JOURNAL OF CATALYSIS **37,** 324–331 (1975)

Activity of Metallic Catalysts

IV. Influence of the Nature of the Support and Effect of Sulfur-Containing Poisons on Two Examples of "Demanding Reactions"[1]

R. MAUREL, G. LECLERCQ AND J. BARBIER

Groupe de Recherches sur la Catalyse en Chimie Organique,
Equipe de Recherches Associée au CNRS, Université de Poitiers,
86022 Poitiers, France

Received March 25, 1974; revised September 27, 1974

Platinum catalysts were prepared from two transition aluminas with respective surface areas of 120 and 180 m^2/g and two α-aluminas. Their metallic surface areas were varied by thermal treatment at various temperatures. Their activities with respect to the hydrogenation of benzene ("facile reaction"), the hydrogenolysis of cyclopentane ("demanding reaction" of the first type) and the exchange between benzene and deuterium ("demanding reaction" of the second type) were measured. It is shown that the effect caused by the support does not arise from a difference in crystallinity, but rather from a selective poisoning brought about by the reduction of sulfate, in certain aluminas.

Moreover, it is shown that certain poisons such as H_2S and SO_2 are "nonselective," i.e., they have the same effect on the three reactions in the same way. On the contrary, the mixture $H_2S + SO_2$, which produces atomic sulfur, is a selective poison which reduces the rate of the hydrogenolysis of cyclopentane more than that of the hydrogenation of benzene, whereas the exchange between benzene and deuterium is far less affected than the hydrogenation.

The cause of this selective poisoning is discussed.

INTRODUCTION

Catalytic reactions on Group VIII metals have been classified by Boudart *et al.* (*1*) into two categories. The first is that of "facile" or "structure insensitive" reactions for which the activity per unit of surface area of the metal is constant whatever the treatment given to the catalyst. If we restrict ourselves to the case of platinum, such is the case, for example, in the hydrogenolysis of cyclopropane (*2*), the hydrogenation of benzene (*3–5*) and of cyclohexane (*6,7*), the oxidation of sulfur dioxide (*8*) and of hydrogen (*9*), the dehydrogenation of 1,1,3-trimethylcyclohexane (*10*) and the epimerization of 1,2-dimethyl cyclohexane (*11*).

The second category is that of those reactions called "demanding" or "structure sensitive," for which activity is not proportional to metallic surface area. These are fewer in number: we can quote the example of the hydrogenolysis of neopentane on platinum (*1*) and of ethane on rhodium (*12*), the dehydrocyclization of *n*-heptane on platinum (*13*) and the exchange between benzene and deuterium on nickel (*14*). In a preliminary paper (*15*) we showed that this last reaction is also "structure sensitive" on Pt-alumina. But its "demands" are not the same as those of the hydrogenolysis of cyclopentane which

---

[1] For previous papers in this series, see Refs. (*11*) and (*23*).

we had previously studied; the curves of variation in activity as a function of metallic area are very much different.

It is important to know to which type each reaction belongs, but the answer is not always clear. Thus the hydrogenolysis of cyclopentane on platinum has been classified among the first (*16*) or the second category (*11*). We showed that the result obtained by varying the metallic area by thermal treatment under hydrogen depends on the catalyst support (*17*), and we attributed this effect to the degree of crystallinity of the support. The activity is in fact proportional to the metallic surface area if the support is α-alumina.

In the present paper we report a more detailed study of this effect of the support. We measured the activity of various $Pt-Al_2O_3$ catalysts on the one hand with respect to the hydrogenolysis of cyclopentane at 300°C (first demanding reaction) and on the other with respect to the reactions of benzene with deuterium at 85°C, namely, addition (facile reaction) and exchange (second demanding reaction). We prepared catalysts deposited on crystallized or amorphous aluminas containing various proportions of sulfate ions. These catalysts were treated under hydrogen at various temperatures so as to vary their metallic surface area and their activity for the three reactions. Moreover, they were poisoned with H_2S, SO_2, a mixture of these two, or by the depositing of a sulfate by impregnation.

The results we obtained have led us to a different interpretation from the preceding one: the nonproportionality of activity to metallic surface area would seem to have its origin in a selective poisoning, elementary sulfur being a *selective* poison in certain demanding reactions, whereas SO_2, H_2S and the product of sulfate ion reduction at 300°C are *nonselective* poisons.

EXPERIMENTAL METHODS

Catalysts

Platinum–alumina catalysts were prepared by impregnation of alumina with a solution of chloroplatinic acid. For the preparation of the catalysts, the support was covered with distilled water, and then the required volume of chloroplatinic acid solution was added in order to prepare catalysts with 0.1 and 1% platinum. The solution was evaporated to dryness. During evaporation the catalyst was stirred continuously. Then it was placed overnight in an oven maintained at 100°C. The metal was then reduced under a hydrogen flow at 300°C. Quite intense thermal treatment (up to 600°C) under hydrogen enabled one to decrease the metallic surface area and diminished the activity of the catalysts.

We used four supports for which the characteristics are given in Table 1.

The aluminas CBL_1 and SCS_9 were commercial products (Rhône-Progil). With CBL_1, activity of $Pt-Al_2O_3$ in the cases of the hydrogenolysis of cyclopentane and

TABLE 1

Alumina	BET surface area (m^2/g)	Crystallinity	Microporosity	Sulfur content (ppm)
CBL_1	180	Low degree of crystallinity	Max at 30 Å	1380
SCS_9	23	α	Nonmicroporous	110
CBL_1-1040	50	Mainly α	Nonmicroporous	960
CBL_p	120	Low degree of crystallinity	Max at 30Å	<10

benzene exchange were not proportional to metallic surface area (*15*). On the other hand, on Pt–SCS_9 alumina hydrogenolysis was apparently "facile" (*17*).

The third support was obtained by heating CBL_1 alumina at 1040°C for 4 hr. The fourth, of a similar texture to that of CBL_1, was prepared in the laboratory from hydrargillite; this hydrate was calcined at 450°C in an electric oven, then washed with water to obtain neutral pH. Alumina was dried overnight in an oven at 100°C, then calcined at 650°C in the electric oven for 10 hr.

Some of these solids contain sulfur introduced during calcination by an oil flame.[2] When the sulfur content was high, the emission of H_2S was detectable during the reduction of the catalyst.

Apparatus and Technique

Hydrogenolysis of Cyclopentane (11)

The reaction was carried out in a continuous flow reactor at normal pressure. The conditions were: T, 300°C; hydrocarbon pressure, 0.1 atm; hydrogen pressure, 0.9 atm; weight of catalyst, 5 to 15 g; total flow rate, 0.214 mole/hr. The analysis was carried out by vapor phase chromatography. Conversion was less than 20%. As previously (*11*), the initial activity of the catalyst was determined by extrapolating the deactivation curve to zero.

Deuteration and Benzene Exchange

A back mixed circulating flow reactor was used. Its volume was 150 cc and the recycling rate was 500 cc/min. The conditions were: T, 85°C; p_{D_2}, 0.7 atm; catalyst weight, 0.1 to 3 g; total flow rate, 3.51 10^{-2} mole/hr. The rate of hydrogenation was measured by chromatography and the rate of exchange by mass spectrometry on the chromatographic effluents. The usual natural isotopic corrections were made.

The space velocity was chosen so that the conversion should be close to 4% for hydrogenation and should not exceed 15% for exchange. A check was made to ensure the nondependence of these rates on the recycling rate.

The activity diminished very slowly and, as in the case of hydrogenolysis, extrapolations to zero were made.

Poisoning

For sulfate poisoning the alumina was impregnated by means of a solution of $(NH_4)_2SO_4$, dried and calcined and 350°C, then impregnated with chloroplatinic acid in the usual way.

Poisoning by H_2S or SO_2 was carried out by injecting a given quantity of these gases into the reactor at 85°C. After recycling in the closed circuit for 0.5 hr, the experiment was carried out in the usual way.

RESULTS

Thermal Treatment of Catalysts on Various Supports

Pt on CBL_1 Alumina

Figure 1 gives the activities for exchange, a_1, (curve 1) and for hydrogenolysis, a_2, (curve 2) as a function of the activity for hydrogenation, a_H, of a series of catalysts at 0.1 and 1% platinum which have been reduced at temperatures which vary between 300 and 450°C. As we have already pointed out (*15*), the activity for hydrogenation of benzene is proportional to the metallic surface area measured by $H_2 + O_2$ (*18–20*) titration on all these catalysts. It would seem then that the reactions of hydrogenolysis of cyclopentane and of

---

[2] We express our thanks to the Societe Rhône-Progil, and especially to Mr. M. Graulier who kindly gave us samples of aluminas and carried out the sulfur titrations for us.

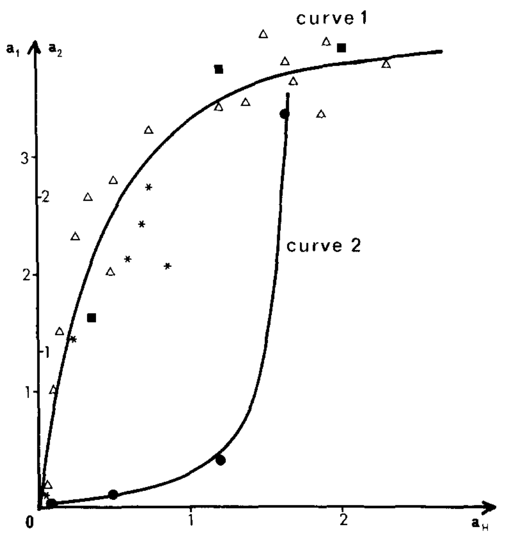

FIG. 1. Pt on CBL$_1$ alumina. (1) Activity in exchange a_1 vs activity in benzene hydrogenation a_H. Catalysts deactivated by thermal treatment: (△) catalysts with 0.1% Pt; (■) catalysts with 1% Pt. Catalysts deactivated by H_2S: (*) catalysts with 1% Pt. (2) Activity in hydrogenolysis of cyclopentane a_2 vs activity in benzene hydrogenation a_H (●).

benzene exchange are "demanding." Moreover, the large difference between curves 1 and 2 shows that the "demands" of these two reactions are not the same.

Pt on SCS$_9$ Alumina

Catalysts containing 1% platinum on SCS$_9$ alumina were treated under hydrogen at increasing temperatures as were the preceding catalysts. For the reactions of benzene with deuterium they give the results set out in Fig. 2 (curve 1). Benzene exchange is thus apparently "facile" in this instance. We, in fact, verified once again that the rate of hydrogenation is proportional to the metallic surface area. Recall that on these same catalysts, the rate of hydrogenolysis of cyclopentane is also proportional to the metallic surface area (*17*). The effect of this particular support seems to show up in "demanding reactions" of quite different types. The enlargement of platinum crystallites resulting from thermal treatment under hydrogen, which brings about a reduction in metallic area, was also verified by X-ray measurements[3]: the average diameter of the crystallites is 15 Å for a catalyst reduced at 300°C, and 19 Å for a catalyst treated at 450°C.

Pt on CBL$_p$ Alumina

Figure 2 (curve 2) gives exchange activity of catalysts containing 1% platinum on CBL$_p$ alumina treated under hydrogen up to 600°C as a function of their activity for benzene hydrogenation. We notice that the result is different from that obtained with CBL$_1$ alumina, even though the surface area, the microporosity and the crystallinity of these two aluminas are analogous.

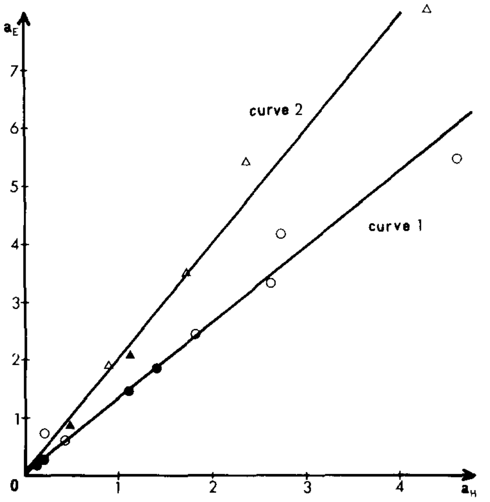

FIG. 2. Pt on SCS$_9$ and CBL$_p$ aluminas. (1) Comparison of a_E (activity in benzene exchange) with a_H (activity in hydrogenation) for Pt-Al_2O_3 SCS$_9$ with 1% Pt: (△) catalysts deactivated by thermal treatment; (▲) catalysts deactivated by hydrogen sulfide poisoning. (2) Comparison of a_E with a_H for Pt-Al_2O_3 CBL$_p$ with 1% Pt: (○) catalysts deactivated by thermal treatment; (●) catalysts deactivated by hydrogen sulfide poisoning.

---

[3] We thank Mr. A. Renouprez who carried out these measurements for us at the Institut de Recherches sur la Catalyse at Villeurbanne.

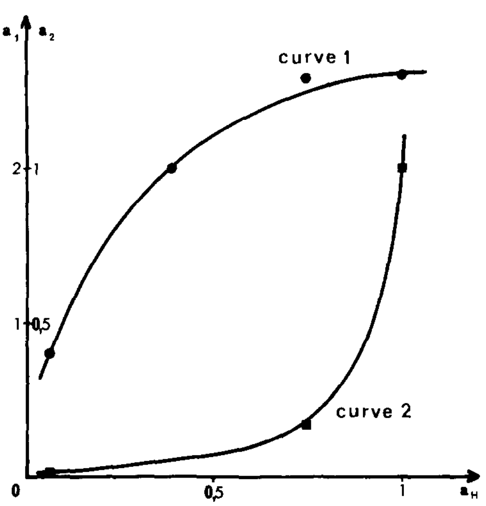

FIG. 3. Pt–Al_2O_3 CBL_1 treated at 1040°C 1% Pt. a_1 activity in exchange [curve I (●)] and a_2, activity in hydrogenolysis [curve II (■)] vs a_H, activity in hydrogenation.

Pt on CBL_1 1040 Alumina

These catalysts, with a 1% platinum content under the same conditions, gave the results in Fig. 3 for the reactions of benzene exchange (curve 1) and of cyclopentane hydrogenolysis (curve 2) as a function of hydrogenation activity. Once again different results are obtained with two aluminas of analogous surface area, porosity and crystallinity, namely, SCS_9 and CBL_1-1040.

Pt-Alumina Catalyst Poisoning

It is clear, according to the characteristics of the four aluminas (Table 1), that the effect of the support on variations in activity for the three reactions does not have its origin in the crystallinity of the alumina as we had previously thought (*17*). On the contrary, it seems to be related to the sulfur content of the support, according to the results obtained with CBL_1 alumina and CBL_1 alumina treated at 1040°C, which both contain quite important quantities of sulfate. This is why we sought to prove that the selective deactivation of certain catalysts was due to a poisoning. The Pt-Al_2O_3 SCS_9 poisoning experiments were carried out on catalysts with a low platinum content (0.1%), so that the latter would be more sensitive to the effect of the poisons. Notice in this respect that the Pt-Al_2O_3 SCS_9 catalysts with 0.1% platinum do not have the same a_E/a_H selectivity as catalysts with 1% platinum. We shall come back to this effect in a future paper.

SO_4^{2-} Poisoning

Catalysts with 0.1% platinum were prepared using SCS_9 alumina previously impregnated with ammonium sulfate with SO_4^{2-} weight contents of 0.12, 0.3 and 0.6%. The exchange and hydrogenation activities of those catalysts reduced at 300°C, diminish with the sulfate content: the catalyst with 0.6% of platinum is seven times less active than the catalyst containing no sulfate, but there is little variation in the hydrogenation/exchange ratio (Table 2).

On the other hand, when these catalysts are treated under hydrogen at a higher temperature, we observe once again a different diminution in activity for the three reactions, as Fig. 4, which refers to the catalyst containing 0.6% sulfate, shows.

TABLE 2

ACTIVITIES OF PT/AL_2O_3 SCS_9 CATALYSTS WITH 0.1% PLATINUM WITH VARIOUS SULFATE CONTENTS, REDUCED AT 300°C

Catalysts	a_H (activity for hydrogenation) (mole/hr/g Pt)	a_E (activity for exchange) (mole/hr/g Pt)	$S = \frac{a_E}{a_H}$
Pt/Al_2O_3 SCS_9 0.1% Pt	0.76	4.5	5.9
Pt/Al_2O_2 SCS_9 0.1% Pt 0.12% SO_4^{2-}	0.76	4.7	6.2
Pt Al_2O_3 SCS_9 0.1% Pt 0.3% SO_4^{2-}	0.44	2.5	5.7
Pt/Al_2O_3 SCS_9 0.1% Pt 0.6% SO_4^{2-}	0.013	0.071	5.5

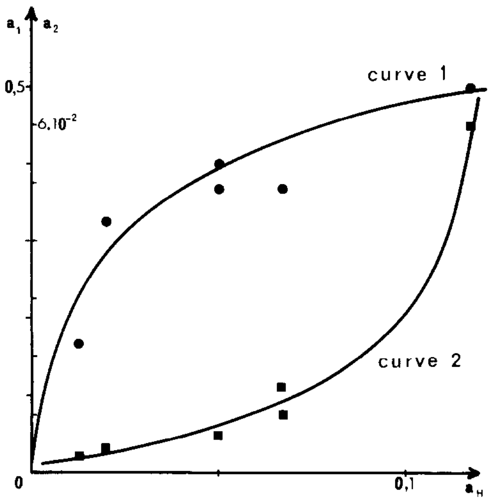

FIG. 4. a_1, activity in exchange [curve I (●)] and a_2, activity in hydrogenolysis [curve II (■)] vs a_H, activity in hydrogenation for a Pt–Al_2O_3 SCS_9 catalyst poisoned with 0.6% SO_4^{2-}.

We can thus conclude that the sulfate ion itself or the product of its reduction at 300°C is a nonselective poison which diminishes activity for the three reactions in the same proportion. The selective poison responsible for the shape of the curves in Fig. 4 should be obtained by a reduction of SO_4^{2-} at a temperature higher than 300°C.

SO_2 Poisoning

As sulfur dioxide can be a product of the reduction of sulfates, we injected it at 85°C in varying quantities on Pt–Al_2O_3 CBL_1 catalysts with 1% platinum and Pt–Al_2O_3 SCS_9 catalysts with 0.1% platinum. The results show that SO_2 is a nonselective poison which diminishes activity without modifying the exchange/hydrogenation ratio.

H_2S Poisoning

Hydrogen sulfide, injected under the same conditions as sulfur dioxide on Pt–Al_2O_3 SCS_9 or Pt–Al_2O_3 CBL_p catalysts whose supports contain no sulfate, is equally a nonselective poison which diminishes exchange and hydrogenation activities in the same proportion (Fig. 2). But the action of H_2S at 85°C on a Pt–Al_2O_3 CBL_1 catalyst with 1% platinum reduced at 300°C, leads to a greater deactivation for hydrogenation than for exchange (Fig. 1) as we can see during deactivation by thermal treatment under hydrogen.

Poisoning by Sulfur Produced in Situ *by the Claus Reaction*

As the injection of H_2S produces selective deactivation of only those catalysts whose supports contain some SO_4^{2-} one could think that this effect is due to a poison resulting from the reaction of H_2S on the sulfate or the product of its reduction at 300°C. This led us to treat the catalysts successively with SO_2 and H_2S in such a way to deposit S on it by Claus reaction.

The results thus obtained on a Pt–Al_2O_3 catalyst with 0.1% platinum are very scattered, these poisonings being of low reproductibility. But the results given in Table 3 show that hydrogenation activity is affected to a greater degree than exchange activity in each case, whereas H_2S and SO_2 taken separately on this catalyst are nonselective poisons.

DISCUSSION

The metallic area diminishes and the average size of the crystallites increases

TABLE 3

POISONING OF PT/AL_2O_3 SCS_9 BY SUCCESSIVE INJECTIONS OF SO_2 AND H_2S

(H_2S/SO_2 = 2)

Activity before injection of SO_2 + H_2S		Vol of SO_2 injected (μl)	Activity after injection of SO_2 + H_2S	
a_H (mole/hr/g Pt)	a_E/a_H		a_H (mole/hr/g Pt)	a_E/a_H
0.70	5.7	30	0.04	10
0.65	5.7	30	0.2	10
0.70	5.7	30	0.10	7
0.75	5.5	10	0.40	8.75
0.70	5	10	0.1	8
0.70	5.7	10	0.22	9.1
0.74	4.6	10	0.13	9.25
0.7	5	20	0.1	8

through thermal treatment of Pt–Al_2O_3 catalysts under hydrogen. Parallel to this, catalytic activity decreases. If the alumina used as a support contains no sulfate, the catalyst activity varies in the same proportion for the three reactions: hydrogenolysis of cyclopentane, hydrogenation and exchange of benzene with deuterium. Moreover, Hightower and Kemball (*21*) have shown that the rate of the exchange in *p*-xylene is practically constant, whether the support is a γ-alumina or an α-alumina from different sources. Therefore it is possible to conclude that if the alumina contains no sulfate the fall in activity is due exclusively to the recrystallization of the platinum.

On the other hand, one observes a diminution which is greater for hydrogenolysis and less marked for benzene exchange if the metal can be poisoned. The experiments described above show that SO_4^{2-}, or the product of its reduction at 300°C, SO_2 and H_2S are nonselective poisons in relation to platinum, and they affect the three reactions in the same way, whereas elementary sulfur is the selective poison responsible for the effects observed with aluminas containing sulfate.

An analogous effect has been observed by Crawford and Kemball (*22*) on nickel films. They found a marked difference between the relative reactivities for the exchange of side chain hydrogens and for that of aromatic hydrogens in alkyl benzenes whether the films were sintered at 200°C or not. The exchange of aromatic hydrogens is diminished by sintering to a greater extent than that of the other hydrogens. But, having suggested that this effect could be brought about by a poison, Crawford and Kemball rule out this hypothesis, pointing out that such an explanation does not seem very compatible with their values of activation energy.

Our results could be interpreted by assuming that the nonselective poisons such as H_2S and SO_2 just diminish the accessible metallic area, whereas the selective poisons such as sulfur act on the metal by an electronic effect which alters the specific activity of the remaining surface area for the different reactions. Thus the platinum atoms modified by the proximity of an adsorbed sulfur atom would have the same activity in the hydrogenation of benzene as normal atoms, but would be less active in hydrogenolysis and more active in benzene deuterium exchange. Under this hypothesis the three reactions studied here would be "facile" for they would take place over the whole of the accessible metallic surface area, the rates of reaction being more or less influenced by the change in electronic structure of the metal caused by the adsorption of a selective poison.

Nevertheless it seems difficult to reconcile this hypothesis with the work done by Crawford and Kemball who, as we have said, eliminate the possibility of an effect caused by poison and consider their results "consistent with a concept of reaction on a few special sites."

We can therefore continue to assume that the reactions of exchange and hydrogenolysis are "structure sensitive." They would be produced on particular sites which would be different from one another. The hydrogenation of benzene, on the other hand, a "structure insensitive" reaction, would occur over the whole surface area.

Our results lead to the following conclusions:

the relative number of sites particular to hydrogenolysis and to exchange is not varied by recrystallization, at least not within the temperature range explored;

the nonselective poisons such as H_2S and SO_2 are adsorbed indifferently on all catalytic sites;

the selective poisons such as sulfur would be adsorbed predominantly on those sites responsible for hydrogenolysis.

We have already discussed the nature of

those particular sites (*17,23*), referring in particular to a review written by Boudart (*24*). For example, as has been proposed, these can be the atoms of certain crystalline faces (*23*) or those of lower coordination than that of the surface atoms (*23,25*) [referred to as B5 sites by Van Hardeveld and Hartog (*14*)]. These selective poisons would avoid those sites responsible for the exchange of benzene and which could in that case be the atoms of the other crystalline faces or those atoms with a coordination equal to 9, situated on the faces. In fact the studies of Van Hardeveld and Hartog (*14*) show that on Ni-Aerosil those catalysts containing the most B5 sites are the least active in benzene exchange.

The selective poisons could therefore be qualified as "demanding poisons" as they are adsorbed only on some special sites.

We are continuing our work in this direction with an aim to determining whether the notion "demanding poison" can be generalized.

REFERENCES

1. Boudart, M., Aldag, A. W., Ptak, L. D., and Benson, J. E., *J. Catal.* **11,** 35 (1968).
2. Boudart, M., Aldag, A., Benson, J. E., Dougharty, V. A., and Harkins, C. G., *J. Catal.* **6,** 92 (1966).
3. Aben, P. C., Platteeuw, J. C., and Stouthamer, B., *Proc. Int. Congr. Catal. 4th,* (1968) (Pap. 31) i, 395 (1971).
4. Nikolajenko V., Bosácek, V., and Danes, V., *J. Catal.* **2,** 127 (1963).
5. Mutin, R., Basset, J. M., and Prettre, M., *C. R. Acad. Sci. Ser. C,* **273,** 1704 (1971).
6. Poltorak, O. M., and Boronin, V. S., *Zh. Fiz. Khim.* **40,** 2671 (1966).
7. Dmitrienko, N. M., Boronin, V. S., and Poltorak, O. M., *Vestn. Mosk. Univ., Ser. II: Khim.* No. 6, 106 (1966).
8. Boreskov, G. K., and Chesalova, V. S., *Zh. Fiz. Khim.* **30,** 2560 (1956).
9. Boreskov, G. K., Slinko, M. G., and Chesalova, V. S., *Zh. Fiz. Khim.* **30,** 2787 (1956).
10. Barbaux, Y., Roger, B., Beaufils, J. P., and Germain, J. E., *J. Chim. phys.* **67,** 1035 (1970).
11. Maurel, R., and Leclercq, G., *Bull. Soc. Chim.* **4,** 1234 (1971).
12. Yates, D. J. C., and Sinfelt, J. H., *J. Catal.* **8,** 348 (1967).
13. Maat, H. J., and Moscou, L., *Proc. Int. Cong. Catal., 3rd, 1964* **2,** 1276 (1965).
14. Van Hardeveld, R., and Hartog, F., *Proc. Int. Congr. Catal., 4th, 1968,* (Pap. 70). **2,** 295 (1971).
15. Maurel, R., Leclercq, G., and Barbier, J., *C. R. Acad. Sci. Ser. C* **277,** 1075 (1973).
16. Mitrofanova, A. N., Boronin, V. S., and Poltorak, O. M., *Vestn. Mosk. Univ., Ser. II: Khim.* **5,** 40 (1966); **1,** 95 (1967).
17. Leclercq, G., Trochet, J., and Maurel, R., *C. R. Acad. Sci. Ser. C* **275,** 857 (1972).
18. Gruber, H. L., *J. Phys. Chem.* **66,** 48 (1962).
19. Benson, J. E., and Boudart, M., *J. Catal.* **4,** 705 (1965).
20. Dorling, T. A., and Moss, R. L., *J. Catal.* **5,** 111 (1966).
21. Hightower, J. W., and Kemball, C., *J. Catal.* **4,** 363 (1965).
22. Crawford, E., and Kemball C., *Trans. Faraday Soc.* **58,** 2452 (1962).
23. Maurel, R., Leclercq, G., and Leclercq, L., *Bull. Soc. Chim.* **2,** 491 (1972).
24. Boudart, M., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 20, p. 158. Academic Press, New York, 1969.
25. Anderson, J. R., Macdonald, R. J., and Shimoyama, Y., *J. Catal.* **20,** 147 (1971).