JOURNAL OF CATALYSIS **37,** 22–36 (1975)

A Study of Benzene Hydrogenation and Identification of the Adsorbed Species with Pt/Al_2O_3 Catalysts

J. M. BASSET, G. DALMAI-IMELIK, M. PRIMET AND R. MUTIN

Institut de Recherches sur la Catalyse, 39, Bd. du 11 Novembre 1918
69100-Villeurbanne, France

Received September 24, 1973; revised April 18, 1974

The turnover number for benzene hydrogenation over various Pt/alumina catalysts has been found to be constant. It does not depend upon the particle size distribution which varied considerably in the "mitohedral" range (10–50 Å), nor did it vary either with the complex of impregnation (H_2PtCl_6) or $Pt(NO_2)_2(NH_3)_2$, or with the chlorine content. The value obtained is very close to that obtained by other authors. The results confirm that benzene hydrogenation is a structure-insensitive reaction. Various infrared investigations have explained the "facile" character of the reaction: all the surface platinum atoms are active sites for benzene or hydrogen adsorption. Benzene is adsorbed on a single platinum atom (as for π arene complexes) with a global transfer of electrons toward platinum, and there is no surface steric requirement for adsorption. Hydrogen responsible for the catalytic activity is reversibly and weakly adsorbed.

In 1966 Boudart *et al.* (*1*) developed a new concept in heterogeneous catalysis concerning "structure-sensitive" and "structure-insensitive" reactions. According to this concept a structure-insensitive or "facile" reaction may be defined as one for which the specific activity of the catalyst is practically independent of its mode of preparation (*2*). In other words for such a facile reaction all the surface atoms are considered to be active sites in the catalytic reaction without any dependence on the coordination number of the metallic site or on the collective properties of the crystallite. If the "turnover number" for a given reaction is characteristic of one metal, without any dependence on its method of preparation, it could be possible in the future to compare in a meaningful way the specific activity of various metals.

The most interesting result leading to this concept of catalysis concerns benzene hydrogenation on supported platinum which has been found by Poltorak, Boronin and Mitrofanoya (*3*) as a facile reaction. This result was corroborated by Aben, Platteuw and Stouthamer (*4*), but in a recent publication (*5*) they observe some anomaly in the case of ultradispersed catalysts ($d < 10$ Å). According to them, the platinum surface may well be heterogeneous to the adsorption of hydrogen: only the platinum sites which are able to adsorb hydrogen weakly are active for benzene hydrogenation. Working with Pt/SiO_2, Dorling and Moss (*6*) found also a constant specific activity of Pt for this reaction when the catalyst was fired below 400°C. Above this temperature of calcination, the specific activity was decreasing, suggesting a kind of structural effect.

We report here our own results concerning benzene hydrogenation on alumina-supported platinum. Platinum dispersion was estimated from chemisorption measurements but also from electron microscopic studies which allowed us to detect platinum particles with a diameter as low as 5 Å. Furthermore we tried to explain by infrared investigations how benzene and hydrogen are adsorbed on platinum and to know whether, and to what

Copyright © 1975 by Academic Press, Inc.
All rights of reproduction in any form reserved.

extent, benzene hydrogenation must be considered as a facile reaction.

EXPERIMENTAL METHODS

a. Catalysts

Various sets of catalysts were prepared. Some properties are given in Table 1 (columns 1, 2, 3). The catalysts are indexed as follows: A 100 represents a catalyst of series A with 1.00% Pt, etc.

Catalysts A were obtained by impregnation of a γ-alumina ($S = 300$ m^2/g, mean pore diameter $= 30$ Å, pore volume $= 0.45$ ml/g) with hexachloroplatinic acid. After a treatment at 100°C under vacuum they were reduced at 500°C under flowing hydrogen followed by a vacuum treatment at the same temperature. In this case there is a strong chemisorption of the platinum complex on the support (*16*). After reduction under hydrogen at 500°C the catalyst still retains a significant amount of chloride ions able to increase the acidic properties of the carrier (*17*). For samples containing 4% Pt, the chloride content is equal to 0.5×10^{-3} Cl^-/g corresponding to about 1 Cl^-/100 Å^2. If we consider that the maximum quantity of chloride that we can fix at the surface of an alumina ranges between 3 and 4 Cl^-/100 Å^2 (*18*), the probability to have an interaction Pt–Cl–Al for the high platinum content catalysts is not negligible.

Catalysts B were obtained by impregnation of the same γ-alumina with the complex $Pt(NO_2)_2(NH_3)_2$. After a treatment at 100°C in air, the complex was decomposed under vacuum by increasing the temperature slowly (5°/min) from room temperature to 570°C. A subsequent reduction at 570°C under hydrogen during 16 hr followed by a vacuum treatment at the same temperature gave a platinum/alumina catalyst which was free of chloride ($Cl^- < 3 \times 10^{-5}$ ion g/g). We have previously shown that during the impregnation the platinum complex precipitates over the alumina as a fiber (*14*). The decomposition under vacuum of the complex seems to be due to a redox reaction between NO_2 and NH_3 ligands producing nitrogen and water (*15*).

Catalysts C, used mainly for infrared

TABLE 1
CATALYST PROPERTIES

Catalyst	Wt % Pt	Alumina surface (m^2/g)	Chloride content 10^{-3} ion g Cl^-/g	Platinum dispersion % chemisorption	Metallic surface (m^2/g of cat.)	Av particle size (Å)	
						Chemisorption	Electron microscopy
A 025	0.25	300	0.1	59	0.41	17	
A 050	0.50	300	0.13	61	0.84	16.5	
A 100	1.0	300	0.25	67	1.85	15	15.5
A 200	2.0	300	0.32	65	3.60	15.5	15.4
A 300	3.0	300	0.40	67	5.50	15	16
A 400	4.0	300	0.50	47	5.20	22	18
B 025	0.25	300	<0.03	39	0.27	26	
B 050	0.50	300	<0.03	31.5	0.44	32	
B 100	1.0	300	<0.03	24.2	0.67	42	
B 200	2.0	300	<0.03	18.2	1	56	
B 300	3.0	300	<0.03	14.5	1.20	70	
B 400	4.0	300	<0.03	12.1	1.33	84	(87)
C 300	3.00	90		—	—	—	15
C 1000	10.00	90		—	—	—	30
D 500	5.0	105	<0.03	17.8	2.50	57	35

spectroscopy, were obtained in the same way as catalysts of series A except that the carrier was a δ-alumina (Degussa aluminum oxide *P*, 110 C, S... 90 m^2/g, nonporous, particle size = 150 Å).

Catalyst D was a commercial catalyst (Matheson Colman). It contained 5% Pt deposited on an alumina support of 100 m^2/g.

b. Metallic Surface Sites Determination

The number of surface platinum atoms was determined by the O_2–H_2 titration performed in a gravimetric system. The balance was an ultrahigh vacuum CAHN RG electrobalance able to work under controlled atmosphere in a large range of temperature and pressure. All the metallic parts of the balance were golden and greases were avoided by means of a liquid nitrogen trap situated between the balance and the vacuum and gas storage system. All the measurements were made under the same conditions of pressure (10^{-4} Torr) corresponding to species irreversibly adsorbed at room temperature (Pt–O, Pt–H).

The pretreatment procedure was the following: 300 mg of reduced sample were outgassed at room temperature under a vacuum of 10^{-5} Torr during 1 hr. Then the temperature was raised slowly (1°C/min) to 500°C. After 20 hr under vacuum at 500°C, 50 Torr of hydrogen were introduced into the balance during 10 hr. Finally, the catalyst was evacuated under 10^{-5} Torr, 20 hr, at the same temperature. After cooling to room temperature many titration cycles were performed at 25°C.

The following cycles were made. Oxygen was first introduced under 50 Torr and the equilibrium was reached in 3 to 4 min. After evacuation a new equilibrium was obtained in 10 min which gave the amount of oxygen irreversibly adsorbed. Then hydrogen was adsorbed under 50 Torr and evacuated. The procedure was repeated 5 to 6 times. Due to the gravimetric procedure employed only oxygen titration uptakes were used for dispersion determination.

c. Electron Microscope Technique

The catalysts were examined in an electron microscope JEM 100 B. Two techniques of sample preparation were used, namely, direct examination and extractive replica technique (*11*). In the direct method, a portion of the catalyst is ground in a mortar, and dispersed in butyl alcohol by ultrasonic treatment. A drop of this suspension is put on a carbon collodion film and dried. The extractive replica technique consists of evaporating under vacuum a carbon film on the catalyst. After immersing in dilute HF, the carbon film was separated from the alumina carrier and the platinum particles remained on the carbon film. It was shown by means of this technique that all the platinum particles were extracted from the support. Platinum particles having a diameter as low as 5 Å could be detected.

The pictures were taken at an enlargment of 120,000 to 180,000. The subsequent photographic enlargments resulted in a final magnification of 500,000 ± 5%.

Many pictures of each sample were taken (at least 20) and the distribution of particle size was determined by measuring the size of at least 1000 particles.

Assuming that the particles are spherical and denoting the particle diameter by d_i and the number of particles of each diameter increment by n_i, the surface average diameter is given by

$$d_s = \frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2}.$$

d. Infrared Spectrosopy

This spectroscopic method was used to identify the state of adsorption of hydrogen and benzene on the platinum surface. The technique used for the preparation of the discs of catalyst has already been described (*13*). In order to avoid pollution of the catalyst, we used sample holders made of quartz. For the same purpose the tightness of CaF_2 discs was obtained with viton O rings or with epoxy resin (Torr Seal from Varian). The various gases used were dried before each experiment on molecular sieves (5A Zeolite, Union Carbide).

In all cases the standard treatment was the following: 500°C under hydrogen for 16 hr followed by a vacuum treatment at the same temperature. The adsorptions were performed after cooling the sample to room temperature.

e. Kinetics Study

Rates of benzene hydrogenation were measured by means of a differential microreactor. Weighed samples of catalyst ranging from 30 to 200 mg were introduced into the reactor, the amount of catalyst being kept as low as possible so that the conversion was always lower than 5%. The standard activation procedure consisted of a treatment at 500°C during 16 hr under flowing nitrogen followed by a treatment at 400°C during 3 hr under hydrogen flow. The activity was measured at 50°C for a hydrogen pressure of 704 Torr and a benzene pressure of 56 Torr. In our experimental conditions the order in respect to benzene was zero.

We must point out here that all the catalysts were first reduced before being tested for catalytic activity or before being studied by electron microscopy. One might wonder whether the variations in pretreatment temperature could bring some differences of structure in the platinum particle. However, it was shown by ir spectrocopy that for a prereduced catalyst, a secondary treatment with hydrogen between 400 and 530°C did not cause any change in the intensity of the $\nu(CO)$ band corresponding to CO adsorbed on platinum.

RESULTS AND INTERPRETATIONS

A. Characterization of the Catalysts

Electron microscopy examination showed that the catalysts of series A are very homogeneous (Plate 1). The Pt particle size distribution in the surface of catalysts A (examples for A_{100} and A_{200} are given in Fig. 1) is very narrow, with a maximum situated between 15 and 19 Å. The B series is less homogeneous (Plate 2). The amplitude of the platinum size distribution in the surface is wide and some multiple distributions are visible (Fig. 1, expt. on B 400). The samples contain both very small particles ($\phi < 10$ Å) and larger ones ($\phi > 60$ Å). However, few particles having a diameter as high as 500 Å are present. For this reason we have only given one mean calculated diameter.

The platinum size distribution of the commercial catalyst is also very narrow: most of the particles have a diameter which ranges between 35 and 45 Å.

The catalysts used for the ir experiments consisted of Pt crystallites deposited on the surface of alumina spheres (Plate 3). The mean diameter of the Pt crystallites is 30 Å for catalyst C 1000 and 20 Å for catalyst C 300.

The results concerning the O_2–H_2 titration are given in Table 1. The platinum dispersion D% was defined as the ratio of surface metal atoms to the total number of metal atoms. Although the matter is still controversial (*7–10*), we have assumed that the stoichiometry (O irreversibly adsorbed)/(surface platinum) = (H irreversibly adsorbed)/(surface platinum) = unity was observed, that is:

$$\text{Pt–H} + \tfrac{3}{4}O_2 \rightarrow \text{Pt–O} + \tfrac{1}{2}H_2O.$$

The good agreement obtained for various catalysts between the average particle size deduced from the titration equation and the electron microscopy justifies

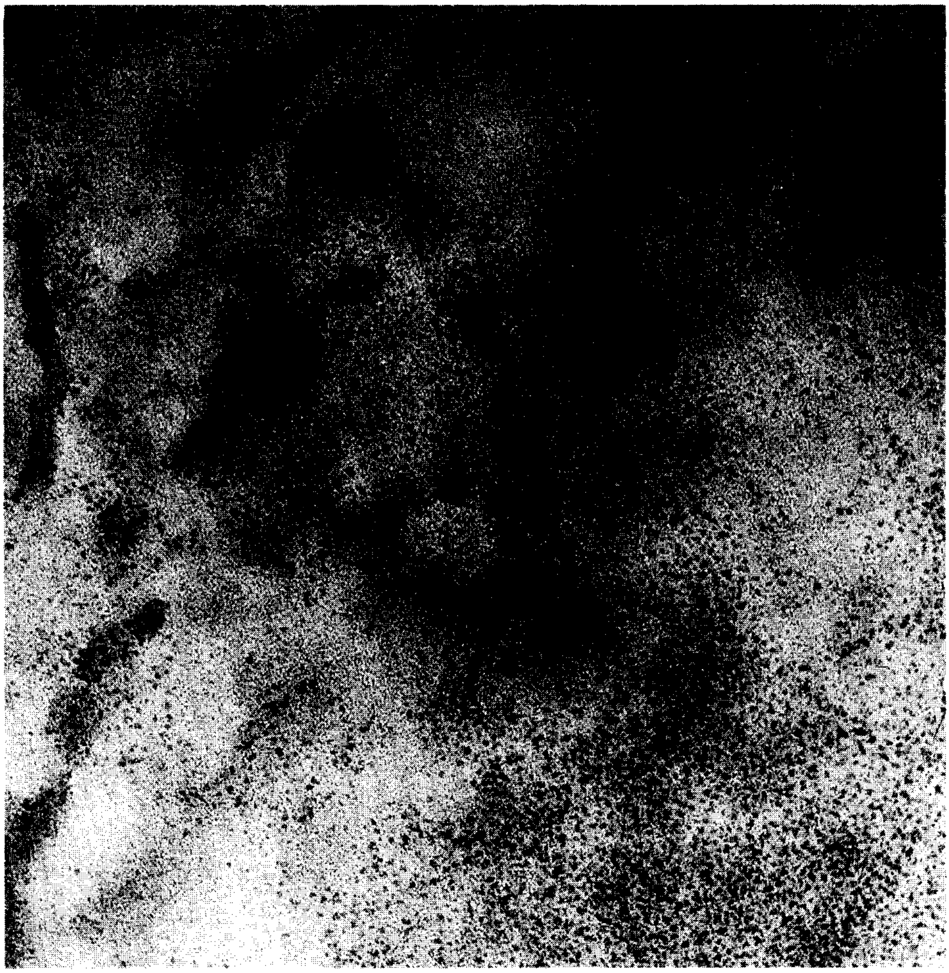


PLATE 1. Catalyst A 200 magnification 500,000 (replica technique).

this assumption: the ratio O_{irr}/Pt_s does not seem to vary with the particle size in the dimension range studied.

Catalysts A have a fairly good dispersion except for the sample containing 4% Pt. It is interesting to notice that an almost constant dispersion of about 65% is observed for a very wide range of platinum content (from 0.25 up to 3% Pt). For the catalysts B the dispersion is rather poor and is decreasing when the platinum content increases.

The platinum area as well as the average particle size in the surface can be deduced from the chemisorption measurements if we make the following assumptions: (111), (110), (100) are the only exposed crystal faces, and they are equally distributed.

The average diameter is equal to $6/\rho A$ (ρ is the volume weight of Pt and A the metallic area).

The results concerning the metal area are given in Table 1. A 20-fold factor is obtained between the lowest B 025 and the highest A 300 platinum surface.

B. Catalytic Activity for Benzene Hydrogenation

The behavior of the reaction rate with time was the same for all the catalysts

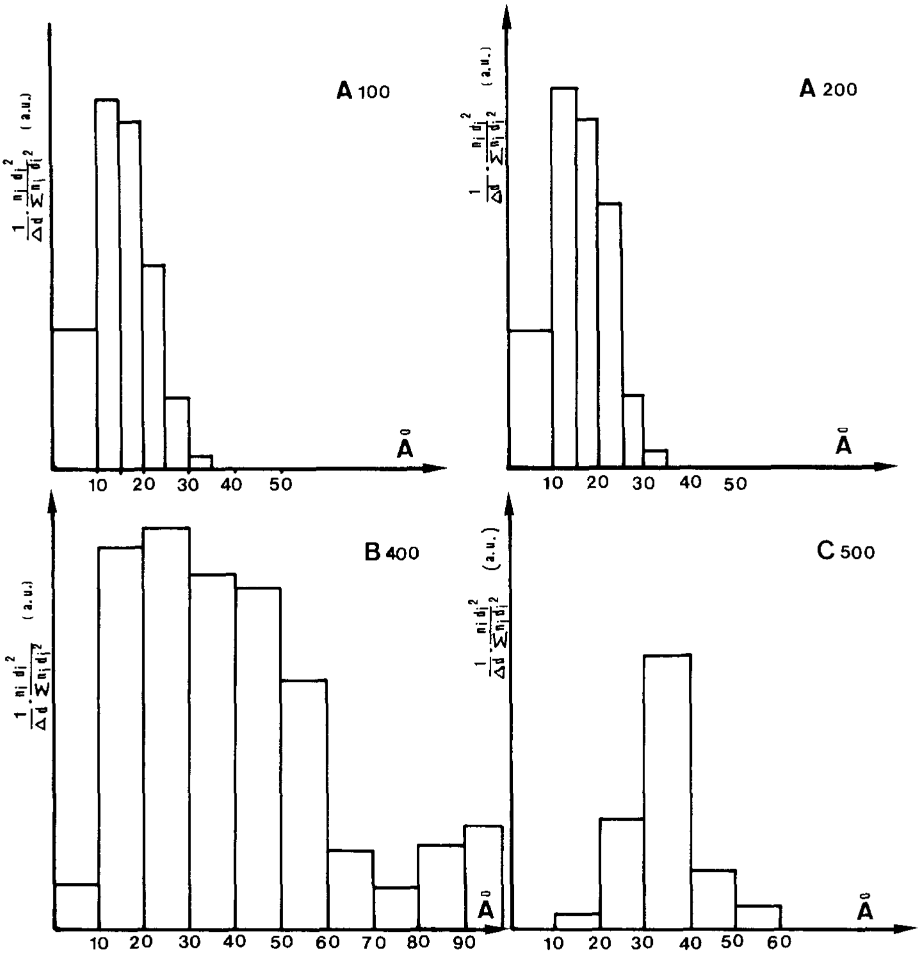


FIG. 1. Particle size distribution in surface for various catalysts.

studied. After a slight decay during the first 15 min the rate was almost constant for 1 hr. We used the value of the activity at this plateau to determine the "turnover number," which is the number of molecules of benzene transformed into cyclohexane in 1 hr at 50°C per platinum site. The results for most of the catalysts are given in Fig. 2. The turnover number is equal to (800 ± 50) molecules of benzene/hr for all the solids studied: a 20-fold factor in the platinum area does not affect the specific activity: this proves definitely that no mass transfer limitation occurs in our experimental conditions (*19*). This activity per platinum site does not depend on the complex used for impregnation (H_2PtCl_6 or $Pt(NO_2)_2(NH_3)_2$). Nor does it depend either on the platinum dispersion (12–67%), the particle size distribution, the surface of the alumina (105 and 330 m^2/g) or the chlorine content of the catalyst (0–0.5 × 10^{-3} ion g Cl$^-$/g).

The apparent activation energies were measured over a temperature range of 40°C. The value obtained (9.7 ± 0.5 kcal/mole) does not depend on the method of preparation of the sample (Table 2).

Dorling and Moss (*6*) have determined the specific activity of platinum for benzene hydrogenation in the case of platinum deposited on silica. Since their experi-

PLATE 2. Catalyst B 400 magnification 500,000 (replica technique).

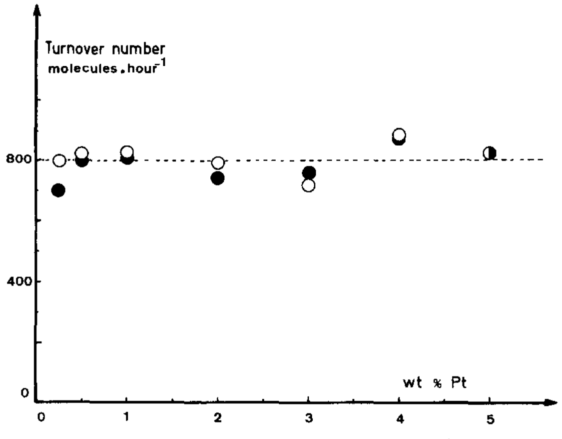


FIG. 2. Turnover number for various catalysts: (●) catalysts of series A; (○) catalysts of series B; (◑) catalyst D.

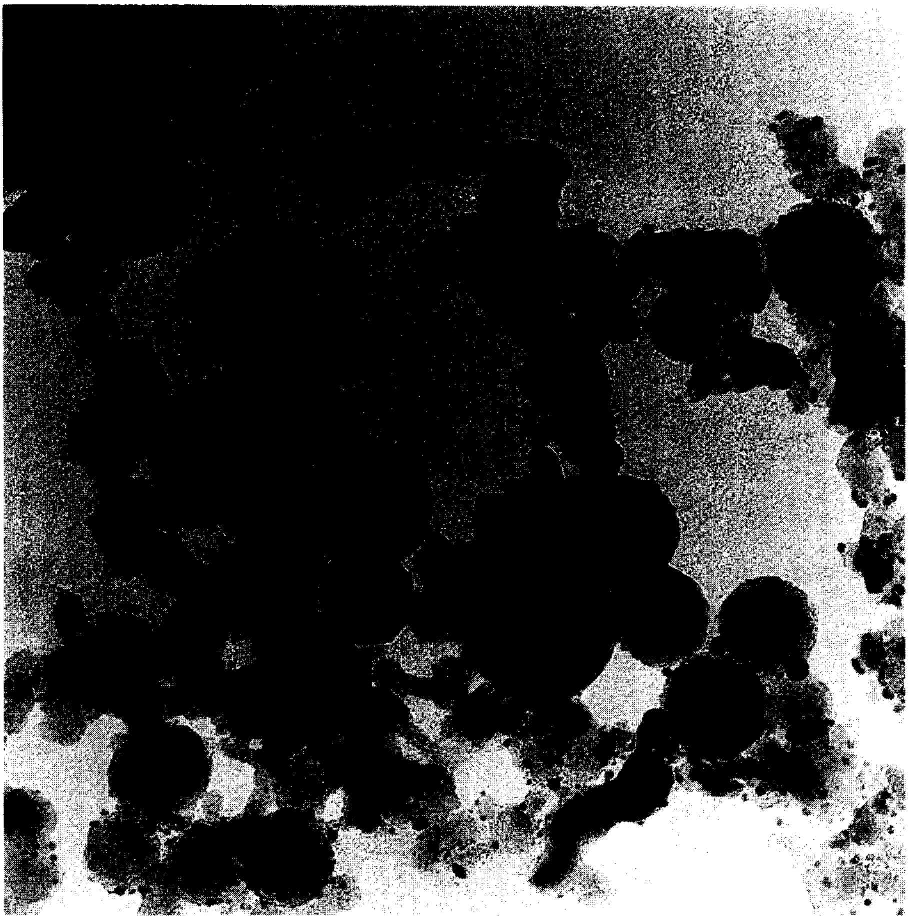


PLATE 3. Catalyst C 1000 magnification 500,000 (direct vision).

mental conditions are very close to ours ($P_{H_2} = 720$ Torr, $T^0 = 25°C$, $P_{C_6H_6} = 39$ Torr) the extrapolation of their results to a temperature of 50°C assuming an apparent activation energy of 9.7 kcal/mole is intersting. The value of turnover number obtained, 517 molecules/hr, is in reasonable agreement with our result (800 ± 50 molecules/hr), especially if we consider the fact that their support was silica and that their platinum dispersion was estimated from CO chemisorption.

TABLE 2
APPARENT ACTIVATION ENERGY FOR BENZENE HYDROGENATION WITH VARIOUS CATALYSTS

Catalysts:	A 025	A 100	A 400	B 025	B 400
Apparent activation energy (kcal/mole)	10	9.5	10	10	10.2

C. Investigation of the Adsorbed Species by Infrared Spectroscopy

a. Hydrogen Adsorption on Platinum

As mentioned in an earlier publication (*13*), among the various forms of hydrogen adsorbed on platinum only the reversible form can be detected by infrared spectroscopy; the band corresponding to this adsorbed species is situated at 2120 cm^{-1} (*20*). It is usually ascribed to the species Pt–H, the atomic hydrogen being right above each surface platinum atom. At

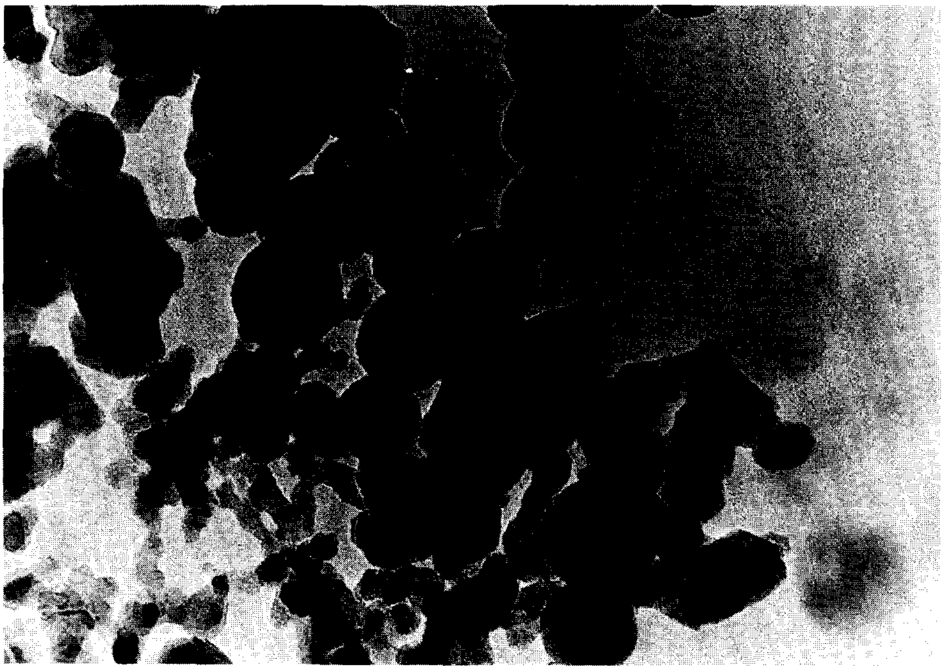


PLATE 4. Carrier of the catalyst C 1000, magnification 500,000 (direct vision).

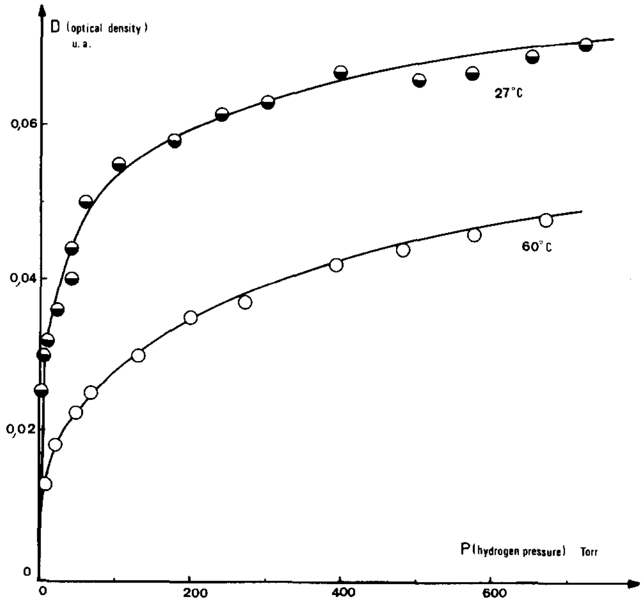


FIG. 3. Pressure dependence of the amount of hydrogen reversibly adsorbed (characterized by the 2120 cm^{-1} band).

room temperature this band can be detected only when the equilibrium pressure is higher than 10^{-1} Torr. For such a pressure a monolayer of hydrogen irreversibly adsorbed ($\Delta H < -18$ kcal/mole) is already attained, and the band corresponds to a species which is weakly ($\Delta H > -10$ kcal/mole) (*7*) and reversibly adsorbed.

By infrared spectroscopy the pressure dependence of the amount of reversibly adsorbed hydrogen was studied. In Fig. 3 this pressure dependence of the 2120 cm^{-1} band is shown for the two temperatures 27 and 60°C. The amount of hydrogen reversibly adsorbed is increasing notably with hydrogen pressure, and the isotherm is completely reversible. Similar experiments have been performed on various Pt catalysts and a good reproducibility was observed.

b. Benzene Adsorption on Platinum

Interaction between benzene and supported platinum has already been the object of various infrared investigations. Erkelens and Eggink-Du Burk (*21*) assumed a strong dissociation of the C–H bands giving rise to self-hydrogenation. They postulated also a reaction between the hydrocarbon and hydrogen adsorbed on the platinum.

Sheppard *et al.* (*22*) find that benzene irreversibly adsorbed on Pt/SiO_2 gives a single weak and broad band near 3040 cm^{-1}. Upon interaction with H_2 all bands from aromatic C–H bands were removed with formation of a stronger CH_2 spectrum. The results obtained are consistent with σ or π bonding interpretation but for intensity arguments the authors retain the hypothesis of a π bonded surface aromatic complex.

In our case all the intensity of the bands corresponding to benzene adsorbed on platinum was too low so that their modifications could not be easily detected. Besides, the carrier adsorbs a significant amount of benzene (*31*), as is also known for silica (*23*).

c. Reaction Between H_2 and Benzene

In a typical experiment benzene was adsorbed on C 1000 at room temperature and evacuated at the same temperature. Hydrogen adsorption resulted in the appearance of bands at 2930 and 2840 cm^{-1} corresponding to adsorbed and gaseous cyclohexane. We must conclude, therefore, that benzene was adsorbed on platinum but not easily detected by ir.

In another experiment hydrogen was adsorbed first on C 1000 and evacuated at room temperature. Benzene adsorption on this surface precovered with hydrogen irreversibly adsorbed did not cause the appearance of any band attributable to gaseous or adsorbed cyclohexane. However, subsequent introduction of molecular hydrogen resulted in the appearance of the bands of cyclohexane, indicating that benzene was in fact adsorbed on the hydrogen-covered platinum surface without formation of cyclohexane.

D. Indirect Investigation of the Adsorbed Species by Infrared Spectroscopy: Competitive Adsorption of CO and Reactants

In a previous paper (*24*) we have explained how CO can be used to determine the interaction metal-adsorbates. When CO is previously adsorbed on platinum ($\theta_{CO} = 0.2$) the subsequent adsorption of Lewis bases or electron donor molecules increases the electronic density of the platinum particles. The back-bonding of metal *d* electrons to antibonding orbitals of CO is thus increased and the ν(CO) vibration is shifted to lower frequencies. The extent of the shift is therefore increasing with the electronic density of the metal particle.

a. Interaction Between CO and Benzene

For this study, a known amount of CO was adsorbed on the catalyst C 300 so that the final platinum coverage was equal to 0.2 (assuming that the CO is not irreversibly adsorbed on the alumina support). Benzene adsorption at room temperature on this solid followed by evacuation at the same temperature shifted the ν(CO) band from 2065 to 2025 cm^{-1} (Fig. 4). The treatment under hydrogen produced instantaneously two bands at 2930 and 2840 cm^{-1}, attributable to cyclohexane which was easily desorbed under vacuum at room temperature. After this treatment the ν(CO) band recovered almost its initial frequency (2055 cm^{-1}) and intensity. This result indicates that benzene is adsorbed on platinum by a mechanism which implies a global transfer of electrons to the metal. Furthermore the adsorbed species which is responsible for this electron transfer is also the adsorbed species active for the catalytic reaction, since the hydrogenation of benzene into cyclohexane suppresses this electron transfer.

In order to study the thermal stability of this adsorbed benzene the following experiment was performed: the catalyst C 300 was contacted with 100 Torr of CO at room temperature and evacuated at 350°C for 10 hr. The resulting ν(CO) band had a frequency of 2050 cm^{-1} (Fig. 5); benzene

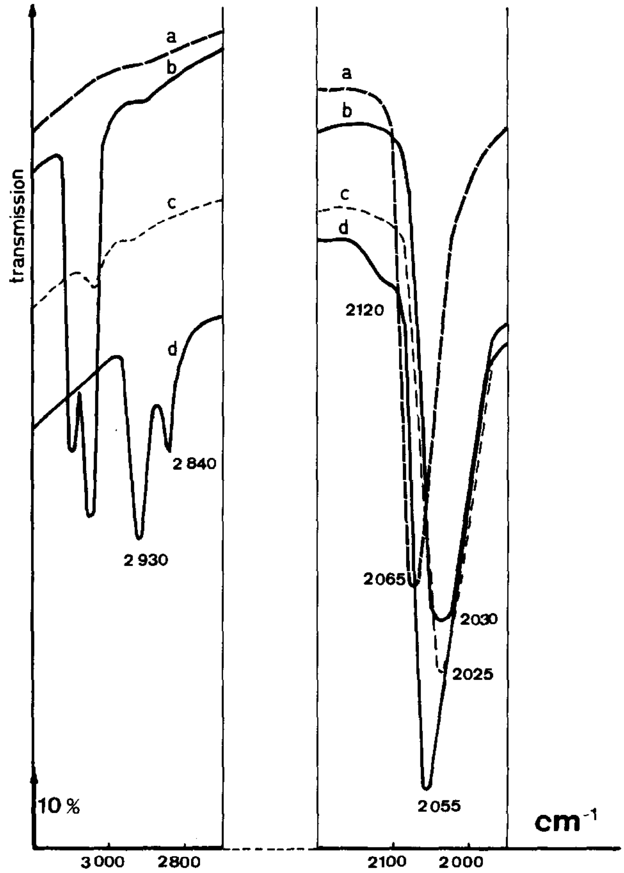


FIG. 4. Infrared spectrum of solid C 300: (a) adsorption of CO ($\theta_{CO} = 0.2$); (b) after introduction of C_6H_6 (50 Torr); (c) after evacuation at room temperature; (d) after introduction of hydrogen (50 Torr) at room temperature.

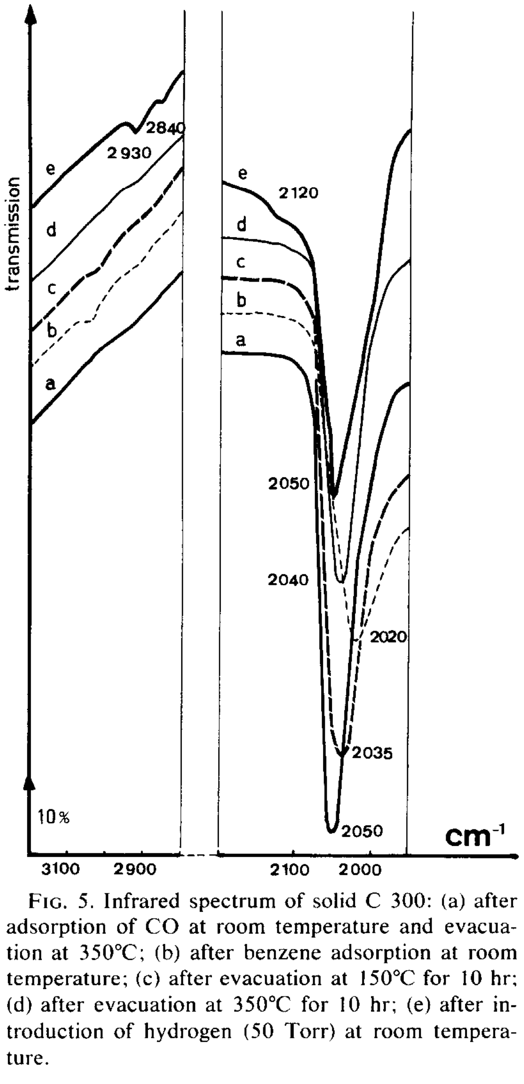


FIG. 5. Infrared spectrum of solid C 300: (a) after adsorption of CO at room temperature and evacuation at 350°C; (b) after benzene adsorption at room temperature; (c) after evacuation at 150°C for 10 hr; (d) after evacuation at 350°C for 10 hr; (e) after introduction of hydrogen (50 Torr) at room temperature.

adsorption at room temperature shifted the band to 2020 cm^{-1}. The solid was then evacuated at increasing temperatures and the ν(CO) band was progressively shifted to higher frequencies which means that benzene was progressively desorbed from the platinum surface. At 350°C the ν(CO) band had not recovered its initial frequency suggesting that benzene was still present on the surface to a certain extent. Indeed, hydrogen adsorption produced cyclohexane detected by bands at 2930–2850 cm^{-1} and instantaneously shifted the ν(CO) band at 2050 cm^{-1}.

In order to compare the strength of the bonds Pt–benzene and Pt–CO two sets of experiments were made. In a first experiment CO was adsorbed at room temperature on C 300 at a pressure of 50 Torr. The evacuation at room temperature did not cause any appreciable decay of the intensity, which supports the hypothesis of a strong and irreversible adsorption ($\theta_{CO} = 1$). Benzene adsorption on this surface covered with CO did not shift the ν(CO) band. After a vacuum treatment at room temperature during 10 min hydrogen was introduced into the cell, but no band indicating the presence of cyclohexane was observed. This result seems to show that the sites responsible for the adsorption of CO are also the sites responsible for the adsorption of benzene, but the latter, less strongly adsorbed, does not displace CO.

This last result has been corroborated by inversing the order of introduction of the reactants. The catalyst was contacted with benzene at room temperature. After a vacuum treatment during 10 min, CO was introduced into the cell. The resulting ν(CO) band had the same frequency and intensity as for CO on bare platinum, suggesting that benzene was displaced by CO. In fact after evacuation a treatment under hydrogen at room temperature did not cause the formation of cyclohexane and did not produce any modification of the infrared spectrum.

b. Interaction Between CO and H_2

Hydrogen adsorption at room temperature on a solid previously treated with a known amount of CO (so that $\theta_{CO} = 0.2$) did not cause any appreciable shift of the ν(CO) frequency and intensity. However, an infrared band at 2120 cm^{-1} indicated that hydrogen was also adsorbed on platinum. The lack of shift of the ν(CO) band upon subsequent adsorption of hydrogen indicates no significant electron transfer from hydrogen reversibly adsorbed to platinum.

If C 300 was treated with CO so that the platinum coverage by CO was unity, hydrogen adsorption did not cause a shift of the ν(CO) frequency either. But in this case no band at 2120 cm^{-1} was observed: the metal sites responsible for the adsorption of CO are also the adsorption sites of hydrogen reversibly and weakly adsorbed.

DISCUSSION

The purpose of this work was to determine whether or not benzene hydrogenation on platinum can be considered as a facile reaction (and to what extent) and if so, to try to explain why in a mechanistic way.

The first result concerns the constancy of the turnover number for the various solids studied. As pointed out by Poltorak, Boronin and Mitrofanoya (*3*) in the "mitohedral method" the properties of surface atoms in crystals depend on their coordination number and collective properties of the lattice. In order to be able to compare the specific activity of the surface atom one has to be sure that the collective properties are not varying in the range of crystal sizes considered. According to Poltorak, Boronin and Mitrofanoya (*3*) the metal lattice possesses an approximately constant specific activity beginning from particles 15–20 Å. The conclusion, therefore, is that the most meaningful results are those which concern particle sizes in the range 20–50 Å; it is in this range of particle size that the most important structural changes in surfaces must be expected.

We can see easily from our particle size distribution curves that we have very different distributions in the range 10–50 Å. The catalyst B 400 has a very wide distribution: 60% of the platinum surface corresponds to particles having diameters ranging between 15 and 55 Å. The catalysts of series A have a very narrow distribution. For the catalysts A 100 and A 200, 90% of the platinum surface corresponds to particles having a diameter lower than 25 Å.

The catalyst D has also a relatively narrow distribution. In this case, about 70% of the metallic surface corresponds to particles ranging between 25 and 45 Å. We consider, therefore, that in the "mitohedral" region determined on a meaningful basis by electron microscopy the specific activity of platinum does not depend at all on the relative number of atoms in different states of the surface (vertices, edges, facets). We are dealing here with a facile reaction and the low variation between the turnover numbers observed between Dorling and Moss (*6*) and ourself supports this conclusion.

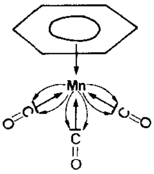
Another feature which deserves to be pointed out is the lack of influence of the nature of the complex of impregnation on this specific activity of platinum: the chlorine content does not play any role on the specific activity. However, it is necessary to say that if we do not know where chlorine is adsorbed (on platinum, on alumina or on both) it is impossible to go further in the interpretation. In fact we have now evidence that chlorine can also be adsorbed on platinum with modification of the oxidation state of Pt (*25*) and therefore one has to be cautious when trying to interpret the data on the basis of platinum-support interactions.

Assuming now that benzene hydrogenation is a "facile" reaction, this result must be explained in a mechanistic way.

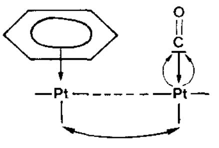
If we consider the numerous kinetic studies of benzene hydrogenation over supported platinum (*4,6,26*), the authors usually agree that the reaction is zero order with respect to benzene and fractional order (sometimes unity) with respect to hydrogen.

Consequently the slow step is certainly the surface reaction between adsorbed benzene ($\theta = 1$) and adsorbed hydrogen ($\theta \leqslant 1$). The constancy of the turnover number suggests that all the surface sites able to chemisorb irreversibly hydrogen or oxygen at room temperature can act as active sites for the catalytic reaction. Since both compounds react in the adsorbed state it results that there should not be any steric requirement for the adsorption of the two reactants. Our infrared data are able to explain this result, which is rather surprising, especially if one keeps in mind the theory of Balandin and Brussow (*27*).

First let us consider benzene adsorption on platinum: the infrared data indicate clearly that the adsorption of benzene takes place with a global transfer of electrons from benzene to platinum and the species responsible for this transfer is also the adsorbed species responsible for the catalytic hydrogenation. Many authors (*28–30*) have already suggested the existence of a π complex for benzene adsorption on platinum. However, the π complex which is suggested is assumed to be a kind of weak adsorption of benzene. In fact a back bonding of metal *d* orbitals to benzene π^* orbitals could explain the very high thermal stability of adsorbed benzene: in this case the electron transfer would be towards the metal. It would be a "surface complex" very close to π arene complexes (Scheme I) and there would not be any steric requirement for the adsorption of one benzene molecule above one platinum (Scheme II). Such a comparison with stable arene complexes has in fact already been proposed by Rooney and Webb (*28*). The interaction between adsorbed benzene and CO would proceed through the lattice, according to a process which is similar to that obtained in the case of π arene carbonyl complexes of maganese:



SCHEME I



SCHEME II

The benzene would be adsorbed flat as can be suggested from the results of Pitkethly and Goble (*31*).

The fact that the ratio (adsorbed benzene)/Pt_s is lower than unity (*31*) is likely to be due to the size of benzene which "prevents" the adsorption of another molecule on an adjacent platinum atom. But, as suggested from the competitive adsorption of CO, all the platinum atoms are potential sites for strong benzene adsorption and the zero order obtained is easily justified.

Concerning the nature of adsorbed hydrogen active for hydrogenation, various results suggest that it is hydrogen weakly and reversibly adsorbed. Indeed, there is no catalytic hydrogenation when benzene is adsorbed on a surface covered with hydrogen irreversibly adsorbed. Besides, the fractional order with respect to hydrogen indicates that the surface coverage with the "reactive" form of adsorbed hydrogen is pressure dependent. Our infrared data show clearly that the species responsible for the 2120 cm^{-1} band obeys this requirement.

Aben, Platteuw and Stouthamer (*4*) deduced from their kinetic data that the heat of adsorbed hydrogen responsible for the catalytic activity in benzene hydrogenation was equal to 10 kcal/mole H_2. We found by calorimetry (*7*) for hydrogen reversibly adsorbed, characterized by the 2120 cm^{-1} band, a heat of adsorption equal to 10 kcal/mole H_2 which is broadly in agreement with the deductions of Aben, Platteuw and Stouthamer.

As for benzene all the platinum surface sites are able to adsorb reversibly hydrogen. The lack of ν(CO) shift after adsorption suggests that this hydrogen is covalently bonded to platinum without significant electron transfer to, or from, the metal.

CONCLUSION

It seems that the most likely mechanism for benzene hydrogenation is the one in which benzene and hydrogen are adsorbed on two adjacent platinum sites. Benzene interacts with only one platinum atom by means of a π complex and the surface geometry would have no effect on the rate of reaction: all the platinum atoms would be active for the reaction. However, another effect, which we can refer to as "electronic," could be the modification of the chemisorption properties of platinum as a function of the metal particle size: a careful study should be made in the range 5–20 Å to determine whether or not the adsorptive properties of Pt are modified in this range of particle size and to look for the interactions with the support which might be detectable in this case.

REFERENCES

1. Boudart, M., Aldag, A., Benson, J. E., Dougharty, N. A., and Harkins, C. G., *J. Catal.* **6**, 92 (1966).
2. Boudart, M., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 20, p. 153. Academic Press, New York, 1969.
3. Poltorak, O. M., Boronin, U. S., and Mitrofanoya, A. N., *Proc. Int. Congr. Catal., 4th,* (Moscow) *1968,* **2**, p. 276 (1971). (Pap. 68).
4. Aben, P. C., Platteuw, J. C., and Stouthamer, B., *Proc. Int. Congr. Catal., 4th,* (Moscow) *1968,* **1**, 395 (1971). (Pap. 31).
5. Aben, P. C., van der Eijk, H., and Oelderik, J. M., *Proc. Int. Congr. Catal., 5th* (Palm Beach, FL) *1972,* p. 717 (1973). (Pap. 48).
6. Dorling, T. A., and Moss, R. L., *J. Catal.* **5**, 111 (1966).
7. Basset, J. M., Theolier, A., Primet, M., and Prettre, M., *Proc. Int. Congr. Catal., 5th* (Palm Beach, FL) *1972,* p. 915 (1973). (Pap. 63).
8. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).
9. Mears, D. E., and Hansford, R. C., *J. Catal.* **9**, 125 (1967).
10. Wilson, G. R., and Hall, W. K., *J. Catal.* **17**, 190 (1970).
11. Dalmai-Imelik, G., and Leclercq, C., *J. Microsc.* 306 (1972).
12. C. Magnan, "Traité de Microscopie Électronique" Hermann, Paris, 1961.
13. Primet, M., Basset, J. M., Mathieu, M. V., and Prettre, M., *J. Catal.* **28**, 368 (1973).
14. Dalmai-Imelik, G., and Leclercq, C., *Congr. Int. Microsc. Electron., 7th,* (Grenoble) *1970.*
15. Mutin, R., Basset, J. M., Primet, M., Mathieu, M. V., and Prettre, M., *Rev. Chim. Min.* **7**, 1101 (1970).
16. Mutin, R., thesis C.N.A.M., Lyon, 1970.
17. Basset, J. M., Naccache, C., Mathieu, M. V., and Prettre, M., *J. Chim. Phys.* **66**, 1264 (1969).
18. Basset, J. M., Mathieu, M. V., and Prettre, M., *Rev. Chim. Miner.* **5**, 879 (1968).
19. Spenadel, L., and Boudart, M., *J. Phys. Chem.* **64**, 204 (1960).
20. Pliskin, W. A., and Eischens, R. P., *Z. Phys. Chem.* **24**, 11 (1960).
21. Erkelens, J., and Eggink-Du Burk, S. H., *J. Catal.* **15**, 62 (1969).
22. Sheppard, N., Avery, N. R., Clark, M., Morrow, B. A., Smart, R. St. C., Takenaka, T., and Ward, J. W., "Symposium on Chemisorption and Catalysis," London, 1970.
23. Galkin, G. A., Kiselev, A. V., and Lygin, V. I., *Russ. J. Phys. Chem.* **36**, 951 (1962).
24. Primet, M., Basset, J. M., Mathieu, M. V., and Prettre, M., *J. Catal.* **29**, 213 (1973).
25. Basset, J. M., and Primet, M., unpublished data.
26. Amano, A., and Parravano, G., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, V. I. Komarewsky and P. B. Weisz, Eds.), Vol. 9, pp. 7, 16. Academic Press, New York, 1957.
27. Balandin, A. A., and Brussow, J. J. Z., *Z. Phys. Chem.* **34**, 96, (1936).
28. Rooney, J. J., and Webb, G. J., *J. Catal.* **3**, 488 (1964).
29. Barnett, J. L., *Catal. Rev.* **5**, 229 (1971).
30. Shopov, D., and Andreev, A., *J. Catal.* **6**, 316 (1966); Volter, J., *J. Catal.* **3**, 297 (1964).
31. Pitkethly, R. C., and Goble, A. G., *Actes Int. Congr. Catal., 2nd,* (Paris) *1960,* **2**, 1851 (1961).
32. Figueras, F., Gomez, R., and Primet, M., *Proc. Int. Congr. Zeolites, 3rd, 1973.* (Pap. No. 43).