3
0.3A	2.43	2
0.5A	3.15	24
0.6A	3.26	23
0.9A	3.50	22
1.0A	3.77	23
0.0B	2.39	0
0.2B	2.38	0
0.3B	2.38	0
0.5B	2.51	2
0.6B	2.40	0
0.9B	2.39	0
1.0B	2.41	0

[a] Recirculation system, P_{H_2} = 760 Torr, T = 773 K.

[b] The calculated hydrogen volume for the Pt(IV) → Pt(0) conversion is 2.30 cm^3(NTP)/g for a 1% in weight of platinum catalyst.

[c] Same as in Table 3.

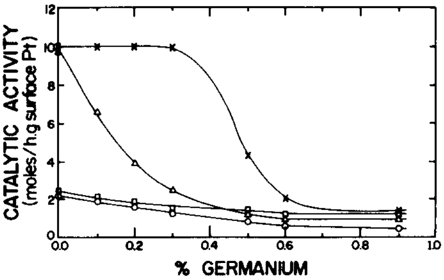

FIG. 5. Catalytic activity for hydrogenolysis and isomerization of *n*-butane vs percentage germanium. (×) Hydrogenolysis activity for Series A. (□) Isomerization activity for Series A. (△) Hydrogenolysis activity for Series B. (○) Isomerization activity for Series B.

action) was observed even at the highest temperature used in the present work.

For the hydrogenation of benzene the only product observed throughout the entire temperature range (343–413 K) was cyclohexane. Previous studies (*18*) show that in our experimental conditions (see experimental section) the reaction is zero-order with respect to benzene and first-order with respect to hydrogen.

Table 5 summarizes the catalytic activity in moles converted/h · g of surface platinum as well as the different activation energies. For the 0.0A and 0.0B catalyst the catalytic activity as well as the activation energy agree with other authors (*19*). For both series the catalytic activity drops with the percentage germanium. The activation energies for Series B remain basically constant throughout the series. For Series A there is a mild increase as the germanium content is increased.

The hydrogenolysis of *n*-butane was performed in the range 573–723 K. The products observed were: methane, ethane, propane, and isobutane (isomerization). *cis*- and *trans*-2-butene were observed only above 673 K. The hydrogenolysis and the isomerization activity measured at 673 K for both series are plotted in Fig. 5 as a function of germanium content. For Series

TABLE 5

Catalytic Activity and Activation Energy for the Hydrogenation of Benzene

Catalyst	Activity[a] (mol/h · g surface platinum)	Activation energy[c] (kcal/mol)
0.0A	5.1	10 ± 1
0.3A	5.0	10 ± 1
0.5A	1.3	11 ± 1
0.6A	1.2	11 ± 1
0.9A	0.4	12 ± 1
1.0A	0.1	13 ± 1
0.0B	5.0	10 ± 1
0.3B	5.0	10 ± 1
0.5B	0.9	11 ± 1
0.6B	0.8	11 ± 1
0.9B	1.0	11 ± 1

[a] Reaction temperature = 373 K, C_6H_6 partial pressure = 40 Torr. Other experimental details are described in the text.

[b] Catalytic activity obtained by extrapolation at zero conversion in mol/h · g surface platinum.

[c] Activation energies calculated from the Arrhenius plots obtained from the activity measurements at different temperatures.

A the hydrogenolysis activity decreases for the catalysts with higher germanium content. For Series B there is a drop in the activity as soon as germanium is introduced on the catalyst. The isomerization activity is much less influenced by the addition of germanium in both series.

Finally, Table 6 summarizes the selectivity ratios obtained in the *n*-butane hydrogenolysis at 673 K. For Series A the C_3/C_1 (propane/methane) ratio stays unchanged (within experimental error) throughout the series. The C_2/C_1 (ethane/methane) ratio decreases while the C_3/C_2 (propane/ethane) ratio increases when the germanium content is increased. For Series B the ratios do not change appreciably with the germanium loading.

DISCUSSION

The results obtained for the two series of catalysts are definitively different. For the catalysts of Series A with a percentage germanium above 0.3 wt% the TPR results as well as the hydrogen consumption at 773 K and 760 Torr agree with the work of McNicol and co-workers (*20*). They worked with a 0.375 wt% Pt/0.25 wt% Ge on Al_2O_3 calcined catalyst. A peak at 553 K corresponding to the reduction of the platinum component and a second peak at 873 K which was assigned to the reduction of germanium were reported. The hydrogen consumption for the second peak was 40% less than the amount of required for the reduction of Ge^{4+} to Ge^0.

TABLE 6

Selectivity Ratios for the Hydrogenolysis of *n*-Butane Reaction at 673 K[a]

Catalyst	C_3/C_1[b]	C_2/C_1[c]	C_3/C_2[d]
0.0A	5.5	3.5	1.6
0.1A	5.6	3.2	1.9
0.2A	5.6	3.2	1.9
0.3A	5.7	3.1	1.9
0.5A	5.7	2.4	2.4
0.6A	5.7	1.7	3.1
0.9A	5.0	1.6	4.1
0.0B	5.4	2.9	2.0
0.1B	5.2	2.8	2.0
0.2B	5.1	2.7	2.0
0.3B	5.1	2.5	2.0
0.5B	5.5	2.6	2.2
0.6B	5.6	2.5	2.5
0.9B	5.8	2.4	2.5

[a] Atmosferic flow system, $T = 673$ K, *n*-butane partial pressure: 60 Torr, total flow rate = 60 cm^3(STP)/min.

[b] Propane/methane ratio obtained from the corresponding amount of each product expressed in terms of converted reactant.

[c] Ethane/methane ratio obtained as in (b).

[d] Propane/ethane ratio obtained as in (b).

In our case, two well-defined temperature regions exist and the percentage germanium reduced is around 40% of the total needed for complete reduction (Ge(IV) → Ge(0)). The temperature of maximum hydrogen uptake (Fig. 2) for the second temperature region is 850 K which is fairly close to the one reported by McNicol and co-workers (*20*).

The reduction experiments carried out at 760 Torr and 773 K agree with the TPR experiments since the catalysts where there is a measurable reduction of germanium (Table 4) are the same which yielded the two temperature regions in the TPR experiments.

In order to discuss the oxidation state of the germanium in the catalysts of Series A it is worthwhile to divide the series into two subseries. The first from 0% Ge up to 0.3% Ge and the second from 0.3% Ge up to 1.0% Ge. For the first subseries TPR experiments (Table 3) as well as hydrogen consumption at 760 Torr (Table 4) indicate that there is no reduction of the germanium so it stays as Ge(IV). For the second subseries TPR experiments (Table 3) indicate an approximate 40% reduction (average oxidation state close to Ge(II)) while Table 4 shows an approximate 23% reduction (average oxidation state between IV and II). The difference might be the temperature range covered in TPR experiments (298–973 K) compared with the temperature used for reduction prior a catalytic reaction (773 K).

Evidently, the amount of hydrogen consumed in the reduction studies, over and above that needed for reducing platinum, can be interpreted either in assuming that a certain amount of germanium is reduced from Ge(IV) to Ge(0), or that a quantity twice as large is reduced from Ge(IV) to Ge(II). To shed some light into this matter XPS experiments were carried out in the reduced 1.0A catalyst. Preliminary results (*23*) show that the germanium $2p_{3/2}$ photoline is centered at 1221.0 eV (this line position is referred to C 1*s* = 284.6 eV). The photoline positions (*24*) for Ge(II) (GeO), Ge(IV) (GeO_2), and Ge(0) are 1221.2, 1220.2, and 1217.2 eV, respectively. This result strongly suggests the absence of Ge(0) in the 1.0A catalyst reduced with H_2 at 500°C and 760 Torr.

It is worth comparing our results with the work of Burch (*10*) who studied the oxidation state of tin in the related Pt–Sn/Al_2O_3 catalyst. For a series of catalysts with different tin loadings a constant percentage reduction close to 45–50% was reported based on the reaction $Sn^{4+} + 2H_2 = Sn^0 + 4H^+$. Our results for the second subseries coincide since the average oxidation state of germanium is independent of the percentage Ge on the catalyst. This makes an ensemble (or dilution) effect unlikely because the fraction of germanium reduced should depend on the germanium content if a small amount of Ge(0) is formed. Similar effects have been reported by other authors (*18*).

Interestingly enough, the temperature of maximum hydrogen uptake (Fig. 3) for the first temperature region for the second subseries increases with the percent germanium. For the first subseries it remains basically constant. Seemingly, there is a minimum amount of germanium at which the reduction starts to show up and at which the activation energy for the hydrogenation of benzene starts to increase.

The hydrogenation of benzene is known to be a structure insensitive reaction (*21*), so the catalytic specific activity should not depend on such parameters as dispersion, preparation of the catalyst, geometric effects, etc. A drop in the specific activity due to an increase in activation energy is very likely to be related to an electronic effect. In our case this is supported by the following: (a) The selectivity ratios summarized in Table 6 show a decrease of the C_2/C_1 ratio, an increase of the C_3/C_2 ratio and a approximate constant value for the C_3/C_1 ratio for the catalysts of Series A with more than 0.3 wt% Ge. Levitskii *et al.* (*22*) summarizing early data has shown that on going from Pt–SiO_2 to Pt–Al_2O_3 a decrease of the relative rates of hydrogenolysis of the bonds between C atoms with a minimum electron density occurs. It was suggested that the higher electron-donating properties of Pt in Pt–SiO_2 compared to Pt in Pt–AlO_3 catalysts were responsible for this behavior. In the case of *n*-butane the carbon atoms with lower electron density are the internal so the production of ethane will be decreased if the platinum in the platinum–germanium catalysts of Series A is more electron deficient than in the monometallic catalyst. (b) Bouwman and Biloen (*12*) working with Pt–Ge/Al_2O_3 catalysts prepared in a similar fashion as our Series A catalysts concluded by XPS that platinum was more electron deficient in the bimetallic catalyst than in the monometallic system, consequently an interaction between platinum and germanium was suggested. (c) Preliminary experiments (*23*) on the adsorption of CO followed by infrared spectroscopy showed a shift to higher frequency for the catalysts of Series A with a percent germanium above 0.3 wt%. These results agree with early data on fluorided catalysts (*14*) and can be interpreted in terms of electron donation from the platinum to the germanium entity (*14*).

From the above discussion it follows that our results (high loading germanium catalysts of Series A) seem to be well explained by the electronic surface model (*10*), where the special catalytic properties of the bimetallic catalyst are due to a change in the electronic properties of the platinum, presumably via electron withdrawal by the reduced germanium ions.

The results for Series B indicate that the germanium after the calcination at 873 K is stabilized in the alumina support in such a way that its reduction does not occur under our experimental conditions; there is no catalysis for the reduction of germanium(IV) by the metallic platinum. Evidently a dilution or geometric effect would be almost impossible under these circumstances. A legitimate question that arises for Series B is why the catalytic activity for the reactions studied drop with the percentage germanium? The dispersion as well as the reduction studies exclude a dilution effect and the catalytic experiments showed no changes in the activation energy (C_6H_6 hydrogenation) as well as in the selectivity ratios (*n*-butane hydrogenolysis) which presumably would neglect a localized electronic effect. XPS and infrared studies are now underway to try to shed more light on this subject.

CONCLUSIONS

1. There is a correlation between reduction and catalytic studies for the higher loading germanium catalyst of Series A.

2. The percentage germanium reduced under normal experimental conditions is approximately constant for the catalysts mentioned in 1. There are no signs of germanium(O) present in these catalysts.

3. For the catalysts calcined at 873 K prior to the addition of platinum and after the addition of germanium (Series B) there is no reduction of the germanium(IV).

4. The special properties of Pt–Ge catalysts are not due to a dilution effect in which germanium atoms divide the surface up into small ensembles of platinum.

5. Changes in the electronic properties of small platinum crystallites are probably responsible for the behavior observed for the bimetallic catalysts (Series A).

ACKNOWLEDGMENTS

The authors with to acknowledge Consejo Nacional de Investigaciones Científicas y Technológicas (CONICIT) for its financial support (Proyecto DDCT-PPQ6) and Hernán Abreu for his technical assistance.

REFERENCES

1. Muller, A. C., Engerlhard, P. A., and Weisang, J. E., *J. Catal.* **56,** 65 (1979).
2. Wagstaff, N., and Prins, R., *J. Catal.* **59,** 434 (1979).
3. Wagstaff, N., and Prins, R., *J. Catal.* **67,** 255 (1981).
4. Sinfelt, J. H., Carter, J. L., and Yates, D. J. C., *J. Catal.* **24,** 283 (1972).
5. Davis, B. H., Westfall, G. A., Watkins, J., and Pezzanite, J. J., *J. Catal.* **42,** 283 (1972).
6. Burch, R., and Garla, L. C., *J. Catal.* **71,** 360 (1981).
7. Coq, B., and Figueras, F., *J. Catal.* **85,** 197 (1984).
8. Bacaud, R., Bussiére, P., and Figueras, F., *J. Catal.* **69,** 399 (1981).
9. Dautzenberg, F. M., Helle, J. N., Biloen, P., and Sachtler, W. M. H., *J. Catal.* **63,** 119 (1980).
10. Burch, R., *J. Catal.* **71,** 348 (1981).
11. Palazov, A., Monev, Ch., Kadinof, G., Shopo, D., Lietz, G., and Völter, J., *J. Catal.* **71,** 1 (1981).
12. Bouwman, R., and Biloen, P., *J. Catal.* **48,** 209 (1977).
13. Romero, T., Tejeda, J., Jaunay, D., Bolívar, C., and Charcoset, H., *in* "Proceedings, the VIIth Iberoamerican Congress in Catalysis," p. 453. La Plata, Argentina, 1980.
14. Bolívar C., Charcosset, H., Primet, M., Arenas, B., and Torellas, R., *in* Proceedings, VIIIth Iberoamerican Congress in Catalysis," p. 162. Huelva, Spain, 1982.
15. Bolívar, C., Charcosset, H., Frety, R., Primet, M., Tournayan, L., Betizeau, C., Leclercq, G., and Maurel, R., *J. Catal.* **39,** 249 (1975).
16. Willard, H. H., Merritt, L. L., Dean, J. A., and Settle, F. A., "Instrumental Methods of Analysis," 6th ed., p. 667. Van Nostrand, New York, 1981.
17. Goldwasser, J., and Hall, W. K., *J. Catal.* **71,** 53 (1981).
18. Amano, A., and Parravano, G., *in* "Advances in Catalysis and Related Subjects" (D. D. Eley, W. G. Frankenburg, V. I. Komavewsky, and P. B. Weisz, Eds.), Vol. 9, p. 716. Academic Press, New York/London, 1975.
19. Bacaud, R., and Figueras, F., *C.R. Acad. Sci. París, Ser. C* **281,** 479 (1975).
20. McNicol, B. D., Paper presented at Surface Reac-

tivity and Catalysis Group Meeting, Nottingham, U.K., 1976.

21. Aben, P. C., Platteuw, J. D., and Stouthamer, *Rec. Trav. Chim.* **89** (1970).

22. Levitskii, I. I., Gyul'maliev, A. M., and Udal't-zova, E. A., *J. Catal.* **58,** 144 (1979).

23. Arenas, B., Bolívar, C., Girón, J., Castro, G., and Goldwasser, J., unpublished results.

24. Wagner, C. D., Riggs, W. H., Davis, L. E., Moulder, J. F., and Muilenberg, G. E., "Handbook of X-Ray Photoelectron Spectroscopy," p. 88. Perkin–Elmer Corp., Minn.