JOURNAL OF CATALYSIS **38**, 47–53 (1975)

Activity of Platinum–Palladium Bimetallic Catalysts

R. GÓMEZ,[1] S. FUENTES, F. J. FERNÁNDEZ DEL VALLE,
A. CAMPERO AND J. M. FERREIRA

Instituto Mexicano del Petróleo, Av. de los 100 Metros N. 152,
México 14, D. F.

Received August 6, 1974

The dispersion of metallic particles on a porous medium is studied by hydrogen and oxygen chemisorption. The catalysts used in this work are made of two noble metals, platinum and palladium, deposited on alumina by the ion exchange technique. Both metals were impregnated either simultaneously or individually on different portions of the support and then mechanically mixed in appropriate amounts to give the desired proportion. The results show that in both cases none of the metals suffer any modification in their individual oxygen adsorption.

Benzene hydrogenation at a low temperature was used as a test reaction for the study of the catalytic activity. The catalytic activity per surface metal atom (N) on the catalyst prepared by the co-impregnation technique was three times smaller than the one on the catalyst prepared by mechanical mixture. From X-ray diffraction data we infer cluster formation on the co-impregnation type catalyst.

INTRODUCTION

The use of bimetallic systems in supported catalysts for the reforming of naphthas has acquired considerable importance recently (*1*). However, surface distribution studies of these systems have been only sparingly reported (*2–4*). Nevertheless, the electronic factor concept and its relation with catalytic activity has been extensively studied, mainly for systems as silver–palladium (*5*), copper–nickel (*6, 7*) and gold–palladium (*8*); in these systems the specific formation of alloys has been thoroughly confirmed, but, for the catalysts utilized in reforming, the present knowledge about these matters, is not appropriate.

It is well known that the chemisorption of hydrogen and oxygen, on group VIII metals, has been frequently utilized in order to find its relationship to the hydrogenation catalytic activity (*9–13*). Because of its importance in chemical technology, the bimetallic system platinum–palladium is the subject of this work. The chemisorption of oxygen and hydrogen on bimetallic platinum–palladium supported on alumina, as well as the catalytic activity of such systems, has been studied.

The catalysts were prepared by a co-impregnation technique, or by simple mixture of catalysts containing either one of these metals. Benzene hydrogenation at low temperature was utilized as a test reaction for the study of the catalytic activity.

EXPERIMENTAL METHODS

Catalysts Preparation

The Pt–Pd/Al_2O_3 catalysts were prepared by the ion exchange method (*14*), the alumina utilized was Pechiney type SCS-350; the impregnation solutions were prepared with chloroplatinic acid and palladium chloride, Merck, analytical quality grade.

---

[1] Present address: Universidad Autónoma Metropolitana, Unidad Iztapalapa, Depto. de Física y Química Apdo. Postal 55-534, México 13, D. F.

The following series of catalysts were prepared:

Series A. Platinum/Al_2O_3 catalysts (Pt% from 0.2 to 1%).

Series B. Palladium/Al_2O_3 catalysts (Pd% from 0.2 to 1%).

Series C. Platinum–palladium catalysts. Prepared by co-impregnation.

Series D. Platinum-palladium catalysts. Prepared by mixing the appropriate amounts of catalysts of Series A and B.

Adsorption Measurements

All catalysts were dried for 12 hr at 120°C in air, the product was reduced *in situ* at 500°C for Series A and at 400°C for Series B, C and D, in a Cahn RG UHV electrobalance, under a hydrogen pressure of 500 Torr for 6 hr, and then evacuated at 10^{-5} Torr for 12 hr at the temperature of reduction. The cleanliness of the vacuum system is insured by an antipollution system previously described (*15*). Matheson oxygen and hydrogen of ultrahigh purity were utilized, and adsorbed at 24°C, at pressures of 100 and 10 Torr, respectively, in order to obtain the 1:1 Pd–H stoichiometric relation (*16, 17*).

Catalysts samples (300 mg) were used for the adsorption measurements. The dispersion and the platinum crystallite size was calculated from the weight of oxygen adsorbed, as determined in the titration tests; crystallite size was estimated supposing spherical shape for the metal particles.

Electron Microscopy

The determination of particle size distribution was made with a Hitachi HU-11B electron microscope with a resolving power of 7 Å. A replica technique was utilized counting each time an average of 500 particles. Crystallite size was calculated by means of the volume/surface ratio $\bar{d} = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$.

X-Ray Diffraction

X-Ray diffraction spectra was obtained with a horizontal goniometer Phillips PW-1380 with a copper tube and a monochromator of graphite.

Catalytic Activity

The catalyst samples (25–50 mg) used for the dispersion measurements were reactivated at 400°C in hydrogen. The rate of benzene hydrogenation was measured in a conventional flow reactor at low conversion (<1%) to avoid heat and mass transfer limitations. The partial pressure of benzene was 56 Torr and that of hydrogen 530 Torr; under these conditions, the reaction is zero order in terms of benzene. Activities were measured for platinum and bimetallic series between 40 and 70°C and 120–150°C for palladium; at these temperatures catalyst aging phenomena were not observed and the reproducibility of the experiments was better than 10%.

RESULTS

Adsorption Data

Benson and Boudart (*18*) and Benson *et al.* (*19*), on supported platinum and palladium, proposed that the sensitivity of the direct chemisorption method could be improved by a factor of three by titrating chemisorbed oxygen with hydrogen; the stoichiometry assumed was:

$$\text{Pt (surface)} + \tfrac{1}{2}O_2 \text{ (gas)} \rightarrow \text{Pt–O (surface)} \ (O_I),$$

$$\text{Pt–O (surface)} + \tfrac{3}{2}H_2 \text{ (gas)} \rightarrow \text{Pt–H (surface)} + H_2O \text{ (support)}.$$

These reactions were completed on supported platinum by Barbaux *et al.* (*20*) who by gravimetric studies introduce the following reaction:

$$\text{Pt–H (surface)} + \tfrac{3}{4}O_2 \text{ (gas)} \rightarrow \text{Pt–O (surface)} + \tfrac{1}{2}H_2O \text{ (support)} \ (O_{II}).$$

The stoichiometry was supported by

TABLE 1

DETERMINATION OF THE RATIO O_{II}/O_I

Metal	%	(μg/g cat)		
		O_I	O_{II}	O_{II}/O_I[a]
Pt	1.0	464	633	1.36
Pd	0.8	452	680	1.50
Pd	0.6	377	565	1.62
Pt–Pd	0.4–0.6[b]	490	793	1.62
	0.2–0.8[b]	490	830	1.69
	0.2–0.3[c]	226	378	1.67

[a] Theoretical value, 1.5.

[b] Co-impregnation technique.

[c] Mechanical mixture; support Al_2O_3.

their observed ratio of 1.5 for oxygen titration/oxygen chemisorption. Other authors proposed different stoichiometric equations (*21*). However, as was pointed out by Wilson and Hall (*22*), the error introduced by that hypothesis is around 16%; we may consider it as a systematic error on dispersion and hence on the turnover number determination. Some limited experiments (Table 1) give a stoichiometry for titration similar to that studied by Barbaux *et al.* (*20*).

The metal dispersion calculated on base of the oxygen titration value (O_{II}) is around 50 and 37% for Series A and B catalysts, respectively (Table 2). The lower dispersion obtained with palladium is expected, since it is well known that palladium is more sensitive than platinum to thermal treatments because of the difference in their melting points (Pd: 1, 557°C, Pt: 1, 769°C).

The mean values for metal dispersion in catalysts Series C and D are not reported, since the adsorption is not selective; nevertheless, in Table 3, results are reported, which show that it is possible to establish a correlation between the theoretical results calculated by adding the individual adsorption values for each metal and the experimental total adsorption of the bimetallic systems (Fig. 1).

The distribution of crystallite sizes, obtained by the independent experimental technique of electron microscopy for Series A, B and C, are shown in Fig. 2. The maximum observed in Fig. 2 agrees quite closely with the results obtained by chemisorption giving good support to our results (Table 4).

Catalytic Activity

Activities are expressed in terms of turnover number *N* (number of millimole-

TABLE 2

ADSORPTION DATA ON Pt/Al_2O_3, Pd/Al_2O_3 CATALYSTS

% Pt	Oxygen adsorption (μg/g cat)	Area (m²/g cat)	Area (m²/g metal)	Dispersion (%)	Crystallite size (Å)
Series A					
0.2	120	0.25	134	48	21
0.4	245	0.55	138	50	20
0.6	390	0.87	145	52	19
0.8	482	1.08	135	49	21
1.0	633	1.41	142	51	20
% Pd					
Series B					
0.2	152	0.32	161	33	31
0.4	340	0.73	183	37	27
0.6	565	1.21	202	41	25
0.8	680	1.47	183	37	27
1.0	850	1.83	183	37	27

TABLE 3

ADSORPTION DATA ON CATALYSTS $Pt–Pd/Al_2O_3$

% Pt	% Pd	Oxygen adsorption (μg/g cat)			
		Total adsorption (experimental)	Individual adsorption[a]		
			$Pt_{(1)}$	$Pd_{(2)}$	$Pt_{(1)} + Pd_{(2)}$
Series C[b]					
0.8	0.2	700	482	152	634
0.6	0.4	755	390	340	730
0.4	0.6	793	245	565	810
0.2	0.8	830	120	680	800
Series D[c]					
0.4	0.1	283	245	75	320
0.3	0.2	332	195	150	345
0.2	0.3	378	120	280	400
0.1	0.4	434	60	340	400

[a] Taken from Table 2.

[b] Co-impregnation technique.

[c] Mechanical mixture.

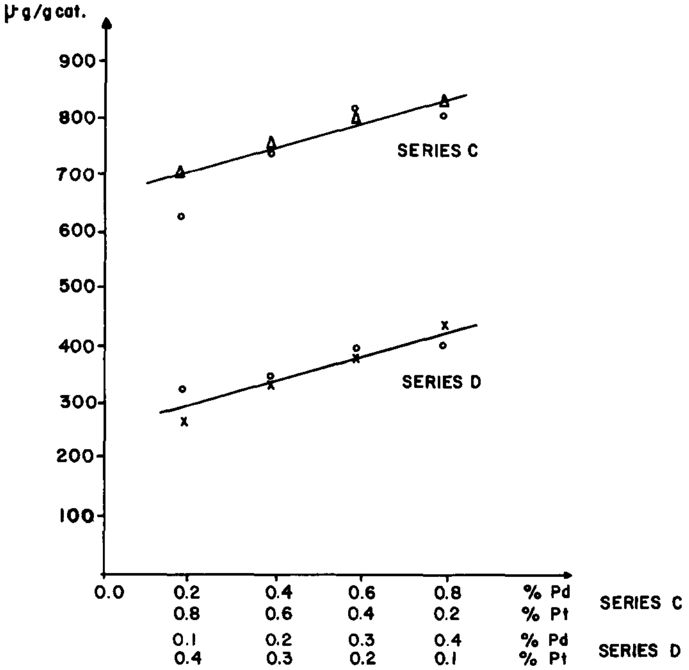

FIG. 1. Oxygen adsorption as a function of metal content. (Δ) co-impregnation preparation (×) mechanical mixture. (○) obtained by addition of the individual metallic adsorptions.

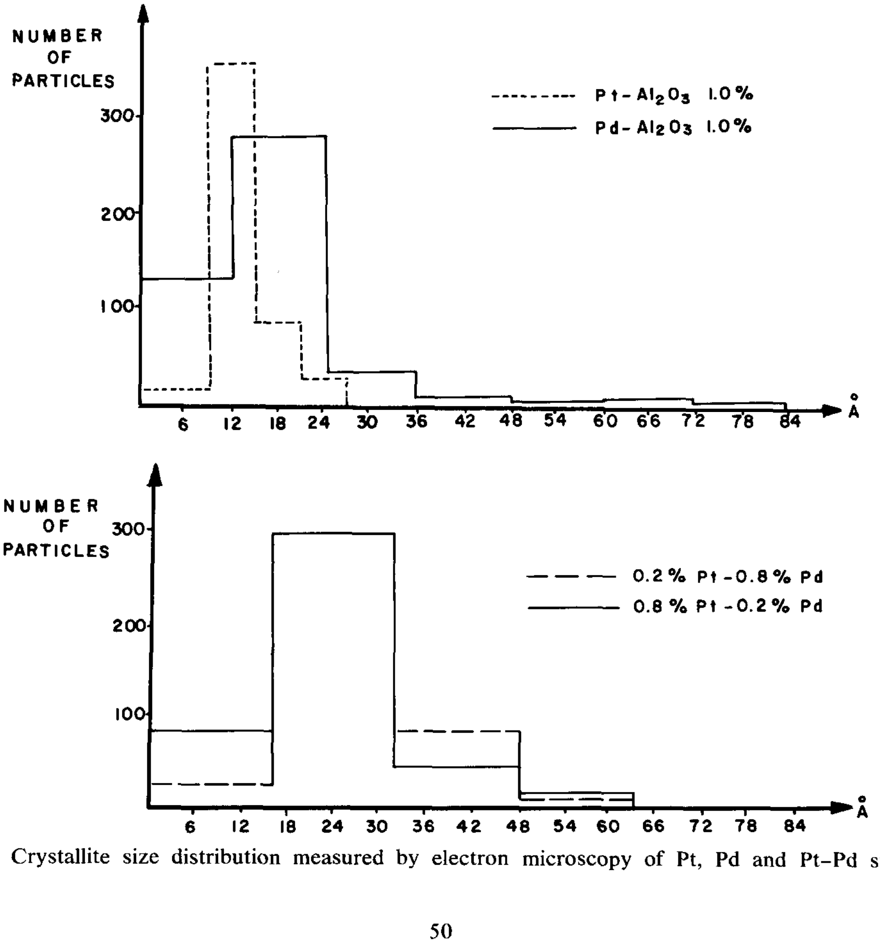

FIG. 2. Crystallite size distribution measured by electron microscopy of Pt, Pd and Pt–Pd supported catalysts.

TABLE 4
COMPARATIVE DATA ON CRYSTALLITE SIZE

Metal content	Mean crystallite size (Å)	
	Electron microscopy data	O_2 chemisorption data
Pt, 1%	19	21
Pd, 1%	32	27
Pt, 0.8%–Pd, 0.2%[a]	27	24
Pt, 0.2%–Pd, 0.8%[a]	30	25

[a] Co-impregnation technique.

cules of benzene which reacts per second per surface metallic atom). For bimetallic catalysts, the palladium adsorption values were not considered for the calculations, because palladium has a negligible catalytic activity under the experimental conditions used. The calculations were made on base of surface platinum atom from the relation:

$$N = \frac{r\,W}{M\,N_0\,D\%} \times 100,$$

where r is the rate (mmolecules/sec g cat); M is the content in weight of the metal (g/g cat); D is the dispersion value, defined as the relation number of active metallic atoms to adsorb the oxygen/number of total metallic atoms contained in the catalysts; W is the atomic weight of the metal; and N_0 Avogadro's number.

The experimental results are reported in Fig. 3, the absence of any significative change in N as the amount of metal is increased being taken as convincing evidence of the lack of influence of transport phenomena under the experimental conditions utilized (*23*).

The values obtained for N ($N = 35$ for platinum and $N = 50$ for palladium) can be compared with previous results reported in the literature under similar experimental conditions; $N = 40$ for platinum (*24*) and $N = 52$ for palladium (*9*). The activation

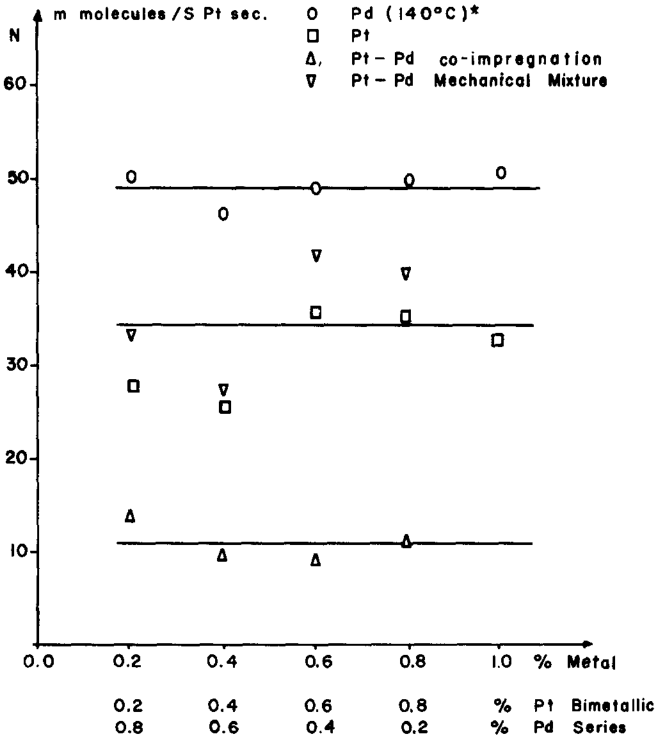

FIG. 3. Catalytic activity for Pt and Pt–Pd/Al_2O_3 catalysts on benzene hydrogenation at 50°C. * Calculated in mmolecules/S Pd sec.

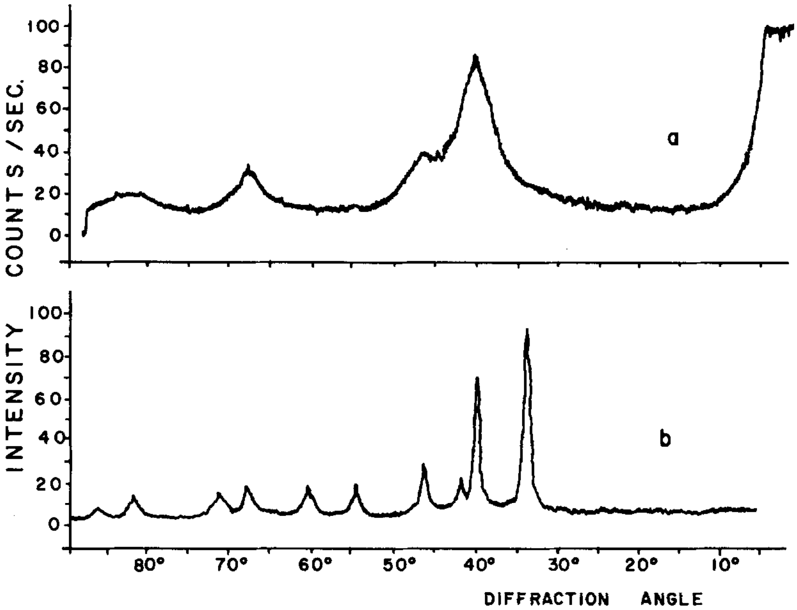

FIG. 4. X-Ray Diffraction spectra for Pt–Pd catalysts. (a) Reduced sample at 400°C under hydrogen atmosphere, (b) heated sample at 700°C under air atmosphere.

energy for the reaction is 10 ± 1 kcal/mole°C.

X-Ray Diffraction

One of the catalysts (0.5% of platinum and 0.5% of palladium), prepared by the co-impregnation method, was reduced at 400°C under a hydrogen pressure of 590 Torr for 6 hr and subjected to a metal extraction technique (*25*) which consists of a treatment of the sample with hydrofluoric acid solution to dissolve the alumina support and subsequently studying the residual metallic phase by X-ray diffraction. There is a broad peak caused by the overlap of the platinum and palladium signals at a diffraction angle (2θ) of 40.25°. Air treatment at atmospheric pressure of this material at 700°C resolves the broad line, giving the characteristic diffraction lines of platinum and palladium oxide, at 2θ angles of 39.7 and 33.7°, respectively. The results obtained are shown in Fig. 4.

DISCUSSION

The adsorption and crystallite size distribution data presented in this work for platinum and palladium catalysts supported on alumina, show that the size distribution is very narrow, so it is possible to have additive chemisorption with Series D (mechanical mixture) powdered catalysts; this can be clearly seen in Table 3 where the individual O_2 adsorption agrees with the values obtained for the catalysts prepared by the co-impregnation technique. It can be seen that the individual chemisorption properties are conserved.

For Series C catalysts (co-impregnation technique) similar adsorption results were obtained; however, for these catalysts, a substantial modification of the individual catalytic properties of palladium and platinum would be expected, since under these experimental preparation conditions, the metals could form some sort of alloy. Our experimental results show evidence of such a phenomenon, because a decrease in the turnover number values is obtained (Fig. 3). The observed results cannot be explained by some hypothesis of overlap of *d*-electron bands, because in this case a change in the chemisorption values would have been obtained.

TABLE 5
CATALYTIC ACTIVITY OF BIMETALLIC CATALYSTS PREPARED BY CO-IMPREGNATION METHOD

Content		Atomic ratio	Turnover no.
Pt (%)	Pd (%)	(Pt/Pd)	(*N* Pt/*N* Pt–Pd)
0.2	0.8	0.13	2.5
0.4	0.6	0.36	2.6
0.6	0.4	0.82	3.5
0.8	0.2	2.15	3.2

The study of the ruthenium–copper and osmium–copper catalytic systems enabled Sinfelt (*26*) to propose a model of "bimetallic clusters, rather than alloys, in referring to highly dispersed supported bimetallic systems where the catalytic behavior indicates significant interaction between the metallic components." In this work, the X-ray diffraction results confirm the formation of "clusters," as proposed by Sinfelt. In catalysts Series C we do not observe modifications in the catalytic activity per metallic site, even when the atomic ratio Pt/Pd increases from 0.13 to 2.1. These experimental data show that at constant metallic dispersion, the stability of the bimetallic phase is independent of the Pt/Pd atomic ratio variation (Table 5).

In conclusion, the results of this work show that a measurement of the metal dispersion in the platinum–palladium bimetallic system can be done by means of the well-established Benson–Boudart stoichiometric model; the individual chemisorption properties of platinum and palladium are conserved in catalysts containing these two metals as was demonstrated in this work by comparing the chemisorption of Pt–Pd catalysts prepared by the standard co-impregnation technique, with that of catalysts obtained by a mechanical mixture of the individual metals. The catalytic activity of such systems shows, however, important differences; the catalysts prepared by co-impregnation have a lower activity than those made by mechanical mixture (by factor of 2.5–3.5).

ACKNOWLEDGMENT

We express our appreciation to the Instituto Mexicano del Petróleo for its support of this work.

REFERENCES

1. Kluksdahl, H. E., *U. S. Pat.* 3, 415, 737 (1968).
2. Menon, P. G., Sieders, J., Streefkerk, F. J., and Van Keulen, G. J. M., *J. Catal.* **28,** 381 (1973).
3. Sachtler, W. M. H., and Jongepier, R., *J. Catal.* **1,** 665 (1965).
4. Baranowski, B., Majchrzak, S., and Flanagan, T. B., *J. Phys. Chem.* **77,** 35 (1973).
5. Christmann, K., and Ertl, G., *Surface Sci.* **33,** 254 (1972).
6. Roberti, A., Ponec, V., and Sachtler, W. M. H., *J. Catal.* **28,** 381 (1973).
7. Sinfelt, J. H., Carter, J. L., and Yates, D. J. C., *J. Catal.* **24,** 283 (1972).
8. Maestas, S., and Flanagan, T. B., *J. Phys. Chem.* **77,** 850 (1973).
9. Aben, P. C., Platteeuw, J. C., and Stouthamer, B., *Int. Congr. Catal., 4th* (Moscow) *1968,* Pap. 31.
10. Gomez, R., and Figueras, F., *C. R. Acad. Sci., Ser. C* **275,** 769 (1972).
11. Figueras, F., Gomez, R., and Primet, M., *Advan. Chem. Ser.* **121,** 480 (1973).
12. Boudart, M., Aldag, A., Benson, J. E., Dougharty, N. A., and Harkins, C. G., *J. Catal.* **6,** 92 (1966).
13. Barbaux, Y., Roger, B., Beaufils, J. P., and Germain, J. E., *J. Chim. Phys.* **67,** 1041 (1970).
14. Samanos, B., Boutry, P., and Montarnal, R., *C. R. Acad. Sci., Ser. C* **274,** 575 (1972).
15. Charcosset, H., Bolivar, C., Frety, R., and Gomez, R., *Conf. Vac. Microbalance Tech. 10th* (Uxbridge, England) *1972,* Pap. 21.
16. Sermon, P. A., *J. Catal.* **24,** 460 (1972).
17. Sermon, P. A., *J. Catal.* **24,** 467 (1972).
18. Benson, J. E., and Boudart, M., *J. Catal.* **4,** 704 (1965).
19. Benson, J. E., Hwang, H. S., and Boudart, M., *J. Catal.* **30,** 146 (1973).
20. Barbaux, Y., Roger, B., Beaufils, J. P., and Germain, J. E., *J. Chim. Phys.* **67,** 1035 (1970).
21. Mears, D. E., and Hansford, R. C., *J. Catal.* **9,** 125 (1967).
22. Wilson, G. R., and Hall, W. K., *J. Catal.* **17,** 190 (1970).
23. Korus, R. M., and Nowak, E. J., *J. Chem. Eng. Sci.* **22,** 470 (1967).
24. Kubicka, H., *J. Catal.* **12,** 223 (1968).
25. Ferreira, J. M., Peralta, A., and Gomez, R., unpublished data.
26. Sinfelt, J. H., *J. Catal.* **29,** 308 (1973).