The State of Platinum on Reforming Catalysts

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Platinum has been deposited on a series of silica–alumina supports with different alumina contents; the dispersion of platinum is found to be constant. The catalytic activity for cyclohexane dehydrogenation increases when the alumina content decreases. The activity for *tert*-butanol dehydration and for perylene cation formation decreases when platinum is deposited on the support. In contrast, the number of sites producing tetracyanoethylene anion increases. The existence of a charge-transfer complex between the metal and the oxidizing sites of the support could explain the variations of platinum activity and redox properties.

INTRODUCTION

Supported metal systems occupy and important place in the field of catalysis by metals; they find wide applications as industrial catalysts. The numerous studies on these catalytic systems have been reviewed (1, 2). Two main problems have been investigated with these solids, namely the possible change of catalytic activity with crystallite size and the influence of the carrier.

For platinum on alumina or on silica catalysts, published results demonstrate that the activity per exposed metal atom is independent of crystallite size, at least for some reactions like hydrogenation of benzene (3), cyclohexene (4), cyclopropane (5); Boudart et al. (5) proposed that these reactions may be considered as "facile reactions," as opposed to "demanding reactions" for which activity should depend on particle size, for example CO adsorption on supported platinum, according to Dorling and Moss (6).

The influence of the carrier on the intrinsic catalytic activity of supported metals is a more controversial subject in the literature: while some deny it (3), Taylor et al. (7) report a substantial influence of the support for the hydrogenolysis of ethane

and cyclopropane over nickel on alumina, silica, and silica–alumina. Some results in our laboratory allow us to suppose that such an effect can arise with platinum on silica–alumina catalysts. In the conversion of *n*-butane at 475°C (8), hydrogenolysis into methane and propane increases greatly when alumina is removed from the support; also, *cis*-butene isomerization (9) reveals that platinum-on-silica–alumina can yield *trans*-butene at −10°C while neither the support alone nor Pt-on-silica or on alumina can give this reaction at the same temperature. The adsorptive capacities of these catalysts for oxygen and carbon monoxide were measured (10) and are discussed in detail below. The present work deals with the catalytic activity of platinum-on-silica–aluminas in the dehydrogenation of cyclohexane. The dispersion of the metal was investigated by electron microscopy and hydrogen adsorption; a special effort was made to study the interaction of platinum with oxidizing sites.

EXPERIMENTAL METHODS

1. Materials

The supports were a commercial silica–alumina (Ketjencat) with 13 wt % alumina

TABLE 1

Support	Surface area (m²/g)	Mean pore radius (Å)	Cl × 10⁶ at./g	Na × 10⁶ at./g
K 13	576	22	3.2	3.8
K 6	680		0.28	0.87
K 1.9	720	20	0.11	0.65
K 0.45	610	20	0.05	0.53

and several other solids obtained from this one by selective extraction of aluminum (*11*). The surface areas of these solids and their chemical composition are given in Table 1; the aluminum content was measured by colorimetry, while chlorine and sodium were detected by radioactivation. A spectrographic analysis could not detect any other foreign ion. On the initial support (K 13) 0.5 wt % SO_4^{2-} was present; on the dealuminated solids sulfates could not be detected and it can be thought that the hydrochloric treatment washes them off.

The platinum catalysts were prepared by impregnation of the carrier with aqueous chloroplatinic acid solution, followed by drying at 110°C for 8 hr. The catalysts were reduced *in situ* with hydrogen at 400°C for 2 hr before use. The platinum catalysts will be denoted Kxy, where x represents the weight percent of alumina and y the weight percent of platinum.

The cyclohexane was an R. P. Prolabo product; no impurity could be detected by gas chromatographic analysis. Hydrogen was passed over reduced copper catalyst (BTS catalyst from BASF) and Linde 5A molecular sieve to remove possible traces of oxygen and water.

2. Procedure

Activity measurements were conducted in a differential flow reactor (*12*); the reaction conditions were: temperature, 230°C; weight of catalyst, 20 mg; partial pressure of hydrogen, 700 Torr; partial pressure of cyclohexane, 59 Torr; total flow rate, 2 cm³/sec. In these conditions no decline in activity was observed after 6 hr on stream. The products of reaction were benzene and hydrogen; no secondary reaction could be

TABLE 2
INFLUENCE OF MASS OF CATALYST AND PARTICLE
SIZE ON CONVERSION, AT 230°C

Catalyst	Av particle size	Mass of sample (mg)	Conversion (%)
K 13-0.6	1 μ	20	0.09
	1 mm	20	0.12
K 6-0.6	1 μ	20	0.3
	1 mm	20	0.29
K 1.9-0.6	1 μ	20	0.4
	1 mm	20	0.4
K 13-0.6	1 μ	5	0.29[a]
	1 mm	50	0.29[a]

[a] The last two runs were made at the same gas hour space velocity.

detected by chromatographic analysis. Table 2 indicates that neither the mass of catalyst nor the particle size affected the reaction rate, so diffusion was not rate controlling.

RESULTS

1. Platinum Dispersion

Four catalysts were examined by electron microscopy; the solids were dispersed and deposited on a collodion film reinforced with carbon. On K 13-0.6, K 1.9-1, and K 0.4-0.16 metal particles are not visible; it can then be assumed that their size is less than 20 Å. On K 0.45-1 crystallites from 20 to 100 Å are clearly visible. No distribution such as that reported in the literature (*6*) was calculated; we can conclude that for the two supports with 13 and 1.9 wt % alumina the dispersion is good and that no great difference can be observed between these supports.

We recall previous results from our Laboratory (*10*) obtained with these catalysts; they are listed in Table 3 and represent the irreversible adsorption of oxygen and carbon monoxide. It can be seen first that both adsorbates give similar results and secondly that no major difference arises between the four supports used: all lead to the same platinum dispersion.

TABLE 3

ADSORPTIONS OF OXYGEN AND CARBON MONOXIDE
[from Ref. (10)]

Catalyst	O/Pt	CO/Pt
K 13-0.6	0.22	0.23
K 9.4-0.6	0.31	0.31
K 1.9-0.6	0.22	0.23
K 0.09-0.6	0.21	0.21

The adsorption of hydrogen was investigated by the chromatographic technique described by Ozaki et al. (13): the measurement of the retention volume of a deuterium pulse in hydrogen gives the extent of reversibly adsorbed gas. The results obtained are represented in Table 4.

TABLE 4

HYDROGEN ADSORBED AT 200°C AS MEASURED
CHROMATOGRAPHICALLY

Catalyst	Hydrogen adsorbed at 200°C (cm³/g)
K 13-0.6	0.5
K 3.4-0.6	0.5
K 1.9-0.6	0.6

These data reveal similar adsorptions on the three silica–alumina catalysts investigated, in good agreement with the preceding methods.

2. Dehydrogenation Activity

The reaction rate was measured under standard conditions; a preliminary study with a Pt–SiO₂ catalyst had shown that the reaction rate was first order relative to cyclohexane. The results are presented in Fig. 1. The catalytic activity suffers a great increase when the carrier is changed from K 13 to K 1.9. With K 0.45 as support, the activity remains constant when the platinum content increases (Pt% > 0.2); this may be interpreted as a decrease of the platinum dispersion in agreement with electron microscopy observations.

The same catalysts were tested in the reverse reaction of hydrogenation of benzene at 80°C and very similar results were obtained for the initial rate of reaction as a function of the alumina content of the support.

3. Dehydration Activity

On these colored solids with low platinum content conventional methods (indicators) of measuring acidity fail. tert-Butanol dehydration can be considered as characteristic of acidic sites (14); this reaction is zero order and gives a measurable rate at 50°C, providing a sensitive test for measuring the number of acid-centers.

Some results are represented in Fig. 2 for pure and platinized K 13 silica–alumina; the activities per unit area fall from 1.6 for the support to 1.1 for the catalyst with 0.6% Pt. The decrease in specific activity shows that platinum covers acidic sites, so it can be supposed that there is an
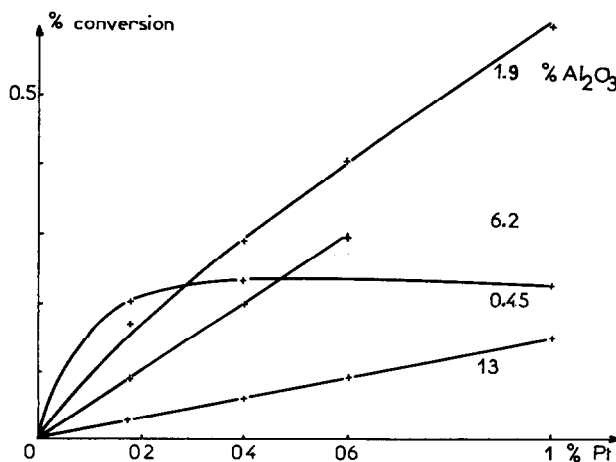

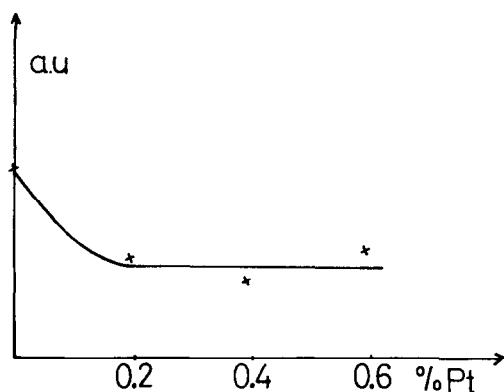FIG. 1. Catalytic activities for cyclohexane dehydrogenation for a series of platinized silica–aluminas.

FIG. 2. Catalytic activities for *tert*-butanol dehydration, expressed in arbitrary units, of pure and platinized K 13 silica–alumina.

TABLE 5

INFLUENCE OF PLATINUM ON REDOX PROPERTIES

Catalyst	Perylene$^+$ signal	TCNE$^-$ signal
K 3.4	1.1	0.6
K 3.4	0.1	3.6
K 13	0.8	0.8
K 13-0.2	0.40	1.0
K 13-0.5	0.95	1.2
K 13-1	0.6	1.2
K 13-1.45	0.7	1.4
K 13	0.8	0.9
K 13-0.6^a	0.5	1.1

^{a} Pt from $Pt(NO_2)_2(NH_3)_2$.

interaction between these sites and some metal atoms.

4. EPR Measurements

Silica–aluminas have a special behavior among usual supports since they possess strong redox properties.

The presence on the surface of silica–alumina catalysts of electron transfer sites capable of oxidizing hydrocarbons to the corresponding cation radicals is well known [15]; according to various authors these oxidizing sites can be identified to some particular acidic sites [16]. The interaction of platinum with these sites was studied through the variations of the EPR signal obtained when perylene is contacted with the solid.

Silica–aluminas also possess reducing sites. Some results allow one to think that platinum atoms may also act as electron-donor centers. Turkevich *et al.* [17] compared the signals produced by tetracyanoethylene (TCNE) adsorption on alumina and palladium-on-alumina. The palladized catalyst gave a higher signal which was connected with palladium content; this was attributed to a charge-transfer complex between the metal and TCNE. Platinum may be supposed to behave as palladium; this led us to measure also the number of (TCNE)$^-$ ions. For these EPR experiments the catalysts were reduced at 400°C under hydrogen, then evacuated and contacted with a benzene solution of the reactant.

The data obtained are summarized in Table 5. For K 3.4, the Pt deposit decreases the Pe$^+$ signal, while (TCNE)$^-$ increases. For K 13 the situation is rather more complex: after an initial decrease for perylene, both signals increase with platinum content. We must keep in mind that platinum has been deposited by impregnation with chloroplatinic acid; it is known that chlorinated compounds create oxidizing sites and destroy reducing centers on alumina [18, 19]. The chlorine content of some reduced platinum catalysts has been measured by radioactivation. The results for some catalysts are reported in Table 6; they show that K 13-0.4 retains much more chlorine than dealuminated supports. We can therefore attribute the variations of Pe$^+$ ion for K 13 to the competitive effect of chlorine and platinum. To check the validity of this hypothesis a covalent compound of platinum $Pt(NO_2)_2(NH_3)_2$ was used to deposit the metal; this complex decomposes under

TABLE 6

CHLORINE CONTENT OF PLATINIZED
SILICA–ALUMINA CATALYSTS
AFTER REDUCTION
AT 400°C

Catalyst	Cl/Pt
K 13-0.4	0.39
K 6.2-0.4	0.13
K 1.9-0.4	0.027
K 0.45-0.4	0.031

vacuum into nitrogen and water. The cata-lyst was treated under vacuum, then under hydrogen at 400°C. For a platinum content of 0.6% on K 13 a clear decrease in pery-lene signal is obtained (Table 5).

Therefore, measurements of perylene ion formation give a confirmation of the inter-action of platinum with silica–alumina sup-ports. The increase of the TCNE signal with platinum content, in good agreement with the results published by Turkevich et al. (17), leads us to propose the existence of a charge-transfer complex between plati-num and tetracyanoethylene.

DISCUSSION

The results reported above demonstrate an interaction between platinum and the oxidizing sites of silica–alumina. The de-crease in hydrogenation activity per plati-num atom can therefore be attributed to a support effect which lowers platinum ac-tivity when the alumina content of the carrier increases.

Support effects are easy to understand with semiconductor materials: in that case, alterations in the electron concentration of the support could induce changes in the electronic properties of the metal (20). Such an effect is not possible with usual in-sulating oxides; however, EPR experiments suggest the possibility of existence of a charge-transfer complex.

A theory describing the interaction of donor D and acceptor A was formulated by Mulliken (21). For weak donors and accep-tors the molecular complex AD is formed by nonbonding van der Waals type forces and to a first approximation is a single state with a slight admixture of a state in which electron transfer takes place giving rise to an ionic species A^-D^+. A typical property of the adduct is its characteristic optical spectrum; an electron transfer process is assumed to be responsible for the optical absorption which leads to the first excited level in which the contribution of the ionic state is greater. For molecules with great donating and accepting power, a complete electron transfer can take place in the ground state; the system is paramagnetic and is expected to show free radical behavior.

Some insulating oxides possess superficial acceptor sites, especially silica–aluminas and chlorinated aluminas (15, 18); dealum-inated silica–aluminas are weaker electron acceptors than K 13 as is shown by the number of sites which can oxidize perylene to the radical cation Pe^+ (Fig. 3). Alumina is not a strong oxidizing agent even in pres-ence of oxygen unless dehydrated above 550°C (22); pure silica is inactive.

If we compare the ionization potentials of an isolated platinum atom (9 eV) and those of the aromatic compounds used in EPR experiments (6.4 to 8.4 eV), it can be supposed that platinum plays the role of an
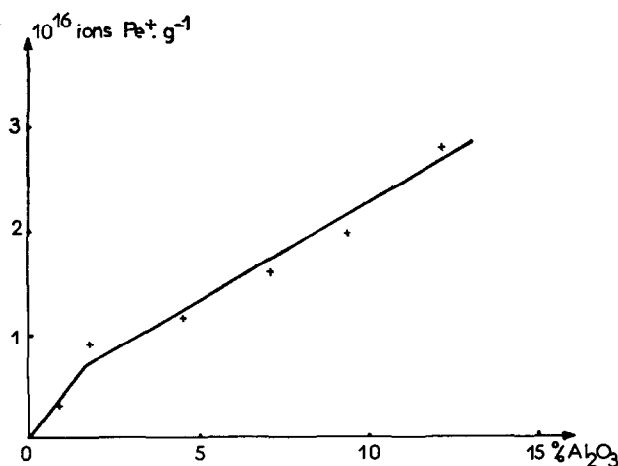

FIG. 3. Number of perylene cations Pe^+ measured by EPR against alumina content of the supports.

electron donor. This is reinforced if we take into account that the metal is actually present in the form of small crystallites, for which the work of electron extraction will be lower than for isolated atoms. Indeed a charge transfer complex is observed between platinum and TCNE which is a strong acceptor. Silica–alumina also has strong acceptor sites and we may suppose that the observed interaction between the metal and oxidizing sites is of the same type, leading to a complex by transfer of one electron from the metal to the support. The loss of this electron would reduce the metallic character, and therefore the dehydrogenation activity.

Some other results (*23*), obtained by studying the dissolution of platinum in HCl, support the thesis of the interaction Pt-carrier. In the absence of oxygen, the metal does not dissolve in HCl solutions at room temperature, so the interaction with the support cannot produce ionic platinum. In the presence of air, the solubilization occurs only if the carrier possesses oxidizing sites which can be either intrinsic ones or induced by the impregnation. When these sites exist initially on the support, the dissolution rate increases with the oxidizing power of the carrier. The role of oxygen finds a simple explanation with the model proposed here since this compound is known to increase the electron affinity of the carrier; this effect can induce a complete transfer of the electron from the platinum to the support, thus leading to an ionic species easily soluble in hydrochloric acid.

All these experimental observations favor the hypothesis of the existence of a complex between platinum and oxidizing sites; the increase of the dehydrogenation activity when dealuminating the support would correspond to the decrease in the amount of platinum interacting with the carrier.

From this viewpoint carrier effects will depend on the ionization potential of the metal and the oxidizing strength of the support. Let us examine the results published in the literature and compare them with this theory. On one hand some authors have used carriers which possess strong oxidizing properties: Taylor *et al.* (*7a*) reported that the specific activity for ethane hydrogenolysis of nickel-on-silica catalysts was about 50-fold higher than that of the nickel on silica–alumina; these authors also reported a clear support effect for hydrogenation and hydrogenolysis of cyclopropane (*7b*). Goble and Lawrence (*19*) published that benzene adsorption is mainly irreversible on platinum-on-alumina catalysts while it is mainly reversible on the chlorinated catalysts; these experiments indicate that platinum is no longer present in its metallic form and the authors propose a surface complex between platinum, chlorine, and a Lewis site. Chlorinated aluminas give strong interactions even with benzene, which has an ionization potential greater than platinum (*18*), so an interaction between the metal and electron acceptor sites is very possible.

On the other hand Aben *et al.* (*3*) found that the activity per exposed metal atom is independent of the support used for nickel, palladium, and platinum. It can be remarked that among the carriers used silica and alumina have no or low electron acceptor properties; silica–magnesia is known to be a weaker acid than silica–alumina, it is also a weaker oxidizing agent; among silica–aluminas it has been recognized that those containing 25% alumina have less acidity and oxidizing properties than those containing 13% alumina. The authors do not specify what kind of silica–alumina was used; in our opinion their data prove that the activity is independent of crystallite size but do not rule out any possibility of support effects, at least with the definition used here.

REFERENCES

1. GERMAIN, J. E., *Bull. Soc. Chim. Fr.* **1966, 22.**
2. SINFELT, J. H., *Amer. Inst. Chem. Eng.* **73,** vol. 63, 16, (1967).
3. ABEN, P. C., PLATTEEUW, J. C., AND STOUT-HAMER, B., *Int. Congr. Catal., 4th, Moscow, 1968,* prepr. no. 31.

4. POLTORAK, O. M., BORONIN, V. S., AND MITRO-
    FANOVA, A. N., *Int. Congr. Catal., 4th, Mos-
    cow, 1968*, prepr. no. 68.
5. BOUDART, M., ALDAG, A., BENSON, J. E., DOUG-
    HARTY, N. A., AND GIRVIN HARKINS, C., *J.
    Catal.* **6**, 92 (1966).
6. DORLING, T. A., AND MOSS, R. L., *J. Catal.* **7**,
    378 (1967).
7. (a) TAYLOR, W. F., YATES, D. J. C., AND SIN-
    FELT, J. H., *J. Phys. Chem.* **68**, 2962 (1964):
    (b) TAYLOR, W. F., YATES, D. J. C., AND
    SINFELT, J. H., *J. Catal.* **4**, 374 (1965).
8. DUBIEN, J., DE MOURGUES, L., AND TRAMBOUZE,
    Y., *Bull. Soc. Chim. Fr.*, **1967**, 114.
9. NICOLOVA, R., BARTHOMEUF, D., CHARCOSSET, H.,
    AND TRAMBOUZE, Y., *C. R. Acad. Sci. Ser. C*
    265, 468 (1967).
10. CHARCOSSET, H., BARTHOMEUF, D., NICOLOVA,
    R., REVILLON, A., TOURNAYAN, L., AND TRAM-
    BOUZE, Y., *Bull. Soc. Chim. Fr.* **1967**, 4555.
11. BARTHOMEUF, D., BALLIVET, D., DEVAUX, R., AND
    TRAMBOUZE, Y., *Bull. Soc. Chim. Fr.* **1967**,
    1435.
12. MENCIER, B., FIGUERAS, F., DE MOURGUES, L.,

AND TRAMBOUZE, Y., *J. Chim. Phys.* **66**, 171
    (1969).
13. OZAKI, A., NOZAKI, F., MARUYA, K., OGASAWARA,
    S., *J. Catal.* **7**, 234 (1967).
14. FIGUERAS, F., NOHL, A., DEMOURGUES, L., AND
    TRAMBOUZE, Y., to be published.
15. FLOCKHART, B. D., SCOTT, J. A. N., AND PINK,
    R. C., *Trans. Faraday Soc.* **62**, 730 (1966).
16. BROUWER, D. M., *J. Catal.* **1**, 372 (1962).
17. TURKEVICH, L., NOZAKI, F., AND STAMIRES, D.,
    Proc. Int. Congr. Catal., 3rd, 1964 **1965**, 586.
18. BASSET, J., NACCACHE, C., MATHIEU, M. V., AND
    PRETTRE, M., *J. Chim. Phys.* **66**, 1522 (1969).
19. GOBLE, A. G., AND LAWRENCE, P. A., *Proc. Int.
    Congr. Catal. 3rd, 1964* **1965**, 320.
20. SCHWAB, G. M., BLOCK, J., AND SCHULTZE, D.,
    Angew. Chem. **71**, 101 (1958).
21. MULLIKEN, R. S., *J. Amer. Chem. Soc.* **74**, 811
    (1952).
22. FLOCKHART, B. D., LEITH, I. R., AND PINK, R.
    C., *Trans. Faraday Soc.* **65**, 542 (1969).
23. FIGUERAS, F., MENCIER, B., BACAUD, R., AND
    URBAIN, H., *C. R. Acad. Sci. Ser. C* **270**,
    769 (1970).