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Role of Molecular Interactions during the Preparation of Pd and Pt/Glass Hydrogenation Catalysts, in Determining the Physical State and Chemical Reactivity of the Metal

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Pd and Pt catalysts on vitreous materials, with measured physicochemical properties, have been prepared starting from the corresponding $M(C_3H_5)_2$ precursors. The catalytic activity in the hydrogenation of 1-hexene was found to be strictly dependent on the metal particle size determined by SAXS techniques. The preparative procedure for the catalysts which involves prior chemical interaction of $M(C_3H_5)_2$ with the –OH groups of the support is demonstrated to be the fundamental step in achieving a good metal dispersion (clusters <30 Å in diameter), the sorber $M(C_3H_5)_2$ species bearing larger and practically unreactive metal particles. The different chemical reactivity between small and large metal particles, suggested by catalysis data, is tested by the reaction of dispersed Pt metal with CO and phosphines to give carbonyl-phosphino complexes; this is discussed and compared with the chemical reactivity of known organometallic clusters.

INTRODUCTION

The availability of suitable supports for metallic catalysts is of fundamental importance in heterogeneous catalysis to modify the physical properties and the chemical reactivity of the metal. Indeed the physical properties of the support can be exploited for catalytic purposes and a better metal dispersion is expected on increasing the support's surface area (*1*, *2*).

We recently prepared from Si, Al, and Na alkoxides a number of vitreous materials useful as supports for Pd metal in the hydrogenation of olefins (*3*, *4*). The metal deposition was carried out analogously to Yermakov's method to prepare highly dispersed metals on silica (*5*), i.e., reacting purely organometallic allyl derivatives with the surface –OH groups of the support and then reducing the anchored allylic species with LiH or H_2.

$$\text{glass} \,|\!-\!OH + M(C_3H_5)_2 \rightarrow \text{glass} \,|\!-\!M(C_3H_5) + \text{propene} \quad (1)$$

$$\text{glass} \,|\!-\!M(C_3H_5) \xrightarrow{\text{LiH,H}_2} \text{highly dispersed metal} \quad (M = \text{Pd, Pt}) \quad (2)$$

The observed high catalytic activity of these materials was related to the high metal dispersion arising from Reaction (2), where the anchored molecular Pd(II) species generate "naked" atoms which collide and coalesce to stable, small clusters.

These phenomena have been suggested previously by Yermakov who, from magnetic measurements, determined in the case of nickel the presence of metal particles with diameters <20 Å (*6*). In a preliminary note, we reported that the Pd metal particle size on our supports was measured by small angle X-ray scattering (SAXS) and we found for these materials a direct relationship between the catalytic activity in the 1-hexene hydrogenation, the degree of metal dispersion, and the number of surface –OH groups of the support (*7*).

The extent of Reaction (1) is clearly determined by the relative ratio between

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the number of available surface -OH groups and the amount of $M(C_3H_5)_2$ introduced, i.e., the reaction is completed in terms of available metal only when the former exceeds the latter. Therefore the results cited above indicate that the chemical reactions that take place on the support during the preparation of the catalysts might play a prominent role in determining the catalytic activity.

To verify these premises a number of glasses have been prepared with different surface areas and holding different concentrations of the surface -OH groups. The glasses have been used for the preparation of catalysts according to Reactions (1) and (2). The physicochemical characterization has been carried out by SAXS measurements with the aim of verifying the above hypothesis on some relationship between the extent of Reaction (1) and the achievement of a high metal dispersion.

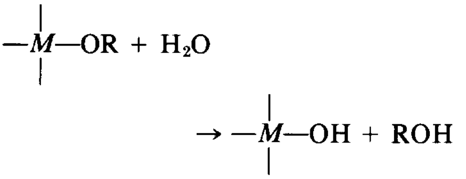
Since the catalytic activity of these materials is greatly increased on lowering the metal particle size (*7*), this implying a different chemical reactivity as a function of the particle dimensions, we have verified the possibility of preparing organometallic complexes via direct synthesis from highly dispersed metal.

Some of the results discussed herein have been reported in a preliminary account (*7*).

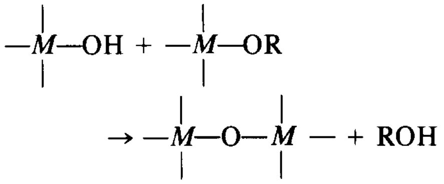
RESULTS AND DISCUSSION

Preparation and Characterization of the Supports

The supports were prepared upon hydrolysis and polycondensation of Si, Al, and Na alkoxides in alcoholic solution. The process is known to involve Reactions (3) and (4) and gives as product a transparent gel. This, when dehydrated by heating, turns into a vitreous material with large surface area and many residual hydroxide groups (*3, 7, 8*). The method is well documented and has been used recently in the synthesis of glasses (*8–10*).



$$-\overset{|}{\underset{|}{M}}-\mathrm{OR} + H_2O \rightarrow -\overset{|}{\underset{|}{M}}-\mathrm{OH} + \mathrm{ROH} \quad (3)$$



$$-\overset{|}{\underset{|}{M}}-\mathrm{OH} + -\overset{|}{\underset{|}{M}}-\mathrm{OR} \rightarrow -\overset{|}{\underset{|}{M}}-\mathrm{O}-\overset{|}{\underset{|}{M}}- + \mathrm{ROH} \quad (4)$$

$(M = \mathrm{Si, Al})$

The surface area was calculated from SAXS and BET measurements (Table 1). Since the examined samples refer to the same $SiO_2/Al_2O_3/Na_2O$ composition, the different surface areas arise from the different experimental conditions used during the preparation.

The surface -OH groups on inorganic supports can be determined either by indirect [ir spectroscopy (*11*)] or direct [titration with $TiCl_4$, BCl_3, or chlorosilanes (*12*)] methods. All these methods suffer from limitations, so that the determination of the exact numbers of -OH groups is in any case difficult because of different exposition and coordination of the hydroxyls on porous materials. We measured the H_2 evolution observed on reacting these supports with LiH in THF suspension. This volumetric method provides a very simple and direct analysis and is suitable even with low surface -OH contents. Owing to the heterogenity of the method, the reaction was carried out under consistent experimental conditions to ensure reliable data.

$$\text{glass} \,|\!-\mathrm{OH} + \mathrm{LiH} \rightarrow \text{glass} \,|\!-\mathrm{OLi} + H_2 \quad (5)$$

In Fig. 1 some typical H_2 evolution plots are reported. As shown, after a faster initial evolution the plot becomes almost linear and continues for long times: hence it is difficult to establish the end of Reaction (5). Thus we chose as a parameter directly

TABLE 1

Preparation Parameters and Physicochemical Properties of the Vitreous Supports

Sample	Heating rate (°C/hr)	Maximum heating temperature (°C)	Surface (m^2 g^{-1}) SAXS	Surface (m^2 g^{-1}) BET	-OH content (ml H_2 g^{-1} [a])
A_{240}	20	240	522	348	10.3
A_{450}	20	450	365	213	6.1
A_{650}	20	650	11	5.4	1.2
A_{950}	20	950	1	0.1	0.3
B_{230}	30	230	350	204	6.2
C_{230}	50	230	634	342	4.2

[a] See Reaction (5).

related to the surface -OH content the volume of H_2 evolved after 60 min (Table 1).

The physicochemical characteristics of these materials (namely, surface area and surface -OH groups) are both dependent on the extent of Reactions (3) and (4). In fact, as a general trend, we found that more rapid hydrolysis conditions lead to an increase in both these properties. Moreover as was previously observed (*3, 7, 8*) an increase in the maximum heating temperature results in lowering of both the -OH group content and surface area of these vitreous supports. These parameters are not strictly related and different surface areas can be obtained depending on the heating rate. We can predict only roughly the physicochemical properties of the reaction products.

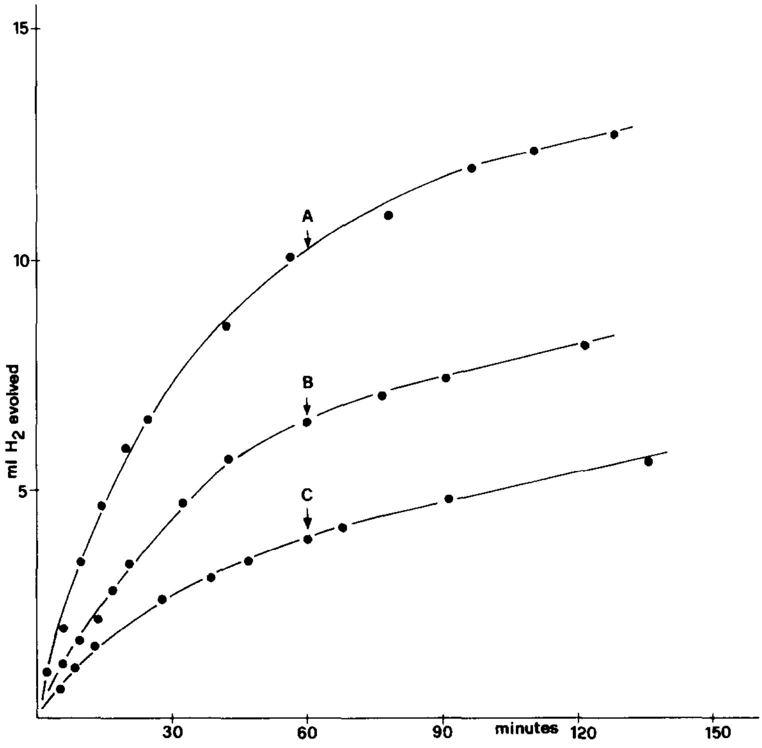
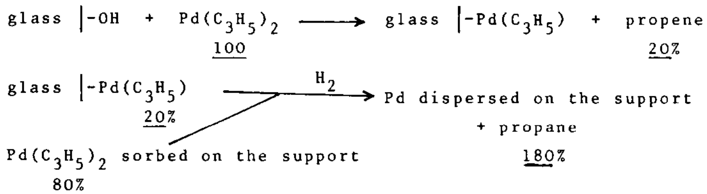


FIG. 1. H_2 evolutions vs time on reacting 1g of the supports with LiH [Reaction (5)].

Preparation and Characterization of the Catalysts

Appropriate amounts of $Pd(C_3H_5)_2$ and $Pt(C_3H_5)_2$ in pentane solution were reacted with weighed amounts of the powdered supports.

As mentioned, the extent of Reaction (1) is thought to be fundamental in achieving good metal dispersion. To elucidate better the details of Reaction (1), the propene evolution was measured gas cromatographically in the case of 10 g of support B_{230} reacting with the amount of $Pd(C_3H_5)_2$ necessary to yield 0.85% of final content of the catalyst. The maximum extent of Reaction (1) was found to be about 20% of the total $Pd(C_3H_5)_2$ introduced. This sample was subsequently brought to dryness and treated with hydrogen in THF suspension. Upon reduction and formation of Pd metal, propane is evolved; quantitative analysis gives a 1.8/1 stoichiometry with respect to palladium in agreement with the extent of Reaction (1). These data indicate unequivocally that $Pd(C_3H_5)_2$ interacts chemically with the support only to a limited extent depending on the availability of suitable -OH groups. Therefore the subsequent reduction with H_2 applies to both the anchored $-Pd(C_3H_5)$ species and the physically sorbed $Pd(C_3H_5)_2$ giving in either case supported Pd metal (Scheme 1).



SCHEME 1

Analogous results were obtained in the case of platinum.

It is noteworthy that the reduction of solutions of bis-allyl Pd and Pt gives very large metal aggregates in contrast to the present case where homogeneously dispersed metal (Pd and Pt) without large aggregates was ascertained by scanning electron microscopy. This fact indicates that these glasses behave as typical inorganic supports such as silica gel or alumina.

In a previous paper we reported on the reactivity of a variety of allyl-Pd(II) complexes toward molecular hydrogen (*13*). The rate of decomposition to Pd metal was found to be strongly dependent on the complex used, a major factor being the nature of the ancillary ligands coordinated to the metal. Thus, for example, $Pd(C_3H_5)_2$ decomposes instantaneously even in the solid state, whereas $(1,Me-C_3H_4)Pd(PPh_3)Cl$ is indefinitely stable. From this standpoint the presence on the support of two different precursors to the metal, namely $M(C_3H_5)_2$ and the anchored $-M(C_3H_5)$ species (M = Pd, Pt), suggests that at least for the case of Pd, about 80% of the metal will be produced very rapidly, the remaining 20% being formed at a lower rate. We can therefore envisage two different stages in the generation of metal particles, which may reflect different physical properties.

In order to evidence different aggregation states of the metal a series of SAXS measurements have been carried out on these catalysts. The results obtained indicate a bimodal volume size distribution for the catalysts on supports B_{230} and C_{230}. The two dimensional ranges exhibited, one of which is under 30 Å, are quantified in column 4 of Table 2, as volume fraction associated with the first peak of the distribution curves. Details on the various problems associated with the SAXS procedure are subject of a forthcoming paper (*14*).

TABLE 2

Physical Properties of the Metal Catalysts

Support	M (%)	D_P (Å)[a]	Fraction with diameters <30 Å[b]	
			(%)	Peak center (Å)
A_{240}	Pd 0.34	12		
	Pd 0.40	18		
	Pd 1.70	16		
A_{450}	Pd 0.85	34		
A_{650}	Pd 0.85	86		
A_{950}	Pd 0.85	104		
B_{230}	Pd 0.85	48	22	12
	Washed Pd 0.32	26	35	11
	Pt 1.0	80	7	26
	Washed Pt 0.31	57	22	28
C_{230}	Pt 1.0	33	46	20
	Pt 0.3	19	51	14

[a] Calculated by using the data treatment from Eq. (7).
[b] Calculated by volumetric distribution functions.

In the case of 0.85% Pd on the B_{230} support (i.e., the catalyst detailed in Scheme 1), the total amount of palladium (Fig. 2A) is split into two ranges of particle size: one centered around 12 Å and the other centered around 56 Å, the former including 22% of the total Pd. There is excellent correlation with the glc determinations. The fact that anchored $-Pd(C_3H_5)$ gives upon reduction small metal clusters, while the sorbed $Pd(C_3H_5)_2$ generates larger aggregates was ascertained with the following experiment. The same sample before reduction with H_2 was washed several times with pentane until colorless washings were obtained, thereby removing most of the physically sorbed $Pd(C_3H_5)_2$. For this washed sample a large drop in the Pd particle fraction with dimensions above 30 Å (Fig. 2B) is observed, while the amount of metal distributed in the 0–25 Å range remains comparable with respect to the nonwashed sample.

The data obtained for other Pd and Pt samples, for which the same behavior applies, are reported in Table 2.

In agreement with Yermakov's results on silica gel, our data underline the fundamental role of "naked" Pd and Pt atoms formed by Reaction (2) which can migrate on the surface to generate small clusters, which in turn are stable enough under the mild experimental conditions used (low temperature and inert atmosphere) not to coalesce to larger aggregates (*15–18*).

The possibility of preparing small, catalytically active, metal particles starting from "naked" atoms dispersed on suitable matrices is a most promising field of research (*19, 20*).

The data obtained in the case of Pd catalysts deserve some additional comments. If we assume the Porod diameter (D_P) as a parameter which quantifies the average particle size independently of the complexity of the distribution, we can observe for samples with the same Pd content, an inverse dependence of D_P with the –OH content of the surface (Fig. 3). Moreover, in the case of support A_{240} with the maximum number of –OH groups, the D_P value is practically independent of the Pd percentage on the support. The achievement of good metal dispersions is therefore related to the availability of supports with high –OH content and again this underlines the importance of performing a molecular dispersion via Reaction (1) before reduction to metal.

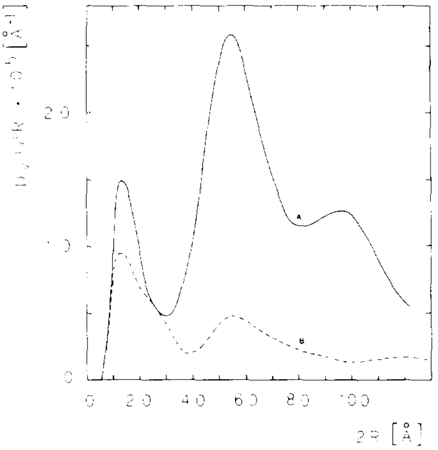


FIG. 2. SAXS determination of the particle size distribution: (A) (0.85% Pd on support B_{230}) nonwashed; (B) (0.32% Pd on support B_{230}) washed before reduction. Quoted also in Ref. (*14*).

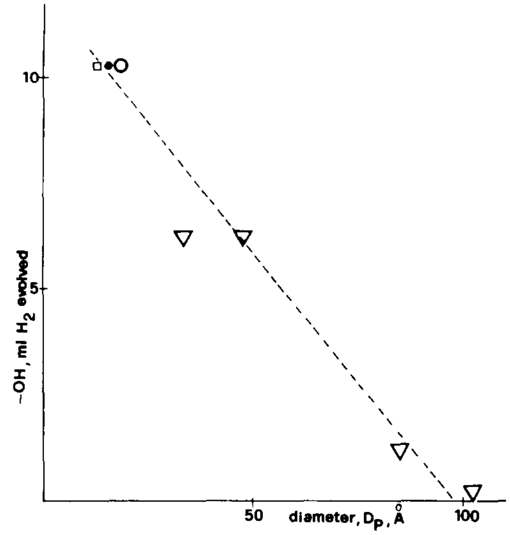


FIG. 3. Inverse dependence of the Porod diameter (D_P) on the -OH content of the support surface. △ = 0.85% Pd; □ = 0.34% Pd; ○ = 0.40% Pd; ● = 1.70% Pd. Data from Tables 1, 2.

Catalytic Behavior and Chemical Reactivity

The catalytic activity of Pd and Pt supported on the above described glasses has been determined for the hydrogenation of 1-hexene at 1 atm H_2 pressure and 25°C in THF suspension. Kinetics were in all cases zero-order in olefin concentration and the k_{obs} determined by gas uptake are summarized in Table 3, where the dimensions of the metal particles are also reported.

The catalytic activity is determined essentially by the clusters with diameter shorter than 30 Å, as shown by comparing the Pd and Pt samples washed after completion of the anchoring reaction [Reaction (1)] to the nonwashed counterparts, although the total metal content is drastically decreased. These data also give a direct interpretation of the already observed leveling effect in the catalytic activity (*3*) of these Pd catalyst on increasing the metal content. The saturation of surface -OH groups, which determine the formation of metal clusters <30 Å, constitutes a limit after which further addition of metal is wasted for catalytic purposes.

Actually, this fact, very interesting from the economic standpoint, has been foreseen some years ago by Renouprez *et al.* (*21*) for platinum on silica catalysts. Analogously, Klabunde *et al.* found that Ni/Al_2O_3 catalysts prepared starting from metal atoms solutions display a maximum catalytic activity at fairly low metal content, the excess of metal being noxious since it probably increases the particle sizes and not the particles number (*19*).

The large difference in catalytic activity between metal particles <30 Å with respect to the larger ones should imply a different chemical reactivity as a function of the particle diameter.

To test the chemical reactivity of metal particles <30 Å and discriminate from larger particles which are present at the same time, 0.3% Pt on C_{230} support, whose distribution plot is shown in Fig. 4A, was treated with phosphines under CO atmosphere. The reaction (see Scheme 2) leads to the formation of Pt-carbonyl complexes already reported in the literature (*22, 23*). SAXS experiments carried out on the "digested" catalyst so obtained (Fig. 4B), show that only the portion of metal with dimensions <20 Å can be extracted from the solid matrix, whereas larger Pt particles remain unreacted.

This experiment underlines the high chemical reactivity of the small Pt clusters

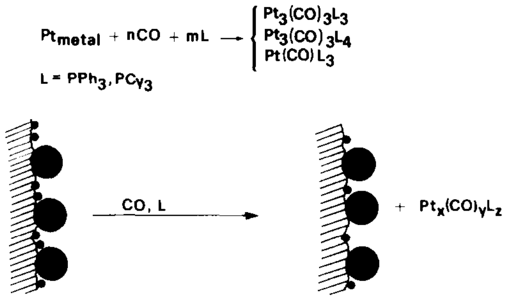
TABLE 3

Catalyltic Activity in the Hydrogenation of 1-Hexene

Metal (%)[a]	Fraction with diameters <30 Å (%)	k_{obs}, M sec^{-1}[b]
Pd 0.85 (nonwashed)	22	4.1×10^{-4}
Pd 0.32 (washed)	35	3.7×10^{-4}
Pt 1.0 (nonwashed)	7	1.3×10^{-3}
Pt 0.31 (washed)	22	1.1×10^{-3}

[a] Support B_{230}.

[b] Rate constants for the hydrogenation of 1-hexene (0.24 M) in tetrahydrofuran at 25°C and P_{H_2} = 760 ± 12 mm Hg with 0.5 g of catalyst.



SCHEME 2

which allows organometallic synthesis directly from the metal. This rapidly expanding area (*24, 25*) has been employed for a variety of metals and requires the use of metallic vapors or monoatomic dispersions in solvent matrices. On the other hand synthesis from metallic powders has been reported by Rieke (*26*) but in the presence of stronger oxidative addition promoters than phoshines or CO, such as allyl, aryl, and alkyl halides. Our results which refer to the reaction of purely metallic Pt clusters with CO and phosphines find a comparable precedent in the recently reported (*27*) Mn–Fe bond cleavage of a trinuclear heterometal cluster performed by the same reactants.

This latter analogy between organometallic clusters in solution and supported metallic clusters leads to a similar metal–metal bond description, i.e., for the latter something very different from the classical metallic bonding. The same parallelism has been already suggested in the hydrogenation of different olefins and dienes with these catalysts (*4*).

EXPERIMENTAL

All chemicals were analytical grade products. Solvents were dried and distilled prior to use according to standard methods. 1-Hexene was purified by filtration through neutral alumina, distilled, and stored in the dark under N_2. $Pd(C_3H_5)_2$ and $Pt(C_3H_5)_2$ were prepared according to literature procedures (*28*). The catalysts were synthetized as previously described (*3*) by reacting the appropriate $M(C_3H_5)_2$ with the vitreous supports and reducing with H_2.

All volumetric measurements were carried out in a 100-ml round-bottomed flask equipped with a side arm fitted with a silicone septum. Two stopcocks allowed connection to a double manifold vacuum-N_2 rack and to a standard gas-uptake apparatus. Temperature was maintained constant (25 ± 0.1°C in all cases) with the aid of a jacket connected to the external circulation of a thermostat. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer.

Gas chromatographic analyses were performed on a HP 5730A gas chromatograph equipped with an automatic integrator.

Preparation of the vitreous supports. The general procedure has been already described (*3, 8*) and utilizes ethanolic solutions of $Si(OEt)_4$, $Al(OBu^{sec})_3$, and NaOMe in a ratio $SiO_2/Al_2O_3/Na_2O$ = 71/18/11. Hydrolysis is performed by passing steam over the boiling solution. The resulting gels were converted to the final glasses according to the following procedure: they were heated at 50°C for 5 hr; then the temperature was raised at a certain rate up to a maximum temperature; as the maximum temperature was reached, the heating was stopped and the glasses cooled down to room temperature while standing in the oven. Individual figures for heating rate and

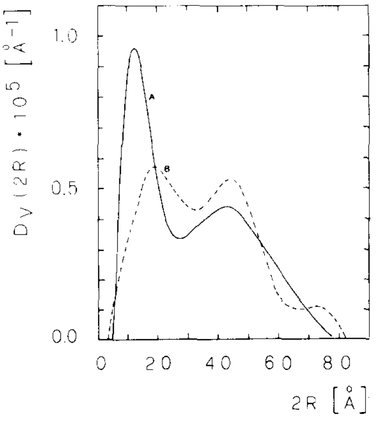


FIG. 4. SAXS determination of the particle size distribution: (A) 0.31% Pt on support C_{230} before and (B) after treatment with CO and PPh_3.

maximum heating temperature are reported in Table 1. All glasses were ground in a ball-mill and the fraction 200–250 mesh was used.

Determination of surface -OH groups. The glass (1 g) is placed in an ampoule, connected to the flask of the above-described apparatus for volumetric measurements, and dried *in vacuo* (10^{-3} Torr) at 80°C for 3 hr. The system is filled with N_2 and dried, N_2-saturated THF (20 ml) is charged into the flask. Large excess of LiH ($\simeq$100 mg) is added under N_2 and equilibration with the gas-uptake apparatus filled with H_2 is achieved. The reaction is started upon tipping the glass in solution by rotating the ampoule. Gas evolution is plotted vs time and the volume of H_2 released after 60 min taken as a measure of surface -OH groups (Fig. 1).

Determination of the relative stoicheiometry of Reactions (1) and (2). A pentane solution (10 ml) containing $Pd(C_3H_5)_2$ (Pd concentration 8.5 mg/ml) was carefully brought to dryness *in vacuo.* Dry degassed THF was added and the resulting solution transferred into a 100-ml flask containing 10 g of B_{230} glass, filled with N_2 and connected to the gas-uptake apparatus to keep the pressure constant (1 atm). After 2 hr the gas phase is sampled (0.3 ml) and propene identified with glc. Quantitative analysis was performed by adding to the gas phase a known amount (10 ml) of propene with a syringe. Then the system was degassed, filled with H_2, and left aside for several hours to ensure complete decomposition. Propane identification and quantitative analysis were performed as above.

Identical procedure was followed for 1% Pt on B_{230}: 10 and 190% with respect to added $Pt(C_3H_5)_2$ for Reactions (1) and (2), respectively.

Catalytic hydrogenation of 1-hexene. The procedure has been already described (*3*).

Reaction with phosphines and CO. Pt (0.3%) on C_{230} catalyst (2.0 g) was placed under N_2 in a 100-ml round-bottomed flask; 10 ml of dry, oxygen-free benzene containing PPh_3 (15 mg) was added. The system was evacuated, placed under CO atmosphere, and refluxed for 1 week. The suspension was filtered under N_2 and the solution ir spectrum showed ν_{CO} at 1935 (s), 1840 (m), and 1785 (s) cm^{-1} attributable (*22*) to the known complexes $Pt(CO)(PPh_3)_3$ and $Pt_3(CO)_3(PPh_3)_4$. Identical procedure can be followed for PCy_3.

SAXS data collection and treatment. SAXS curves were recorded using a Kratky camera aligned to obtain the "infinite" beam condition and equipped with an electronic programmed step-scanner. Zr filtered Mo$K\alpha$ radiation with a pulse height discriminator and a scintillation detector was used. Front slits were used to achieve angular resolution of about 600 Å in Bragg space. To ensure satisfactory statistics each diffraction curve was measured a number of times in succession by the preset counts mode. For the determination of the absolute scattering intensity, the primary beam intensity was measured by means of a Lupolen standard sample (*29*).

The total surface areas of support materials, homogeneously dispersed inside plate-like sample holders, have been determined following the Porod method (*30, 31*), according to the relationship:

$$S = \frac{\lim_{h\to\infty} h^3 J(h)}{\pi^2(\Delta\rho)^2 I_e(h)} \qquad (6)$$

where h is the modulus of the diffraction vector (i.e., $4\pi\lambda^{-1}\sin\theta$, with 2θ = scattering angle and λ = X-ray wavelength); $J(h)$ is the slit-smeared scattered intensity; $\Delta\rho = \rho_1 - \rho_0$ is the electron density difference between heterogeneities responsible of SAXS and matrix; and $I_e(h)$ is the scattering intensity of a single electron in the same experimental conditions. Equation (6) predicts that in the higher angle tail of the diffraction curve $h^3J(h)$ must be constant. Actually we observed a positive linear deviation from the theoretical behavior: Porod law is obeyed after a correction for the sample background scattering (*32*).

With regard to catalysts, to observe the SAXS characteristics of the metallic phase alone, "pore maskant" method was used in order to eliminate the interferences between metal and holes scattered intensities (*33–35*). 1,1-Dibromo-ethane as "pore maskant" liquid was used since its electron density is very close to that of the glass. The difference in SAXS between the catalyst and a similar treated support eliminates effects arising from the pores inacessible to the liquid and leads to the metal particle scattering. Mathematical treatment was performed on this obtained intensity curves. All reported distributions were normalized by the X-ray attenuation factors.

The Porod diameter employed to represent the average linear dimensions of the metal particles, supposedly of spherical shape, is defined as:

$$D_P = \frac{3 \int_0^\infty hJ(h)\, dh}{2(1-c) \lim\limits_{h\to\infty} h^3 J(h)} \qquad (7)$$

where c is the volume fraction of the scattering phase.

With the assumption of spherically shaped particles, widely and randomly separated, an expression for the scattered intensity can be obtained which involves an integral over the particle size distribution functions. This relationship for the scattering intensity in the pinhole geometry, $I(h)$, may be written as

$$I(h) \propto (\Delta\rho)^2 \int_0^\infty D_V(R) R^{-3} V^2(R) i_0(hR) dR \qquad (8)$$

where $D_V(R)$ is the volumetric distribution function that states the volume of all particles defined by the size parameter R and $i_0(hR)$ is the intensity scattered by a single particle. By the least-squares method, we obtained an inversion of the integral Eq. (8) for our experimental data; to this end we used a computer program which has been made available by C. G. Vonk (*37*).

All calculation, starting from slit-smeared intensity value, were performed with a CDC computer, at the Centro di Calcolo of Venezia University.

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