Influence of Preparation Variables on the Activity and Selectivity of Pd/AlPO₄ Catalysts

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In this work we have studied the influence of various preparation variables on the activity and selectivity of Pd catalysts supported on aluminum orthophosphate in the liquid-phase reduction of benzylideneacetone with dihydrogen. Sodium tetrachloropalladiate, tetraamminepalladium(II) chloride, palladium(II) nitrate dihydrate, and palladium(II) acetylacetonate and acetate have been used as precursor salts. The catalysts have been obtained by calcination of the impregnated salts at 598 K and subsequent reduction either in a hydrogen stream or with α-phellandrene under reflux. The interaction between surface OH groups and strongly basic ligands gives rise to variable amounts of PdO upon calcination. The thermal decomposition of sodium tetrachloropalladiate and tetraamminepalladium(II) chloride yields palladium exclusively. Under our working conditions, the process is zero order in hydrogen pressure and benzylideneacetone concentration. Active sites of different coordination number are responsible for the competitive generation of 4-phenyl-2-butanone and 4-phenyl-2-butanol. © 1986 Academic Press, Inc.

INTRODUCTION

Silica and alumina, alone or combined (either with each other or with different metal oxides), are the most frequently used metal supports. The activity and selectivity exhibited by a metal catalyst in a given process are dependent on the nature of the metal, the preparation variables (*1, 2*), and the type of support used (*3, 4*). In most hydrogenation processes the support is not inert, its influence being exerted through the formation of new chemical species (*5*), modifications in the electron density of the metal particles (*6, 7*), cooperation in the adsorption of hydrogen via the "spillover effect" (*8*) or hindrance of the adsorption of reactants through steric effects (*6, 9*). The results obtained in many instances have been attributed to a different strong metal–support interaction (SMSI) (*10–13*). Aluminum orthophosphates gelled in various media are stable solids with large specific surfaces, are moderately acidic, and have been used as metal supports and applied to the reduction of different organic functions

(*14–16*), either with dihydrogen (*17*) or by hydrogen transfer (*18*), with excellent results. On the other hand, the reduction of palladium salts with various olefins (*19, 20*) is also well known.

We thought it interesting to study the activity and selectivity of the catalysts prepared by reduction of various precursor metal salts. This synthetic procedure offers some advantages over the classical reduction method: it requires fairly uncomplicated instrumentation and low temperatures, and the reductant is converted simultaneously to a product of interest (*p*-cymene). In this work we have studied the influence of several preparation variables on the activity and selectivity exhibited by Pd/AlPO₄ in benzylideneacetone reduction.

EXPERIMENTAL

Catalysts. The support used in this work ($S_{BET} = 156 \ m^2 \ g^{-1}$) was an aluminum orthophosphate gelled in an ammoniacal medium. Its synthesis and texture properties were described elsewhere (*21, 22*). The acidity of this support ($3.6 \times 10^{-4} \ eq \ g^{-1}$)

288

was assessed by a spectrophotometric method (23), using cyclohexylamine (pK_a = 10.60) as titrant.

We have used a series of Pd catalysts supported on the above-mentioned solid and obtained by impregnation from aqueous solutions of sodium tetrachloropalladiate and tetraamminepalladium(II) chloride, or from *N,N*-dimethylformamide (DMF) solutions of palladium(II) nitrate dihydrate, palladium(II) acetylacetonate, or palladium(II) acetate. In naming the systems, we have used the symbol of the metal, a subscript denoting the palladium content (percentage) and the letter M, N, O, P, or Q according to whether the precursor salt used was sodium tetrachloropalladiate, tetraamminepalladium chloride, Pd(II) nitrate dihydrate, Pd(II) acetylacetonate, or Pd(II) acetate, respectively.

The impregnated mass thus obtained was subject to three different processes:

—air calcination from 363 to 598 K raising the temperature linearly 1° min⁻¹, keeping the last temperature constant for 30 min;

—air calcination as above and, subsequently, cooling the solid and again subjecting it to the same thermal procedure while a hydrogen stream is passed at a flow rate of 60 ml min⁻¹.

—air calcination as above and chemical reduction with α-phellandrene [which is readily dehydrogenated to *p*-cymene and is capable of reducing Pd(II) to Pd(0)]. In this case, the process involves placing the solid together with the reductant under reflux with magnetic stirring in a silicone bath in order to keep the temperature constant. After 1 h, the mixture was cooled and the reduction liquids were wasted, the catalyst being washed with several ethanol portions and then dried at low pressure.

The theoretical metal loading of the synthesized systems agrees with that determined by atomic absorption with a variation less than 1%.

Differential scanning calorimetry (DSC) assays. To determine whether the Pd(II)

compounds used in the impregnation process underwent any decomposition because of the thermal treatment to which they had been subjected, DSC assays were carried out on the systems with 3% metal in a manner similar to that used for the calcination process. These experiments were performed on a Mettler DSC 20 apparatus.

Determination of metal surface. The metal particle size was determined by TEM for systems with a Pd loading less than 2%, and by X-ray diffraction for systems with higher loadings.

The metal surface was subsequently calculated assuming the spherical-particle model.

Transmission electron microscopy (TEM) measurements. TEM measurements were carried out on a Philips AM-300 instrument working at 100 kV. Samples were prepared by an extractive replica method, and metal size distribution was determined by counting 1400–3000 particles. The average diameter was obtained from the volume-to-surface ratio.

X-ray diffraction (XRD) measurements. The XRD analysis of aluminum orthophosphate shows this to be an amorphous solid. X-Ray diffractograms of the catalysts were recorded on a Philips 1130/00/60 apparatus, using the Cu$K\alpha$ radiation, with λ = 1.5418 Å. The half-peakwidth was calculated graphically, with an angle 2θ = 40.1° corresponding to the (111) plane of Pd, taking a value of 0.89 for constant K of the Debye–Scherrer equation (24). Both the (101) and the (002) reflections for PdO were detected at 2θ = 32.5° in some unreduced calcined samples.

Catalytic activity. Hydrogenation runs were carried out on a conventional low-pressure Gerhardt hydrogenator furnished with a pressure gauge which continuously monitors the hydrogen pressure in the reaction vessel. Reactions were accomplished in a 1.25 M solution (20 ml) at 300 K, under an initial hydrogen pressure of 5 bar. An amount of 0.1 g of catalyst, concentrations in the range 0.3–2.5 M, pressures between

Catalyst	S_{met} $(m^2 \ g_{Pd}^{-1})$	$10^3 \ r_m$ $(mol \ s^{-1} \ g_{Pd}^{-1})$
$Pd_{0.5}Q$	176	5.8
Pd_1Q	160	8.3
Pd_2Q	149	9.0
Pd_3Q	143	6.0
Pd_5Q	105	6.0
Pd/C (10%)[a]	63	10.4

Note. $C = 1.25 \ M$, $P_{iH_2} = 5$ bar, $T = 300$ K, $g_{Pd} = 3 \times 10^{-3}$, V_T: 20 ml, S_{met} = metal surface, r_m = catalytic activity (per g).

[a] Commercial catalyst (Merck Reference 75990).

3 and 6 bar, and temperatures from 290 to 320 K were used in the study of the kinetics of the process. The reaction temperature was controlled by pumping water from a thermostatic bath through the vessel jacket.

The reaction rate was calculated by taking the initial slope of the plot of the decrease in the hydrogen pressure vs time. Blank tests were performed prior to obtaining kinetic data to check the absence of phenomena other than those inherent in the catalytic process. Neither the support nor any other part of the reactor used proved to be active in the reduction of benzylideneacetone. No diffusion phenomena were observed with shaking at a rate of over 200 shakes min^{-1}, and no interparticle diffusion occurred while working with catalyst sifted through 70–230 mesh.

The rate of hydrogen transfer from the gas phase to the reaction medium was shown not to be the rate-determining step of the process. Under our working conditions, we have shown that the initial rate of reaction increases linearly with the amount of catalyst used.

Product analysis. The reaction products were analyzed by using a Hewlett–Packard 5830A chromatograph fitted with a H-P 18850 GC terminal. The column was packed with 5% Carbowax 20M on 80/100 Chromosorb G-AWDMCS. The nature of

the products was confirmed by coupling the GC apparatus to a Hewlett–Packard 5992B mass spectrometer.

RESULTS AND DISCUSSION

We have synthesized a series of catalysts of different metal loading by impregnation with palladium(II) acetate and assessed their activity in the liquid-phase hydrogenation of benzylideneacetone. The results obtained are listed in Table 1. The maximum metal surface corresponds to a catalyst containing 0.5% Pd in weight, although the highest catalytic activity (per gram) corresponds to a catalyst with 2% Pd in weight. A metal loading of 3% was chosen for the synthesis of the remaining catalysts since, although these do not yield the best catalytic activity values, they do have a suitable amount of metal to facilitate determination of the metal particle size by X-ray diffraction and to be subject to DSC assays. All determinations of metal particle size were carried out by X-ray diffraction, except for catalysts with metal loadings less than 2% in weight, which were assessed by transmission electron microscopy.

The classical procedures for determination of metal particle size (CO adsorption, XRD, and TEM) are somewhat controversial as different authors use divergent correction factors (25–27). In our case, we have found good consistency among the results obtained with the three methods assuming the spherical-particle model and a CO adsorption factor of 1.15 (28).

Kinetic assays for benzylideneacetone reduction were performed on catalyst Pd_3Q in the absence of diffusion phenomena.

Figure 1 shows that the transfer of hydrogen from the gas phase to the catalyst is much higher than any of the initial reaction rates obtained; thus, the occurrence of diffusion phenomena can definitely be ruled out. Likewise, we have checked (by means of blank tests) that no part of the reactor takes part in the catalytic process.

The process conforms to a rate law of the type
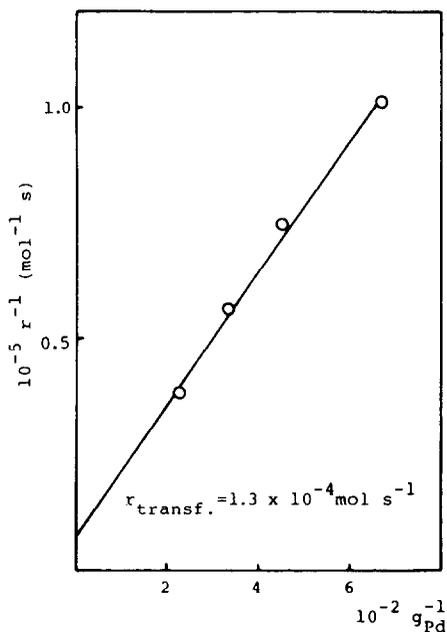
FIG. 1. Hydrogen transfer rate.

$$v = K(g_{cat})$$

i.e., zeroth order in hydrogen pressure and benzylideneacetone concentration, over the pressure range 2–6 bar for the former and the concentration range 3×10^{-1} to 2.5

M for the latter. An apparent activation energy of 9.1 kcal mol^{-1} is inferred from the Arrhenius plot (Fig. 2).

In Fig. 3 are listed the results obtained in the DSC assays of synthesized catalysts. The heating gradient was applied in a manner similar to that used for synthesis of the catalysts labeled "calcined." All Pd(II)-supported salts undergo decomposition at temperatures above 598 K (sodium tetrachloropalladiate shows a thermal signal at 583 K). As a rule, all salts containing the Pd–O bonds decompose at temperatures lower than those for salts bearing Pd–N or Pd–Cl bonds. Complexes of the type K$_2$(PdX$_4$) are relatively stable as compared to other Pd(II) compounds, the Pd–X bond having an estimated 40% covalent character (29).

The decomposition products of the impregnated salts were characterized by X-ray monitoring (Fig. 4). All the salts used yielded metal Pd on decomposition, as shown in the diffraction patterns for the catalysts subject to calcination only. No other species were detected in the case of sodium tetrachloropalladiate, tetraammine-palladium(II) chloride, and Pd(II) nitrate.
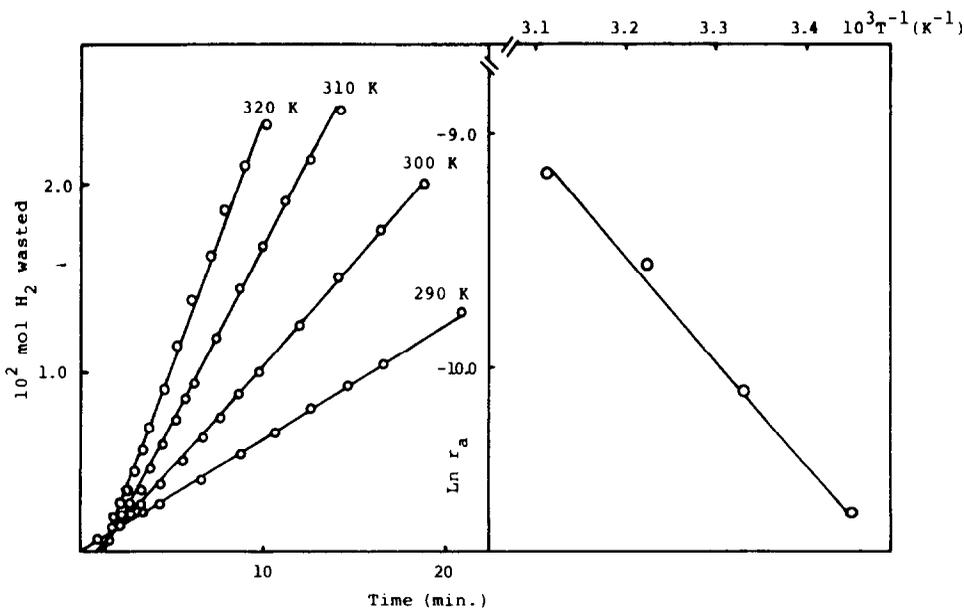
FIG. 2. Initial rates and Arrhenius plot.

ALBA ET AL.
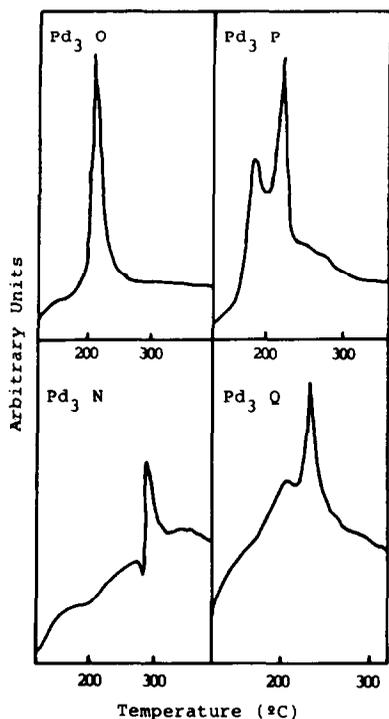
FIG. 3. DSC of the impregnated systems.

On the other hand, some PdO was also detected for palladium(II) acetate and acetylacetonate.

Several adsorbed species have been assumed to result from the interaction between some Pd(II) complexes and the surface OH groups in silica or alumina (30). In the synthesis of Pd catalysts on silica by impregnation from $Pd(NH_3)_4Cl_2$, species such as $Pd(NH_3)_2(SiO)_2$ may be generated through interaction with surface silanol groups in which Pd(II) preserves square coordination. A similar type of interaction has been described for catalysts prepared by impregnation from Pd(II) acetylacetonate on alumina (31).

The strength of this type of interaction must be related to the number and acidic strength of surface OH groups, as well as to the nature of the counterion or ligand bound to the metal atom which undergoes substitution. Aluminum orthophosphate is moderately acidic (3×10^{-4} eq g^{-1} vs cyclohexylamine). Therefore, its surface protons

will only be reactive toward strong bases such as acetate or acetylacetonate, giving rise to surface Pd–O bonds. Thermal decomposition of the surface species would yield PdO. The excess of impregnating salt added (3.3×10^{-3} mol) to obtain a metal loading of 3%, which does not interact with the hydroxyl groups of the support, would yield metal Pd. The great strength of Pd–N and Pd–Cl bonds, together with the low basicity of the nitrate anion, does not favor, in our case, the interaction with surface OH groups. Thermal decomposition of the impregnated salts would yield—at least partly—metal Pd (32).

In Table 2 are listed the metal surface values of the catalysts synthesized from the different Pd(II) salts, which show the influ-
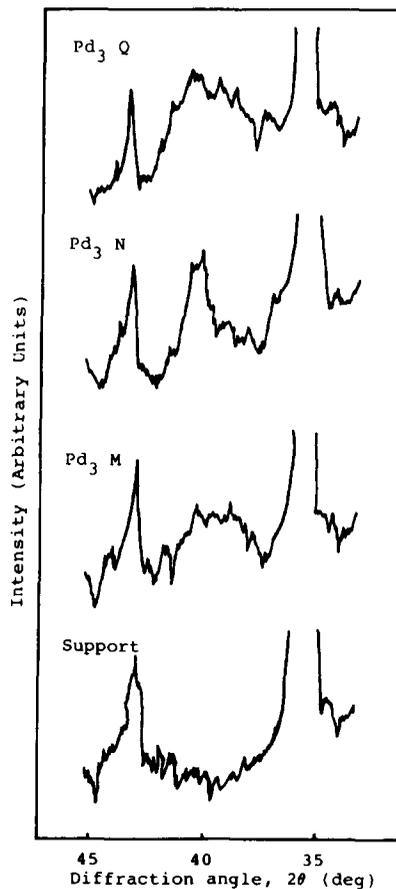
FIG. 4. X-Ray diffractograms of the support and some calcined samples.

TABLE 2

Metal Surfaces (m^2 g$_{Pd}^{-1}$) for Various Catalysts as a Function of the Reduction Treatment Used

Catalyst	Calcined	Calcined and reduced with H$_2$	Calcined and reduced with α-phellandrene
Pd$_3$M	69	36	64
Pd$_3$N	72	30	67
Pd$_3$O	148	71	139
Pd$_3$P	150	99	161
Pd$_3$Q	146	129	143

ence of the type of reduction procedure followed after calcination on the metal surface.

The metal surface of the catalysts "activated" with α-phellandrene under reflux does not change in any case; however, those reduced in a hydrogen flow have a drastically decreased metal surface as a rule. The results obtained cannot be accounted for by considering a higher or lower degree of reduction of the deposited species. On the other hand, Boudart (33) found no changes in particle size after subjecting small Pd particles deposited on silica to alternating oxidations and reductions. Reduction with α-phellandrene is carried out in liquid phase at 453 K, whereas that involving the use of hydrogen is performed in a flowing system at 598 K. These last conditions favor the mobility of

the particles, which can regroup to form larger crystals (34).

Catalytic Activity Tests

The catalysts subjected to different reduction treatments were tested on the reduction of benzylideneacetone in methanol, at an initial hydrogen pressure of 5 bar. The results are given in Table 3. Divergent conclusions can be drawn from these results depending on whether specific reaction rates, catalytic activities (per g), or specific catalytic activities (per m^2) are compared.

The specific reaction rate is higher for reduced catalysts, especially for those treated with α-phellandrene. Thus, such a treatment seems to result in more active catalysts than calcination or reduction with hydrogen. A further advantage of this treatment over that of the reduction with hydrogen lies in its simplicity and economy.

However, different conclusions can be drawn by comparing the results for specific reaction rate. Thus, the reduction of benzylideneacetone can be classified as structure sensitive (35) or structure insensitive, depending on whether catalysts only subjected to calcination or catalysts subjected to calcination and reduced with hydrogen or α-phellandrene, respectively are used. Therefore, the fraction of metal atoms with

TABLE 3

Influence of the Procedure Followed to Reduce the Catalysts on the Hydrogenation of Benzylideneacetone

Catalyst	Calcined		Calcined and reduced with H$_2$		Calcined and reduced with α-phellandrene	
	$10^5\ r_a$ (mol^{-1} m$_{Pd}^{-2}$)	$10^3\ r_m$ (mol^{-1} g$_{Pd}^{-1}$)	$10^5\ r_a$ (mol^{-1} m$_{Pd}^{-2}$)	$10^3\ r_m$ (mol^{-1} g$_{Pd}^{-1}$)	$10^5\ r_a$ (mol^{-1} m$_{Pd}^{-2}$)	$10^3\ r_m$ (mol^{-1} g$_{Pd}^{-1}$)
Pd$_3$M	2.4	1.6	7.5	2.7	4.5	2.9
Pd$_3$N	2.3	1.7	6.6	2.0	3.5	2.3
Pd$_3$O	2.3	3.5	5.9	4.2	3.8	5.2
Pd$_3$P	2.2	3.4	5.4	5.3	5.2	8.3
Pd$_3$Q	2.4	3.5	2.7	3.5	4.2	6.0

Note. $C = 1.25\ M$, $P_{iH_2} = 5$ bar, $T = 300$ K, $g_{Pd} = 3 \times 10^{-3}$, $V_T = 20$ ml, $r_a =$ specific catalytic activity (per m^2), $r_m =$ catalytic activity (per g).

TABLE 4

Selectivity (%) toward 4-Phenyl-2-butanol
after a 2-h Reaction

Catalyst	Calcined	Calcined and reduced with H_2	Calcined and reduced with α-phellandrene
Pd₃M[a]	16.6	6.2	9.5
Pd₃N	8.0	3.1	1.0
Pd₃O	10.4	6.0	6.4
Pd₃P	4.4	2.3	1.0
Pd₃Q	6.4	5.4	1.8

Note. $C = 1.25\ M$, $P_{iH_2} = 5$ bar, $T = 300$ K, $g_{Pd} = 3 \times 10^{-3}$, $V_T = 20$ ml, overall conversion = 100%.

[a] n-Butylbenzene traces begin to appear when the selectivity toward 4-phenyl-2-butanol exceeds 6%.

different coordination number seems to be a more realistic criterion than the dispersion of the crystallite size to define the activity or selectivity of a catalyst (36).

We have studied the selectivity toward 4-phenyl-2-butanol yielded in the reduction of benzylideneacetone with the synthesized catalysts. The results obtained are presented in Table 4. This compound originates directly from benzylideneacetone rather than from the 4-phenyl-2-butanone also yielded.

Reduction of the olefinic double bond in the hydrogenation of 4-phenyl-2-butanone under the same conditions used for the reduction of benzylideneacetone does not yield 4-phenyl-2-butanol, even after 8 h reaction. By adding the reactant after the benzylideneacetone has been completely reduced, the ratio of 4-phenyl-2-butanol in the final mixture is increased: under our working conditions, 4-phenyl-2-butanol and 4-phenyl-2-butanone originate at different

active sites of the catalyst. These activity and selectivity results cannot be accounted for on the basis of a different metal–support interaction as observed in some Ni/AlPO₄ systems (37). On the other hand, this effect would be compensated as the same support was used for all the catalysts. The alcohol and ketone appear to originate at different active sites.

We may think that the metal surface is not homogeneous, containing at least two different—geometric and energetic—types of active sites (38). Each type of site would take part in the one-step reduction of benzylideneacetone to 4-phenyl-2-butanone or 4-phenyl-2-butanol, respectively. The results obtained can be accounted for on the basis of Scheme 1.

The hydrogenation to the alcohol or ketone takes place in one step at a particular type of active site onto which benzylideneacetone has been initially adsorbed. Once 4-phenyl-2-butanone has been generated, this is not readsorbed by the catalyst for further hydrogenation. The different selectivity exhibited by the catalysts is related to the presence of different populations of active sites, which in turn is a function of the synthetic variables used (precursor salt, thermal treatment, prereductant, etc.).

We have been unable to determine the nature of each of the different types of sites proposed, although, according to Scheme 1, they must differ in coordination and steric requirements since they originate in different zones in the crystal (irregularities, faces, edges) according to the particular synthetic procedure followed (39, 40).
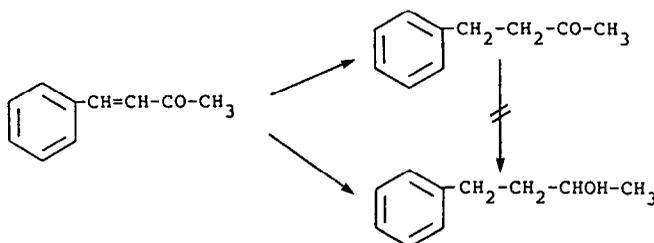
Scheme 1

REFERENCES

1. Rylander, P. N., "Catalytic Hydrogenation in Organic Synthesis." Academic Press, New York, 1979.
2. Freifelder, M., "Catalytic Hydrogenation in Organic Synthesis. Procedures and Commentary." Wiley, New York, 1978.
3. Moss, R. L., Pope, D., Davis, B. J., and Edwards, D. H., *J. Catal.* **58**, 206 (1979).
4. Gallezot, P., Datka, J., Massardier, J., Primet, M., and Imelik, B., *in* "Proceedings, VIth International Congress on Catalysis," Vol. 2, p. 696. Chem. Soc., London, 1977.
5. Fleisch, T. H., Hicks, R. F., and Bell, A. T., *J. Catal.* **87**, 398 (1984).
6. Schwarb, G. M., *Adv. Catal.* **27**, 1 (1978).
7. Dalla-Betta, R. A., and Boudart, M., *in* "Proceedings, Vth International Congress on Catalysis, Miami Beach, 1972," p. 1329.
8. Neikan, W. C., and Vannice, M. A., *in* "Proceedings, Vth International Congress on Catalysis, Miami Beach, 1972," p. 609.
9. Campelo, J. M., García, A., Luna, D., and Marinas, J. M., *Appl. Catal.* **10**, 1 (1984).
10. Vannice, M. A., and Garten, R. L., *J. Catal.* **63**, 255 (1980).
11. Campelo, J. M., García, A., Gutiérrez, J. M., Luna, D., and Marinas, J. M., *Appl. Catal.* **7**, 307 (1983).
12. Tanster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100**, 170 (1978).
13. Imelik, B., Naccache, C., Coudurier, G., Praliaud, H., Mériaudeau, P., Gallezot, P., Martin, G. A., and Védrine, J. C. (Eds.) "Metal-Support and Metal-Additive Effects in Catalysis." Elsevier, New York, 1982.
14. Pery, I. B., *Discuss. Faraday. Soc.* **52**, 55 (1971).
15. Moffat, I. B., *in* "Topics in Phosphorus Chemistry" (G. Griffith, Ed.). Interscience, New York, 1980.
16. Marcelin, G., Vogel, R. F., and Swift, H. E., *J. Catal.* **83**, 42 (1983).
17. Aramendía, M. A., Borau, V., Jiménez, C., and Marinas, J. M., *Bull. Soc. Chim. Belg.* **91**, 743 (1982).
18. Aramendía, M. A., Borau, V., Jiménez, C., Marinas, J. M., and Pajares, J. A., *J. Catal.* **78**, 188 (1982).
19. Livingstone, S. E., "The Chemistry of Ruthenium, Rhodium, Palladium, Osmium, Iridium and Platinum." Pergamon, London, 1973.
20. Gorewit, B., and Tsutsui, M., *Adv. Catal.* **27**, 227 (1978).
21. Jiménez, C., Marinas, J. M., Pérez-Ossorio, R., and Sinisterra, J. V., *An. Quim.* **73**, 1164 (1977).
22. Jiménez, C., Marinas, J. M., Sinisterra, J. V., and Borau, V., *An. Quim.* **73**, 561 (1977).
23. Marinas, J. M., Jiménez, C., Campelo, J. M., Aramendía, M. A., Borau, V., and Luna, D., *in* "Proceedings, VIIth Iberian–American Symposium on Catalysis, 1980," Vol. 1, p. 79.
24. Moss, R. L., "Experimental Methods in Catalytic Research" (R. B. Anderson and P. T. Dawson, Eds.), Vol. 2, p. 43. Academic Press, New York, 1976.
25. Farrauto, R., *AIChE Symp. Ser.* **70**, 9 (1974).
26. Mallat, T., and Petro, J., *React. Kinet. Catal. Lett.* **11**, 307 (1979).
27. Mustard, D. G., and Bartholomew, C. H., *J. Catal.* **67**, 186 (1981).
28. Aramendía, M. A., Borau, V., Gómez, M. C., Jiménez, C., and Marinas, J. M., *Appl. Catal.* **8**, 177 (1983).
29. Martell, A. E., and Sillén, L. G., "Stability Constants of Metal–Ion Complexes," Chem. Soc. Spec. Pub. No. 17 (1964).
30. Gubitosa, G., Berton, A., Camia, M., and Pernicone, N., "Preparation of Catalysts. III," p. 431. Elsevier, Amsterdam, 1983.
31. Boitieaux, J. P., Cosyns, J., and Vasudevan, S., "Preparation of Catalysts. III," p. 123. Elsevier, Amsterdam, 1983.
32. Farran, R., and House, J. E., Jr., *J. Inorg. Nucl. Chem.* **34**, 2219 (1972).
33. Lam, Y. L., and Boudart, M., *J. Catal.* **47**, 303 (1977).
34. Domrachey, G. A., Varyukhin, V. A., and Nesterov, B. A., *React. Kinet. Catal. Lett.* **22**, 281 (1983).
35. Boudart, M., and Djéga-Mariadassou, G., "La cinétique des réactions en catalyse hétérogène." Masson, Paris, 1982.
36. Corma, A., Martin, M. A., and Pérez, J., *J. Chem. Soc. Chem. Commun.*, 1512 (1983).
37. Marcelin, G., and Vogel, R. F., *J. Catal.* **82**, 482 (1983).
38. Somorjai, G. A., *Adv. Catal.* **26**, 1 (1977).
39. Burton, J. J., *Catal. Rev.* **9**, 209 (1974).
40. Gallezot, P., *Surf. Sci.* **106**, 459 (1981).