JOURNAL OF CATALYSIS **102,** 21–28 (1986)

Effect of Presulfurization on the Formation of Coke on Supported Metal Catalysts

J. BARBIER AND P. MARECOT

Faculté des Sciences de Poitiers, U.A. CNRS 350, 40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France

Received February 1, 1985; revised December 16, 1985

Presulfurization of Pt/Al_2O_3, Ir/Al_2O_3, and $Pt\text{-}Ir/Al_2O_3$ catalysts induces an increase in the amount of coke deposited during decomposition of cyclopentane. There is strong indication that such an increase could be the consequence of a higher production of olefinic compounds whose polymerization on the acidic sites of the alumina results in extensive coke deposition on the support. In the opposite sense is the observation that sulfur is able to inhibit the autodeactivation of the metal, which is thus protected from the coking reaction. Such a feature could explain the greater stability observed on sulfided reforming catalysts.

INTRODUCTION

Naphtha reforming catalysts are usually sulfided. In spite of the poisoning effect, addition of small quantities of sulfur improves the behavior of the catalysts, increases their stability and favors their start-up (*1–3*).

Sulfur, through its adsorption, can block a fraction of the metallic surface which then becomes inaccessible to catalytic reaction. As a result, the activity of supported platinum for such reactions as hydrogenation of benzene, exchange of benzene with deuterium and hydrogenolysis of cyclopentane are lowered by sulfidation of the platinum. Nevertheless, selectivities for exchange related to hydrogenation, and for hydrogenation related to hydrogenolysis are significantly enhanced (*4, 5*). The reason why sulfidation improves the behavior of industrial catalysts can probably be explained by the high toxicity of sulfur for hydrogenolysis reactions.

On the other hand, coke deposited during hydrocarbon reactions is also a selective poison. In previous work, we have already shown that the toxicity of coke (defined as the number of accessible platinum atoms deactivated by one atom of carbon) was 2.5 for cyclopentane hydrogenolysis, 0.6 for benzene hydrogenation, and 0 for exchange of benzene with deuterium (*7*).

The selective poisoning by coke or sulfur can be accounted for by the heterogeneous surface of the catalysts (*8*). Therefore, just as some reactions are structure sensitive and occur only on a fraction of the metallic surface area (e.g., hydrogenolysis of cyclopentane or exchange of benzene with deuterium) (*4, 9, 10*), poisoning can be selective if the poison is adsorbed on particular catalytic sites. This is why the catalytic activity of reactions occurring on such sites is strongly lowered by adsorption of the poison under consideration. From the comparable selective effect of coke and sulfur, it can be inferred that sulfur adsorption and coke formation occur preferentially on hydrogenolysis sites, avoiding exchange sites. In agreement with this hypothesis, Lankhorst *et al.* (*11*) showed that treating silica-supported Pt catalyst at 450°C with a hydrocarbon/hydrogen mixture resulted in much more severe deactivation for the samples containing larger particles than for those containing smaller particles. Engels *et al.* (*12*) have also proved that highly dispersed platinum catalysts are less sensitive to coke formation. Then, in a recent work

0021-9517/86 $3.00

(*13*), we have pointed out that both the reactions of coke formation by cyclopentane injection and of hydrogenolysis of cyclopentane have exactly the same structure sensitivity. This is why in the case of Pt supported on alumina increasing crystallite size leads to enhanced catalytic activity for both hydrogenolysis of cyclopentane and coking (*10*). As a consequence, sulfur, on account of its important toxicity for cyclopentane hydrogenolysis, has to be adsorbed on large platinum particles. This hypothesis also accounts for the greater sulfur resistance observed with the small particles of Rh (*14*) and Pt (*15*). According to Gallezot *et al.* (*15*) this is due to the electronic properties of these small particles, which differ from those of bulk metal. Therefore, when the size of the crystallites is decreased, transfer from metal to support causes an electron-deficient character to appear on the metal. The deficiency in electrons could explain the reduced aptitude of the small platinum particles for adsorbing an acceptor compound such as sulfur.

Thus, coke formation, hydrogenolysis of cyclopentane, and sulfur adsorption reactions probably take place on the same metallic reactive sites. From these observations it follows that presulfurization of catalysts should decrease the extent of the coking reaction, thereby resulting in a greater stability as observed on sulfided reforming catalysts. The present study was undertaken to investigate whether sulfur is able to inhibit coke formation on Pt/alumina and Pt-Ir/alumina supported catalysts. We have also studied the influence of the nature of the support, the influence of the metallic accessibility and the influence of the composition of bimetallic Pt-Ir catalysts on the changes of coking rates affected by sulfurization of all the catalysts. The coking agent employed was cyclopentane and the products of decomposition of this hydrocarbon during the coking reaction at 430°C were analyzed by gas chromatography. Then, in order to study the effect of sulfur on the accumulation of carbonaceous deposits on platinum, some experiments were carried out on platinum black, without any support.

EXPERIMENTAL

The supported metallic catalysts (Pt, Ir, and Pt-Ir) were made by impregnation of two high-purity γ-Al_2O_3 powders (Al_2O_3 Degussa oxide C 100 m^2/g (low acidity) and Al_2O_3 GFS 400 Rhone Poulenc 210 m^2/g (high acidity) with aqueous solutions of chloroplatinic and chloroiridic acids in the appropriate concentrations to give catalysts of different metal loading (Pt/Al_2O_3 and Ir/Al_2O_3) or various atomic percent [Ir/(Ir + Pt) ranging from 0 to 100]. HCl was added in order to obtain a constant chlorine content. After impregnation the catalysts were dried overnight at 100°C, then calcined under an air stream for 8 h at 500°C, and finally reduced under flowing hydrogen for 8 h at 500°C. The platinum black catalyst was prepared by alkaline fusing according to Adams *et al.* (*16*).

Dispersion values were determined with a gas volumetric system. A vacuum in the system of 10^{-6} Torr was created with a turbomolecular pump. Prereduced samples were reduced again for 2 h at 500°C, then outgassed at this temperature and cooled to 25°C. Metal accessibilities were obtained by H_2 chemisorption, O_2 chemisorption, and H_2–O_2 titration (*17*).

The catalysts were sulfided at 500°C for 90 min under a flow of H_2S and H_2 with a H_2S/H_2 volume ratio of 5/100 and a flow rate of 60 $cm^3\ min^{-1}\ (g \cdot cat.)^{-1}$. After sulfidation the samples were treated with flowing hydrogen for 8 h at 500°C. Under such experimental conditions we have previously shown (*5*) that the sulfur coverage (θ_S = S/acc. metal) is almost 0.5, and can vary slightly with the nature of the support and the nature of the metal (*6*).

The coking reaction was carried out at atmospheric pressure in a classical flow reactor; 1 g of the prereduced catalyst was reduced again under flowing hydrogen at 500°C for 2 h and cooled to 430°C for 1 h.

TABLE 1

Catalyst Characteristics

Catalysts	Al_2O_3	Metal loading (%)	Cl (%)	Dispersion (%)	$\bar{d}$ (Å)
Pt/Al_2O_3 G_1	GFS	0.56	1.3	47	18
G_2	GFS	0.56	1.2	22	38
G_3	GFS	0.56	1.5	12	71
Pt/Al_2O_3 D_7	Degussa	0.56	0.6	56	15
D_9	Degussa	1.85	1.1	57	15
D_1	Degussa	5.45	1.2	29	29
D_{10}	Degussa	10.1	1.1	11.3	75
D_4	Degussa	10.9	1.0	7.9	107
Ir/Al_2O_3 I_4	Degussa	0.56	0.9	71	11
I_1	Degussa	1.01	1.0	66	12
I_5	Degussa	1.52	1.2	67	12
I_2	Degussa	1.20	0.9	40	20
I_3	Degussa	1.04	0.7	15	52
$Pt\text{-}Ir/Al_2O_3$					
(72-28)	Degussa	Pt + Ir = 1.58	1.1	63	13
(51-49)	Degussa	Pt + Ir = 1.72	1.1	65	13
(39-61)	Degussa	Pt + Ir = 1.53	1.1	60	14

Cyclopentane (Fluka purum) was employed as reactant and was introduced at 2 cm^3/h into the gas flow with $P_{C_5H_{10}} = 0.3$ atm and $P_{H_2} = 0.7$ atm.

In the case of sulfided catalysts, coking and sulfurization were carried out in the same reactor without exposure to air of the catalyst.

Analysis of coke deposition was made by temperature-programmed oxidation (*19*), with the temperature increasing from 25 to 550°C at the rate of 13°C min^{-1}. Analysis of the CO_2 produced was carried out at intervals of 1 min by gas chromatography.

RESULTS

I. Effect of Presulfurization on the Formation of Coke on Metallic Supported Catalysts

Different Pt/Al_2O_3 and Ir/Al_2O_3 monometallic catalysts and $Pt\text{-}Ir/Al_2O_3$ bimetallic catalysts were coked by the cyclopentane reaction for 60 min. The characteristics of these catalysts are summarized in Table 1.

1. Pt/Al_2O_3. Table 2 allows a comparison to be made between the amount of coke deposited on the sulfided catalysts (C_s) and the nonsulfided ones (C_n). It is worth noting that in all cases coking is more extensive on sulfided catalysts.

Furthermore, the change in coke deposition is not affected by metallic accessibility, since the C_s/C_n ratio is almost constant whatever the dispersion. However, when considering the two Pt/Al_2O_3 series it can be noticed that:

(i) C_n for the high acidity, high surface

TABLE 2

Comparison of Coking Extents on Sulfided and Nonsulfided Pt/Al_2O_3 Catalysts

Catalysts	$\bar{d}$ (Å)	θ_S	C_n = %C (nonsulfided catalyst)	C_s = %C (sulfided catalyst)	C_s/C_n
G_1	18	0.51	0.95	1.20	1.26
G_2	38	0.81	0.63	0.83	1.32
G_3	71	0.83	0.34	0.44	1.29
D_7	15	0.45	0.62	0.97	1.56
D_9	15	0.53	1.80	2.80	1.55
D_1	29	0.41	1.25	2.01	1.61
D_{10}	75	0.49	0.86	1.39	1.62
D_4	107	0.51	0.78	1.32	1.69

TABLE 3

Comparison of Coking Extents on Sulfided and Nonsulfided Ir/Al_2O_3 Catalysts

Catalysts	$\bar{d}$ (Å)	θ_S	C_n = %C (nonsulfided catalyst)	C_s = %C (sulfided catalyst)	C_s/C_n
I_4	11	0.91	0.14	0.45	3.21
I_1	12	0.84	0.25	0.71	2.84
I_5	12	0.88	0.34	0.93	2.73
I_2	20	0.64	0.15	0.45	3.00
I_3	52	0.58	0.10	0.28	2.80

area support is only 50% higher than C_n for the low area, low acidity support for the same metal loading and dispersion (G_1 and D_7). This result can be explained by assuming that metal produces coke precursors which can be polymerized on the acidic sites of the support. At low working time (1 h), the amount of coke is comparable on both Degussa and GFS aluminas. However, at higher working time (10 h), we have shown that the coke content on catalyst D_7 (Pt/Al_2O_3 Degussa) is 1.1% while on catalyst G_1 (Pt/Al_2O_3 GFS) the coke content is 4.1%.

(ii) The nature of the support plays a prominent part in the C_s/C_n ratio which is lower on GFS alumina than on Degussa alumina.

2. Ir/Al_2O_3. Iridium catalysts supported on Degussa Al_2O_3 were coked in the experimental conditions previously described. The C_s/C_n ratios, collected in Table 3, point to an important effect of the sulfurization on the coking of Ir/Al_2O_3 catalysts.

3. Pt-Ir/Al_2O_3. Some Pt-Ir/Al_2O_3 catalysts were coked by cyclopentane injection. The same experiments were also carried out on presulfurized catalysts. Table 4 shows that the amount of coke deposited on the whole catalyst decreases from pure platinum to pure iridium supported catalysts. Moreover, sulfurization induces an increase in coke level which is more important on iridium than on platinum and the C_s/C_n ratio varies monotonically from pure platinum to pure iridium. In parallel with this, θ_S, measured in a previous work (*6*), increases monotonically from pure platinum to pure iridium.

II. Effect of Catalyst Presulfurization on Selectivity in the Transformation of Cyclopentane during the Coking Reaction

In previous work (*20, 21*) it was pointed out that the amount of coke deposited during the reaction of cyclopentane is always proportional to the activity in dehydrogenation yielding cyclopentadiene. In this work our interest has turned to the study of the effect of catalyst presulfurization on the activity for cyclopentane disappearance, and *n*-pentane, cyclopentene, and cyclopentadiene formation. Table 5 summarizes the results obtained on some samples of catalysts. It is worth mentioning that on all catalysts, presulfurization induces an important lowering in hydrogenolysis activities when concentrations in dehydrogenation products are increased; this is very much the case for catalysts supported on Degussa alumina.

III. Effect of Presulfurization on the Deposition of Coke on the Metal of Pure Metallic or Supported Metallic Catalysts

In previous work it has been proved that coke deposited on the metal is oxidizable at

TABLE 4

Comparison of Coking Extents on Sulfided and Nonsulfided Bimetallic Pt-Ir/Al_2O_3 Catalysts

Catalysts	θ_S	C_n = %C (nonsulfided catalyst)	C_s = %C (sulfided catalyst)	C_s/C_n
Pt/Al_2O_3 (D_9)	0.53	1.80	2.80	1.55
Pt-Ir/Al_2O_3 (72-28)	0.63	1.30	2.18	1.68
Pt-Ir/Al_2O_3 (51-49)	0.68	0.91	1.56	1.71
Pt-Ir/Al_2O_3 (39-61)	0.75	0.56	1.08	1.93
Ir/Al_2O_3 (I_5)	0.84	0.34	0.93	2.73

TABLE 5

Effect of Catalyst Presulfurization on the Activity in Cyclopentane Transformation

Catalyst	Coking extent	Composition of the gas phase (%)				
		Cyclopentane	*n*-Pentane	Cyclopentene	Cyclopentadiene	Light hydrocarbons
D_4 (1.0 g)	0.78	58.82	24.63	3.81	0.30	12.44
D_4 sulfided (1.0 g)	1.32	88.84	4.03	5.43	0.61	1.09
I_1 (1.0 g)	0.25	74.06	4.49	2.85	0.20	18.40
I_1 sulfided (1.0 g)	0.71	70.87	16.37	4.30	0.43	8.03
I_5 (1.0 g)	0.34	69.79	4.02	2.34	0.25	23.6
I_5 sulfided (1.0 g)	0.93	61.32	23.84	3.96	0.41	10.47

a lower temperature than is required to oxidize coke deposited on the support (*7,13*). In Table 6 are collected the amounts of coke oxidizable at 300°C on some sulfided and nonsulfided catalyst samples which have been coked for 60 min by the cyclopentane reaction. The systematic lowering for sulfided catalysts clearly demonstrates that the coverage of the metal by coke is decreased by sulfurization when coke accumulation on the whole catalyst is increased.

To provide direct evidence that sulfided platinum is less sensitive to coke formation than pure metal, a study of the effect of presulfurization was carried out on platinum black. In order to increase the accuracy of analysis, these experiments were made at 400°C without hydrogen in the cyclopentane flow.

Table 7 shows that coke deposition on platinum is markedly inhibited by sulfurization of the metal, and Table 8 lists the amounts of coke deposited on alumina when in a mechanical mixture with platinum black during the coking reaction by cyclopentane. The results clearly show that coke deposition is enhanced when platinum is sulfided.

Finally, the neutralization by KOH of the acidic sites of alumina is able to decrease the amount of the coke deposited on this support by more than 90% (*21*). Thus, when Pt/Al_2O_3 catalysts are treated with KOH, the coke accumulated on this catalyst is essentially deposited on the metal. One sample of Pt/Al_2O_3 catalyst was thus neutralized by KOH at 5% in aqueous solution. One part of this catalyst was coked by cyclopentane while a second part was sulfided before coking. The results, given in Table 9, bring additional proof that sulfurization of metal inhibits coke deposition on this metal.

TABLE 6

Effect of Catalyst Presulfurization on the Amount of Coke Oxidizable at 300°C

Catalysts	at. C/(g cat.) × 10^{19}
D_1	3.70
D_2 sulfided	3.17
D_4	3.97
D_4 sulfided	3.27
G_1	2.90
G_1 sulfided	2.17

TABLE 7

Effect of Catalyst Presulfurization on the Amount of Coke Deposited on Platinum Black

Catalysts	θ_s	at. C/(g cat.) × 10^{19}
Pt black nonsulfided (S = 2 m^2/g)	0	1.53
Pt black sulfided	1.1	0.90

TABLE 8

Effect of Metal Presulfurization on the Amount of Coke Deposited on the Alumina

Catalysts	at. C/(g Al_2O_3) × 10^{19}
Al_2O_3 Degussa with nonsulfided Pt black	1.00
Al_2O_3 Degussa with sulfided platinum black	1.67

DISCUSSION

In previous work performed on sulfided Pt/Al_2O_3, Ir/Al_2O_3, or $Pt\text{-}Ir/Al_2O_3$ catalysts, Menon and Prasad (*22*), Apesteguia *et al.* (*5, 23, 24*), and Barbier *et al.* (*6*) pointed out that treatment at 500°C in a H_2 atmosphere induces only partial removal of the adsorbed sulfur. They noted that the remaining sulfur is localized on the metal. This resulting strong or "irreversible" sulfur will be present on the reforming catalysts and, according to Engle (*25*) and Haensel (*26*) it is able to prolong the life of these catalysts. Hayes *et al.* (*27*) suggested that essentially all the platinum interacts with sulfur to form a platinum–sulfur complex whose reactivity is lower than that of the original platinum so that coke normally produced through excessive dehydrogenation does not occur. On the other hand, the comparable effects of sulfur and coke on the activity and selectivity of platinum catalysts (*7*) have brought us to the conclusion that sulfur adsorption and coke formation take place on the same catalytic sites. From this we inferred that sulfur could prevent coking of metallic catalysts.

Contrary to such hypotheses, this work has now shown that presulfurization of alumina-supported metallic catalysts induces increased coverage of the catalyst by coke deposition. This result can be explained by taking into account the high cyclopentadiene production on sulfided catalysts. It was in fact previously shown that the amount of coke deposited on a supported Pt/Al_2O_3 catalyst during coking by cyclopentane is always in a linear relationship with the partial pressure in the diolefine which is able to induce accumulation of carbonaceous deposits on the support as result of polymerization on the acidic sites of the alumina. This enhanced activity of sulfided catalysts in dehydrogenation reactions has been previously described (*28, 29*) and can be explained in different ways. First, sulfurization of platinum catalysts has been shown by a kinetic study to induce a decreasing adsorption energy for olefinic compounds. Second, as a result of poisoning of hydrogenolysis activity, sulfur could be able to increase the production of those olefinic compounds which are not destroyed by the hydrogenolysis reaction. Finally, as has been suggested here, sulfur could inhibit the autodeactivation of metals, thus preserving their dehydrogenation activity.

The protection of the metal from the coking reaction was obviously demonstrated by using pure metallic catalysts or alumina-supported platinum catalysts deprived of acidic sites by KOH treatment. However, in the case of platinum black, coke deposition is only reduced by half when platinum is sulfided. Yet is well known, for example, in HDS operation, that metallic sulfides can be covered by coke deposition. From this observation it follows that olefine polymerization yielding coke formation can also be produced on the sulfided platinum atoms. In return, the coking reaction is largely inhibited on sulfided platinum supported on nonacidic alumina.

All these results are in agreement with

TABLE 9

Comparison of Coking Extents on Sulfided and Nonsulfided KOH-Treated Pt/Al_2O_3 Catalysts

Catalysts	at. C/(g cat.) × 10^{19}
D_7 + KOH	4.27
(D_7 + KOH) sulfided	0.90

many patents (*1, 3, 25, 26, 31, 32*) which recommend the presulfurization of catalysts in order to improve their lifetimes. The effect of sulfur adsorption would be to protect the metal from the coking reaction. Such protection can be said to be the consequence of the heterogeneous metallic surface if one assumes that the hydrogenolysis reaction, coke formation, and sulfur adsorption take place on the same metallic reactive sites.

On the other hand, the same protection of the metal can be explained by assuming that coke production, like the hydrogenolysis reaction, require large ensembles of sites. Sulfur adsorption could be able to break up the periodicity of the surface and as a result prevent coke formation on the metal or the hydrogenolysis reaction.

Alternatively, changes in the activity and selectivity of partially poisoned catalysts can be attributed to a "ligand effect" which involves the assumption that the nature and the strength of a chemical bond between an adsorbate and a metallic surface atom is influenced by the neighbors of that surface atom. Also, assuming that cyclopentadiene is the precursor of coke, it is likely that its adsorption will be all the more stabilized as the metal is more able to donate electrons, thus resulting in the formation of a species very similar to the stable cyclopentadienyl ion. In the case of sulfided platinum, it has been clearly shown (*15*) that an electronic transfer from platinum to adsorbed sulfur induces an electron deficiency on the metal. Cyclopentadiene adsorption would then be more stabilized on nonpresulfurized platinum. It is also more likely to react with another cyclopentadiene molecule, in order to induce more polymerization, on nonsulfided platinum catalysts.

In conclusion, as a first estimate, presulfurization of alumina-supported platinum catalysts induces an increase in coke formation on the whole catalyst. This increase could be the consequence of a higher production of olefinic compounds in the gas phase leading to an extensive coke deposition on the support as a result of polymerization on the acidic sites of the alumina. On the other hand, sulfur is able to inhibit the autodeactivation of the metal which is thus protected from the coking reaction. This observation agrees with the greater stability observed in sulfided reforming catalysts.

REFERENCES

1. Baldwin, D., U.S. Patent 3,244,962 (1965).
2. Hayes, J. C., U.S. Patent, 3,481,861 (1969).
3. Capsuto, L., U.S. Patent 3,330,761 (1967).
4. Maurel, R., Leclercq, G., and Barbier J., *J. Catal.* **37,** 324 (1975).
5. Apesteguia, C. R., and Barbier, J., *J. Catal.* **78,** 352 (1982).
6. Barbier, J., Marecot, P., Tifouti, L., Guenin, M., and Frety, R., *Appl. Catal.* **19,** 375 (1985).
7. Barbier, J., Marecot, P., Martin, N., Elassal, L., and Maurel, R. R., "Catalyst Deactivation" (Studies in Surface Science and Catalysis), Vol. 6, p. 53. Elsevier, Amsterdam, 1980.
8. Barbier, J., Morales, A., Marecot, P., and Maurel, R., *Bull. Soc. Chim. Belg.* **88,** 569 (1979).
9. Boudart, M., "Advances in Catalysis," Vol. 20, p. 153. Academic Press, New York, 1969.
10. Barbier, J., Marecot, P., Morales, A., and Maurel, R., *Bull. Soc. Chim. Fr.* **I,** 309 (1978).
11. Lankhorst, P. P., de Jongste, H. C., and Ponec, V., in "Catalyst Deactivation" (Studies in Surface Science and Catalysis), Vol. 6, p. 43. Elsevier, Amsterdam, 1980.
12. Engels, S., Drescher, D., Wehle, P., and Wilde, M. *Chem. Tech.* (*Leipzig*) **29,** 456 (1977).
13. Barbier, J., Corro, G., Zhang, Y., Bournonville, J. P., and Franck, J. P., *Appl. Catal.* **13,** 245 (1985).
14. Del Angel, G. A., Coq, B., and Figueras, F., *Nouv. J. Chim.* **7,** 173 (1983).
15. Gallezot, P., Datka, J., Massardier, J., Primet, M., and Imelik, B., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (J. W. Hightower, Ed.), p. 696. The Chemical Society, London, 1977.
16. Adams, R., Voorhees, V., and Shriner, R. L., *Inorg. Synth.* **1,** 463 (1964).
17. Corro, G., and Gomez, R., *React. Kinet. Catal. Lett.* **9,** 325 (1978).
18. Barbier, J., Charcosset, H., Pereira, G., and Rivière, J., *Appl. Catal.* **1,** 71 (1981).
19. Barbier, J., Corro, G., and Marecot, P., *React. Kinet. Catal. Lett.* **28**(2), 245 (1985).
20. Barbier, J., Elassal, L., Gnep, N. S., Guisnet, M., Molina, W., Zhang, Y., Bournonville, J. P., and Franck, J. P., *Bull. Soc. Chim. Fr.* **I,** 245 (1984).

21. Barbier, J., Elassal, L., Gnep, N. S., Guisnet, M., Molina, W., Zhang, Y., Bournonville, J. P., and Franck, J. P., *Bull. Soc. Chim. Fr.* **I,** 250 (1984).
22. Menon, P. G., and Prasad, J., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976," p. 1061. The Chemical Society, London, 1977.
23. Parera, J. M., Apesteguia, C. R., Plaza De Los Reyes, J. F., and Garetto, J. F., *React. Kinet. Catal. Lett.* **15,** 167 (1980).
24. Apesteguia, C. R., Barbier, J., Plaza De Los Reyes, J. F., Garetto, J. F., and Parera, J. M., *Appl. Catal.* **1,** 159 (1981).
25. Engel, W. F., Dutch Patent 84,714 (1957).
26. Haensel, V., U.S. Patent 3,006,841 (1961).
27. Hayes, J. C., Mitsche, R. T., Pollitzer, E. L., and Homeier, E. H., *in* Preprints, 167th meeting Amer. Chem. Soc., Los Angeles, 1974.
28. Aeyach, S., thesis. Strasbourg, 1982.
29. Allinger, L., Cava, M. P., De Jongh, D. C., Johnson, C. R., Lebel, N. A., and Stevens, C. L., "Ediscience," McGraw-Hill (1971).
30. Apesteguia, C. R., and Barbier, J., *Bull. Soc. Chim. Fr.* **I,** 165 (1982).
31. Bicek, E. J., Belg. Patent 645,402 (1964).
32. Lovell, P., U.S. Patent 3,565,789 (1969).