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Location and Dispersion of Platinum in PtY Zeolites

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Location and dispersion of platinum in reduced PtY zeolites were studied by X-ray diffraction, small angle X-ray scattering and chemisorption. In the case of a 300°C activation most of the Pt^{2+} ions are found in supercages. On reducing at 300°C, 6–13 Å platinum agglomerates fitting into supercages are formed, and they remain stable up to 800°C. Hydrogen chemisorption gives $H/Pt = 1$ and the stoichiometry of titration corresponds to that proposed by Wilson and Hall for very small particles. At 900°C structure breaks down and simultaneously agglomerates are transformed into crystallites of 25–30 Å diameter occluded in the bulk of an amorphous solid. In the case of a 600°C activation, most of the Pt^{2+} ions are in sodalite cages; on reducing at 300°C, the platinum is atomically dispersed in these cages and does not chemisorb hydrogen. On evacuating at higher temperatures, Pt-agglomerates and Pt-crystallites are gradually formed at the expense of isolated atoms, and the chemisorption increases up to 800°C ($H/Pt = 0.65$). At 900°C the platinum is in the same state of dispersion as in the previous case.

INTRODUCTION

Some years ago, Rabo *et al.* (*1*) claimed that atomically dispersed platinum can be obtained by reduction of platinum-exchanged zeolites. Since this pioneering work the problem of platinum dispersion in zeolites has led to contradictory results (*2–7*) essentially for two reasons: (i) the stoichiometry of the titration method (H_2, O_2) used was not sufficiently known for highly dispersed metals and (ii) at least a part of the published investigations were not carried out on materials treated in appropriate conditions. The work of Dalla Betta and Boudart (*7*) greatly helped to clarify the situation. They pointed out the importance of pretreatment conditions for obtaining the highest platinum dispersion. They also gave evidence that platinum encaged in the zeolite forms clusters in which all the atoms are exposed and chemisorb according to the stoichiometry proposed by Wilson and Hall (*4*) for very small particles. However, further investigations are needed in order to characterize these metal clusters better and to learn more about their adsorptive and catalytic properties. Moreover, dispersion and adsorption data are liable to change according to the platinum location in the different cages of the zeolite. Thus, in a previous paper dealing with a PdY zeolite (*8*) we have shown that Pd atoms remain trapped in sodalite cages upon reduction and do not chemisorb hydrogen. X-Ray diffraction proved to be well suited to determine the initial position of cations and the final positions of metal atoms in the zeolite cages as well as the size of crystallites eventually formed after the sintering of platinum atoms. The present paper aims at giving a complete picture of the various location, dispersion and adsorption properties that platinum exhibits when supported on Y zeolite, stress being laid on the variation of these parameters occurring as a function of thermal treatment. Crystal structure analysis, small angle X-ray scattering (SAXS) and adsorption measurements were used for this purpose. Some preliminary results have been published in a note (9).

EXPERIMENTAL METHODS

A. Materials

A Linde NaY zeolite (SK 40) was ion-exchanged in an ammonia solution of $PtCl_2$ which provides exchangeable $[Pt(NH_3)_4]^{2+}$ cations. The solution was stirred at room temperature for 24 hr then filtered. The powder was washed with ammonia solution to eliminate the Cl^- ions. Required exchange levels were obtained by allowing the zeolite to equilibrate in a solution containing the suitable amount of platinum. The zeolite composition was determined by chemical analysis of platinum and sodium on calcined material, and proton concentration was estimated by difference. Two samples were selected: $Pt_{10}Na_{17}H_{19}Y$ (sample I, 14 wt% of Pt), and $Pt_4Na_{48}Y$ (sample II, 5.8 wt% of Pt). It appears that, especially for sample I, some Na^+ ions have been exchanged by NH_4^+ ions from the ammonia solution.

B. Thermal Treatments

Well-defined pretreatment conditions of PtY zeolites are required to obtain homogeneous platinum dispersion and reproducible results. Thermal activation for removing H_2O and NH_3 molecules is a very critical step especially when heavily metal-loaded zeolites and/or large amount of powder are treated because reduction and subsequent sintering of platinum is liable to occur when the $[Pt(NH_3)_4]^{2+}$ complex cation decomposes within the 250–300°C temperature range. Zeolite samples were heated in a rapid flow of oxygen (30 liters/hr) dried over activated molecular sieves. The U-shaped cell shown in Fig. 1 produces a fluidized bed which improves solid–gas contact. The temperature was slowly raised at 1°C/min up to 220°C and at 0.25°C/min up to 300°C. Samples were then evacuated (10^{-5} Torr) for 15 hr at 300, 500 or 600°C. The vacuum line was grease-free thus avoiding contamination and untimely reduction. After oxygen and vacuum treatments the U-shaped cell was sealed off the vacuum line and the powder was transferred into a connected cell designated for reduction and adsorption measurements. Reductions were carried out under 300 Torr of hydrogen pressure at 300°C for 15 hr, then samples were evacuated at 300°C or higher temperatures for 4 hr. Lindemann glass capillaries could be connected to this cell for the X-ray investigation. It is noteworthy that samples were never reexposed to air during the whole process including adsorption and X-ray data collection.

Samples were designated according to the following examples. "I 600" means zeolite I (14 wt% of Pt) pretreated at 600°C, and "I 300 R 800" means zeolite I pretreated at 300°C, reduced (at 300°C) and evacuated at 800°C. (The reduction temperature was always 300°C, and therefore it is not mentioned.)

C. Gas Uptake Measurements

The amount of gas taken up during the reduction or adsorption was measured with a conventional volumetric apparatus on about 100 mg of pretreated zeolite. Volumes of gas adsorbed or reacted were calculated from the change in gas pressure measured with a Texas Instrument pressure gauge. The volume of dead space was determined with helium. The adsorption cell could be evacuated at high temperature and the volume of desorbed gas was deduced from the pressure change in the reservoir-bulb of the vacuum system, the rotary pump being disconnected. The volume of hydrogen actually used for the re-

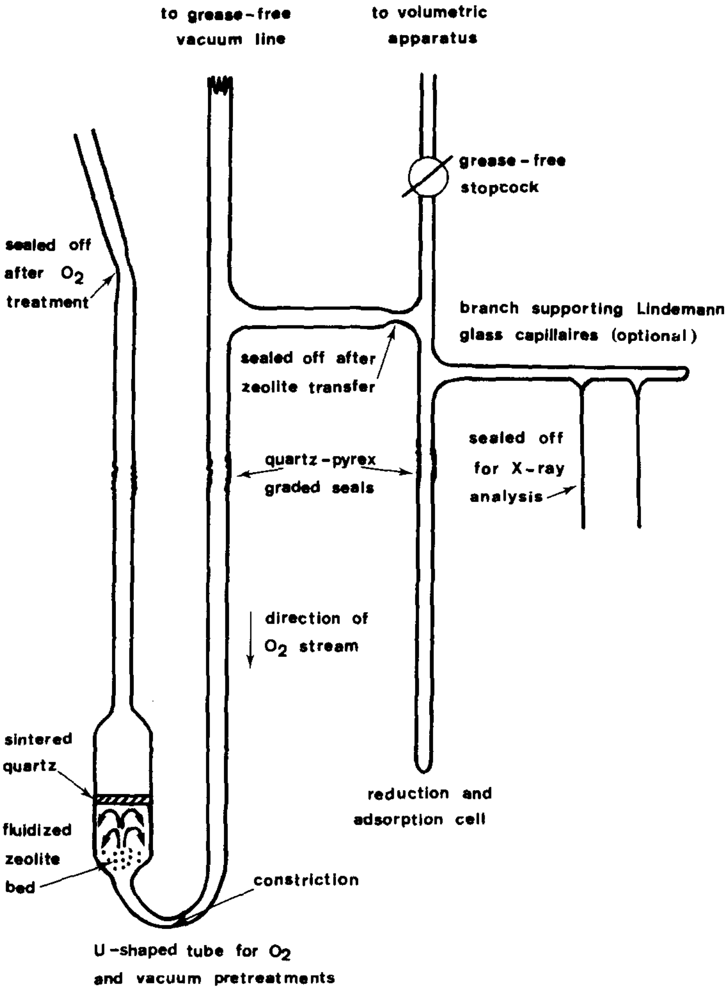


FIG. 1. Device for oxygen and vacuum activation, hydrogen reduction and adsorption measurements.

duction is the difference between the consumed and desorbed volumes.

Hydrogen, oxygen, and carbon monoxide adsorptions were measured at 25°C under 10 Torr gas pressure. Equilibration of gases was complete within 5–10 min. Measurements were corrected for adsorption by the support using blank samples of NaHY zeolites containing the same amount of sodium ions as the PtY zeolites. Corrections were negligible for H_2 and O_2 chemisorption but amounted to 8% for CO adsorption. It was checked that extrapolation of the adsorption isotherm to zero pressure gave a similar adsorbed volume in every case. Hydrogen titration was performed after the evacuation at room temperature of the Pt zeolite covered by oxygen.

D. X-Ray Diffraction Procedures

The crystal structure of the zeolites was determined from powder data according to the experimental technique and resolution methods previously described (*10–11*). Platinum atoms at random positions in the zeolite cages were localized using the liquid scattering functions of Simpson and Steinfink (*12*) which have already been successfully applied in previous work (*8*).

A Guinier-type camera (Cu $K\alpha_1$ wavelength) providing very good peak to background ratio was used to detect the broad diffraction lines of platinum crystallites. A relative and rough estimate of the amount of crystallites in the sample could be made from the intensities of platinum reflections calibrated with an internal standard. The average diameter of the platinum crystallites was calculated from the integral width of the 111 and 200 lines using the Scherrer formula.

E. X-Ray Small Angle Method

The low angle scattering has undergone considerable progress in recent years and we have fully described its application to the case of a three phase system (air, oxide, metal) (*13*). Experiments on the characterization of supported metallic catalysts (*14*) have clearly demonstrated that even for low metal concentration (0.6% Pt on alumina), distribution curves of the particle diameters can be obtained which are comparable to electron microscopy results. Moreover, one of the main advantages of the technique is the possibility to obtain directly a parameter proportional to the metallic surface area. Let us examine briefly how the data are handled and how the parameters are computed. The multiple scattering treatment is applied to the transmitted beam. A Fourier transformation procedure leads to the function $P(r)$, identical to the Patterson function calculated in the structure determination of crystalline materials. Hence, the metallic area S is derived:

$$S = -4 \cdot P'(0)/\mu^2,$$

where μ is the difference of density between the metal and the framework.

Various distribution functions of the metal particle diameters can be calculated:

$$f_v(D) = -(D^3/3) \cdot \mathrm{d}\,[P''(D)/D]/\mathrm{d}D \text{ and}$$
$$f_s(D) = -[P''(D) - DP'''(D)]/2\,P'(0),$$

$f_v(D)$ and $f_s(D)$ are called volume and surface distributions as they are proportional to the volume and surface fraction of the particles whose diameters are between D and $D + dD$. The metallic surface area is a parameter independent of any assumption about the shape of the particles, but the distribution functions are calculated on the basis of a regular spherical shape. Experimentally, the data are collected with a low angle goniometer (*15*) equipped with a linear collimation system. When very small particles are to be detected, the scattering is spread over a very large angular domain, and therefore the Mo $K\alpha$ radiation is more appropriate than Cu $K\alpha$. The difference of density between zeolite and platinum is especially favorable, as the scattered intensity is proportional to μ^2. Moreover, as the pores are regularly arranged in the zeolite, the scattering produced by the support is very weak. Therefore about 95% of the low angle X-ray diffraction intensity is related to platinum.

RESULTS

A. Determination of Crystal Structures

The most heavily loaded platinum zeolite (sample I) was used to obtain accurate positions and population parameters for Pt atoms. Crystal structure of six samples have been determined. Treatment conditions, population and coordinates of extraframework atoms are given in Table 1. The complete list of crystallographic parameters including framework atoms and the listing of observed and calculated structure factors can be supplied upon request to the authors. Before examining the results some limitations encountered in the structure refinements need to be discussed.

The high number of strongly scattering Pt^{2+} ions give very conclusive results especially when they occupy the cation sites on [111] axes [for a description of the faujasite structure and site nomenclature, see Smith (*16*)]. Whenever the Pt^{2+} ions are out of these special positions they have too

TABLE 1

POPULATION AND COORDINATES OF EXTRA-FRAMEWORK ATOMS

Samples[a]	Final R index[b] and unit cell constant (±0.01 Å)	SI	SI′ (0.044)	SI′ (0.065)	SII (0.23)	U[c]
I 600 (600)	$R = 0.114$ $a = 24.68$	6 (1) Na^+ 0.0	9.8 (5) Pt^{2+} 0.0444 (2)		18 (1) Na^+ 0.234 (1)	
I 600 R 300 (600, 300, 300)	$R = 0.125$ $a = 24.70$	8 (1) Na^+ 0.0		3.0 (5) $Pt^{(0)}$ 0.065 (1)	14 (1) Na^+ 0.233 (1)	8 (3) $Pt^{(0)}$ 0.125
I 600 R 600 (600, 300, 600)	$a = 24.50$	8 Na^+		3 $Pt^{(0)}$	14 $Na^\pm$	6 (3) $Pt^{(0)}$ 0.125
I 500 (500)	$R = 0.095$ $a = 24.68$	6 (1) Na^+ 0.0	8.5 (5) Pt^{2+} 0.0440 (5)		24 (1) Na^+ or 1Pt + 16Na 0.231 (1)	
I 300 (300)	$R = 0.11$ $a = 24.71$	5 (1) Na^+ 0.0	3.8 (5) Pt^{2+} 0.046 (1)		19 (1) Na^+ 0.233 (1)	
I 300 R 300 (300, 300, 300)	$R = 0.098$ $a = 24.74$	4 (1) Na^+ 0.0		2.0 (2) $Pt^{(0)}$ 0.063 (1)	9 (1) Na^+ 0.236 (1)	

[a] Treatment conditions in parentheses: activation temperature, reduction temperature, evacuation temperature (°C).

[b] $R = \Sigma||F_o| - K|F_c||/\Sigma|F_o|$.

[c] Site U is a 2.5 Å radius sphere centered at $x = y = z = 0.125$.

low an occupancy factor and therefore cannot be detected. Moreover, an absolute identification of extra-framework atoms cannot be achieved exactly; for instance, some Na^+ ions may well share the same type of site as Pt^{2+} ions although the reported results indicate no Na^+ ions on these positions. Consequently, the errors given for coordinates and population of atoms are often greatly underestimated, in particular for Na^+ cations.

The method of handling randomly dispersed Pt atoms in structure refinement has given rise to some difficulties. The X-ray scattering of platinum distributed at random in the zeolite cages contributes both to the incoherent scattering background and to the intensities of reflections at low Bragg angles. This last part can be taken into account in the structure refinement by means of liquid scattering functions (*12*). They are calculated for a model where the atoms are randomly distributed throughout a sphere of given radius (or throughout the volume between two concentric spheres) centered on a given position in the porous network. This method has been quite effective to locate and count the Pt atoms in sodalite cages but has failed to give reliable results whenever Pt atoms are supposed to occupy the supercages. This may be due to the steep decrease of scattering functions as the third power of sphere radius. Thus the scattering of Pt atoms in small sodalite cages would strongly contribute to low angle reflections, whereas the scattering of Pt atoms inside supercages would mainly be incoherent. Disorder in cage filling may also play a major role. As discussed below, Pt atoms are probably clustered in a few supercages leaving most of the cages unoccupied. Such clumps of Pt atoms at random positions in the crystal can hardly contribute to the structure factors of the zeolite lattice but mainly produce incoherent scattering. On the other hand, a homogeneous distribution of Pt atoms over the sodalite cages (i.e., regular occupancy of cages) is likely to occur; these atoms actually contribute to the low Miller indexes structure factors thus allowing the refinement of platinum population in sodalite cages.

Samples I 600, I 500, and I 300

In these samples the scattering matter at $x = y = z = 0.044$ was attributed to Pt^{2+} ions. Results are shown in Table 1. Population of the SI′ (0.044) site increases as a function of the activation temperature: in I 600 nearly all Pt^{2+} ions are fixed in sodalite cages, whereas in I 300 it is likely that most of them still occupy the supercages. These ions have not been detected because they are probably outside the [111] axis.

Samples I 600 R 300, I 600 R 600, and I 300 R 300

The reduction of I 600 at 300°C (I 600 R 300) induces a complete removal of Pt^{2+} ions from SI′ (0.044) sites. Three Pt atoms are then found to occupy SI′ (0.065) sites and eight Pt atoms are randomly distributed in a sphere of 2.5 Å radius centered at $x = y = z = 0.125$. Scattering matter at SI′ (0.065) and in the 2.5 Å sphere nearly overlaps. It is highly probable that statistically 3 out of the 10 Pt atoms present in sodalite cages occupy the SI′ (0.065) sites because they slightly interact with the six-membered oxygen ring.

The X-ray diffraction pattern of I 600 R 600 exhibits a very poor resolution of diffraction lines because the dehydroxylation of the zeolite framework has created lattice defects. The crystal structure has been tentatively determined with only (hkl) reflections such that $h^2 + k^2 + l^2 \leqslant 75$. The atomic parameters were fixed at the values obtained for I 600 R 300; thus refinement only concerns the population of the 2.5 Å sphere. Although this can hardly yield quantitative results it is noteworthy that sodalite cages still contain Pt atoms after 600°C evacuation.

Crystal structure determination of I 300 R 300 sample failed to detect the reduced Pt atoms in supercages for the very reasons mentioned above. However, there is indirect X-ray evidence that Pt atoms have a very high state of dispersion (inside the supercages since sodalite cages are empty): high background level on the X-ray films suggests that these atoms mainly give incoherent scattering; moreover, very few platinum crystallites were observed. This is consistent with a model in which the Pt atoms form agglomerates accommodated in a few supercages scattered at random in the zeolite.

B. Amount and Size of Platinum Crystallites

Reduced samples were heated in vacuum to 1000°C and diffraction patterns were recorded at various steps of heating. As previously stated, the number of crystallites formed can be estimated on a relative basis with a rough accuracy especially when only a few crystallites are present.

The number of crystallites formed when I 300 R 300 was evacuated at 300, 500, 800, and 900°C are in the ratios 0 : 1 : 1.2 : 10. Thus a small number of crystallites appear at about 500°C and the number does not change appreciably up to 800°C. The conspicuous feature is the large increase of the number of crystallites between 800 and 900°C. On the other hand, the ratios are 1 : 2 : 5 : 10 for sample I 600 R 300 evacuated at the same temperatures. In this case platinum crystallites gradually appear up to 800°C followed by a twofold increase between 800 and 900°C. In both cases the number of crystallites does not increase further at temperatures higher than 900°C.

The mean crystallite diameter by line

broadening analysis is about 25 ± 5 Å. No appreciable sintering occurs above 900°C. This strongly suggests that platinum crystallites are formed inside the volume of zeolite microcrystals, which structure is destroyed in the temperature range 800–900°C.

C. SAXS Results

Table 2 and Fig. 2 show the various parameters determined. Samples I 300 R 300 and I 300 R 800 give similar parameters: the metal area derived from the value of $P'(0)$ corresponds to 240 ± 10 m^2/g and the diameter calculated from this value is 12 Å; the distribution curve f_s (D) has a maximum at 12 Å. Therefore one can conclude that these agglomerates have diameters ranging between 6 and 13 Å. In the case of the sample I 300 R 900, the metal area measured by SAXS is reduced by a factor 5, and the particle diameter calculated from this area is 60Å. However, the distribution curve is very sharp and its maximum is situated at 30Å. At the same time, the background at large angles (beyond the usual domain of SAXS) is greatly increased. These results can be interpreted if it is assumed that platinum has two states of dispersion in sample I 300 R 900, namely, crystallites of 30 Å mean diameter (also detected by X-ray diffraction) and isolated atoms or very small clusters not detected by SAXS. These species do not contribute to the metallic surface derived from $P'(0)$ so that the equivalent particle diameter is artificially too large.

Measurements on samples I 600 R 300 (Table 2, Fig. 3) and I 600 R 800 lead to a value of $P'(0)$ corresponding to 120 and 130 m^2/g for the metallic area. However, the two samples are completely different with respect to the mean parameters. I 600 R 300 gives distribution curves very similar to I 300 R 300 (maxima at 9 Å and diameters between 6 and 10 Å), but a large amount of platinum scattering at larger angles (coherent and incoherent) is not detected. On the other hand sample I 600 R 800 is composed of larger particles: the maximum of the curve is situated at 18 Å and some 30–40 Å crystallites appear. This is in accordance with the value of the diameter calculated from the metallic area (20 Å); in that case all the Pt atoms are detected.

D. Gas Uptake Measurements

Gas adsorptions were measured on zeolites I and II after various pretreatments. Measurements were always duplicated starting from fresh samples treated in the same conditions and checked by X-ray diffraction. Results for H_2, O_2 and CO chemisorption and for H_2 titration are given in Fig. 4 and Table 3.

TABLE 2
PLATINUM DISPERSION PARAMETERS GIVEN BY SAXS

Samples	$P'(0)$	$S(m^2\ g^{-1})$	Equivalent diam (Å)	Mean geometric diam (Å)[a]	Maximum of the distribution (Å) curve
I 300 R 300	3000	240	12	7	11
I 300 R 800	3000	240	12	7	10
I 300 R 900	600	50[b]	60[b]	25	30
I 600 R 300	1500	120[b]	21[b]	7	9
I 600 R 800	1600	130	20	14	18
I 600 R 900	600	50[b]	60[b]	28	32

[a] The geometric diameter is a geometric average weighted by the surface distribution function. It is more sensitive to the finest grain fraction.

[b] Value calculated on the hypothesis that all Pt is detected.

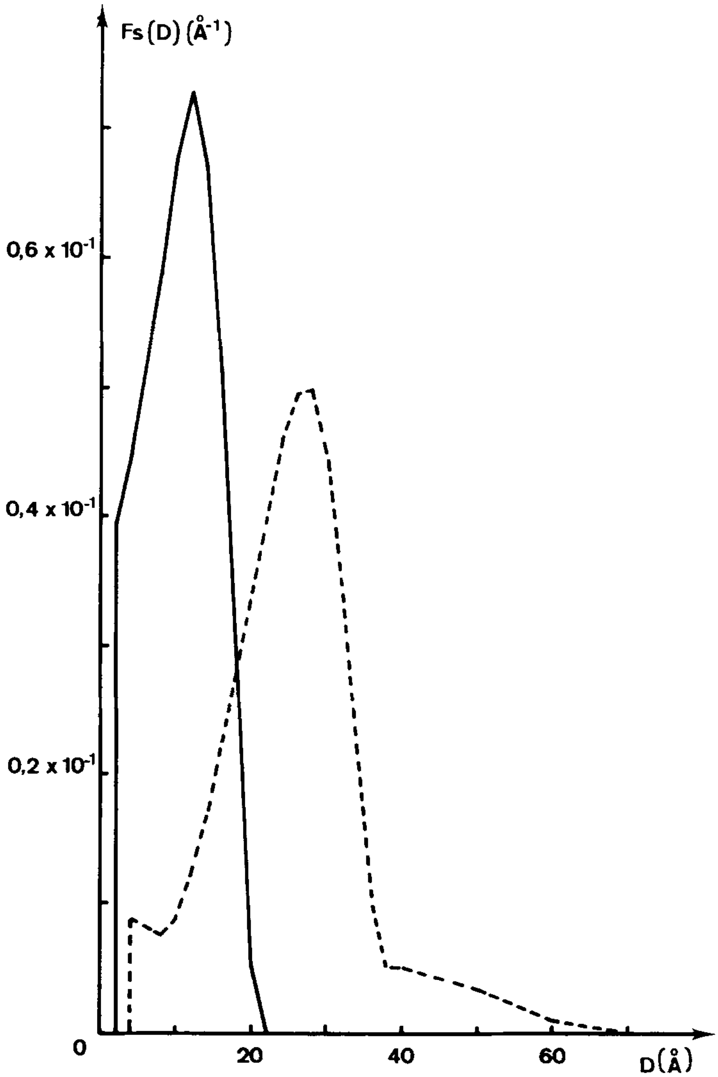


FIG. 2. Distribution of metal particle diameters deduced from SAXS measurements on a reduced PtY zeolite pretreated at 300°C. (——) Sample evacuated at 300° or 800°C (I 300 R 300 and I 300 R 800); (– – –) sample evacuated at 900°C (I 300 R 900).

The PtY zeolites pretreated either at 300 or 600°C begin to take up a significant amount of hydrogen at 80°C, but the reduction is much faster at higher temperatures. Reductions were performed at 300°C for 15 hr under 300 Torr hydrogen pressure, followed by evacuation at 300°C or higher temperature. It was checked that the reduction was complete: the difference between the amounts of hydrogen taken up and subsequently desorbed yields $H_2/Pt = 1$ within experimental error.

Hydrogen chemisorptions were measured after evacuating the reduced zeolites from 300 up to 1000°C. The volume of hydrogen chemisorbed per gram of metal and the ratio H/Pt are plotted in Fig. 4 as a function of the heating temperature. The ratio H/Pt obtained for samples pretreated at 300°C does not deviate appreciably from 1 between 300 and 800°C. On the other hand H/Pt ratios increase from 0.25 to 0.65 for samples pretreated at 600°C. In both cases the dispersion steeply de-

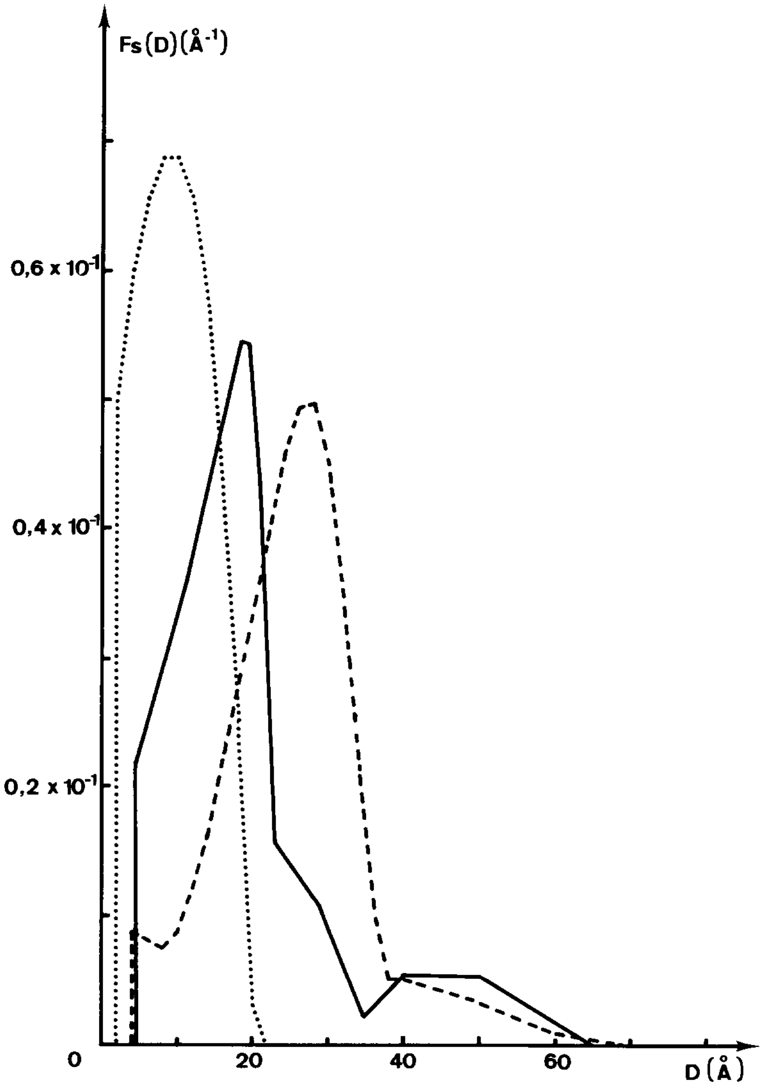


FIG. 3. Distribution of metal particle diameters deduced from SAXS measurements on a reduced PtY zeolite pretreated at 600°C. (· · · ·) Sample evacuated at 300°C (I 600 R 300). (——) sample evacuated at 800°C (I 600 R 800). (——) sample evacuated at 900°C (I 600 R 900).

creases to H/Pt = 0.15 on heating at 900°C and does not change between 900 and 1000°C.

Oxygen and carbon monoxide adsorptions were measured on samples I pretreated and reduced at 300°C and evacuated at 500°C. Table 3 shows that the zeolite adsorbs about half as much oxygen or carbon monoxide as hydrogen; the stoichiometry is therefore near 1 O or 1 CO/2 Pt atoms. Hydrogen titration of platinum covered by oxygen requires about twice as large a hydrogen volume as hydrogen chemisorption. The ratios of H_2 chemisorption, O_2 chemisorption and H_2 titration are 1:0.5:2.

DISCUSSION

Three states of platinum dispersion will be considered:

i. atomically dispersed platinum, i.e., isolated monoatomic $Pt^{(0)}$ atoms encaged in sodalite units or dispersed in an amor-

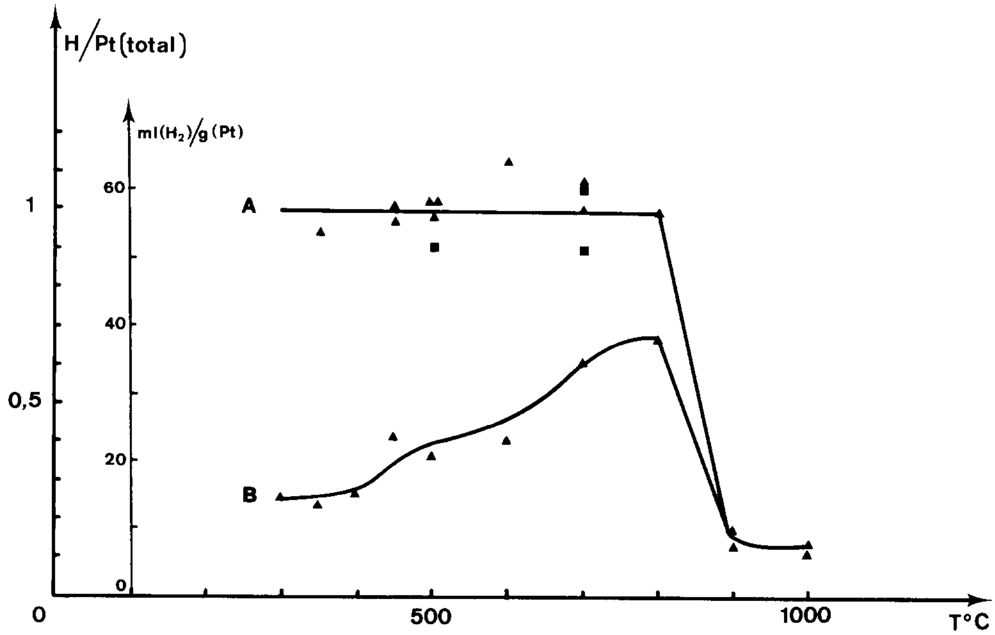


FIG. 4. Hydrogen chemisorption data on reduced PtY zeolites pretreated at 300°C (curve A) and at 600°C (curve B) after evacuation at different temperatures. (▲) Zeolite I (14 wt% of Pt); (■) zeolite II (5.8 wt% of Pt).

phous matrix when the framework is destroyed at high temperature.

ii. platinum agglomerates, i.e., particles of several Pt atoms which can fit into the supercages.

iii. platinum crystallites, i.e., metal crystals of a size generally greater than 15 Å which can be detected by X-ray diffraction.

A. Platinum Dispersion in PtY Zeolite Pretreated at 300°C

300–800°C Temperature Range

X-Ray diffraction indicates that Pt^{2+} ions mainly occupy the supercages when PtY zeolites are pretreated at 300°C. After a reduction at 300°C (I 300 R 300), platinum remains inside the porous network since no crystallites can be detected before 800°C. As shown by SAXS, most of these atoms form 6–13 Å agglomerates, fitting into the supercages. In this range of size all or nearly all the atoms are exposed at the surface and should chemisorb hydrogen with H/Pt = 1 as previously found by Dalla Betta and Boudart (7). This is corroborated by the present adsorption data showing that H/Pt = 1 over the whole 300–800°C range. The growing process and high thermal stability of the agglomerates is probably due to the particular conformation of the supercages. After the reduction at 300°C, Pt atoms are no longer bonded to the oxygen anions of the framework and can easily migrate along the cage walls and through the 7.5 Å aperture of the supercages. They can meet other Pt atoms and form the agglomerates which grow in some supercages scattered throughout the zeolite crystal at the expense of Pt atoms migrating from neighboring cages. Most of

TABLE 3
CHEMISORPTION AT 25°C ON SAMPLE I (14 wt% Pt)

Gas adsorbed	H or O or CO/Pt
H_2	0.98
O_2	0.42
H_2 (titration)	1.80
CO	0.41; 0.56

the agglomerates detected by SAXS are too large to pass through the 7.5 Å apertures. They are thus trapped and stabilized inside the supercages until the breakdown of the structure occurs. Hydrogen chemisorption indicates that all Pt atoms are accessible. But this can happen even for particles containing up to 20 atoms [for example an octahedron with 3 Pt atoms along the edges would have 18 out of 19 atoms on the surface (*17*)]. From SAXS results it turns out that an appreciable fraction of these agglomerates fills up the volume of a few supercages instead of forming smaller particles dispersed in a greater number of cages. As previously stated, this description would also account for the difficulties encountered in detecting platinum agglomerates by crystal structure analysis. In the same way the complete filling of some cages can possibly explain the comparatively low value of the O/Pt ratio (see end of Sect. A). On the other hand, particles smaller than 5 Å would agglomerate as they are able to pass through the 7.5 Å apertures of the cages. All of these considerations allow one to conclude that the size of platinum agglomerates ranges from 6 to 13 Å. They could contain from 8 to 14 Pt atoms so that about 1 supercage out of 10 would be occupied by a metal agglomerate. No suitable data are available so far to describe the arrangement of Pt atoms: however, a probable structure could be the thermodynamically stable icosahedral packing of 13 atoms (*18*).

800–1000°C Temperature Range

Growing and crystal organization of agglomerates into 25–30 Å crystallites occur between 800 to 900°C as shown by line broadening and SAXS. Simultaneously hydrogen chemisorption undergoes a drastic decrease: the H/Pt ratio falls from 1 to 0.15. On the other hand X-ray diffraction proves that a complete breakdown of the zeolite structure occurs after the 900°C treatment. Thus crystallite formation and lattice collapse seem to occur simultaneously. It is therefore highly probable that the agglomerates are able to sinter when they are destabilized by cage collapse. Since no further size increase occurs one is led to conclude that the crystallites are formed in the bulk of the solid, the glassy silicoalumina preventing any further growing of crystallites.

However, the low value of the H/Pt ratio and of the metallic area measured by small angle scattering should correspond to particles of 50–60 Å. These particles are not detected by diffraction and they do not appear in the SAXS distribution curves; moreover, the sample color is dark-brown whereas it should be completely black if some large crystallites were present on the external surface. The only explanation is the presence of an appreciable fraction of Pt atoms or small clusters embedded inside the glassy silicoalumina in such a way that they are not accessible for gases. This is corroborated by a large increase of the Laue scattering measured at comparatively large angles.

Chemisorption Properties of Platinum Agglomerates

Platinum agglomerates provide a good model for high and homogeneous platinum dispersion and can therefore be used to check the stoichiometry of adsorption on very small particles. As previously stated, every Pt atom is exposed on the surface of these agglomerates which actually give H/Pt ratios equal to unity even after heating at 800°C (Fig. 4). On the other hand oxygen chemisorption measurements give O/Pt = 0.42 and hydrogen titration H/Pt = 1.8. These ratios fit well with those previously found by Dalla Betta and Boudart (*7*) for similar samples and they correspond to the stoichiometry 1:0.5:2 for HA, OA and HT that Wilson and Hall (*4*) have proposed for very small particles. However, the O/Pt and H/Pt (titration) are smaller than 0.5 and 2, respectively. Although these discrepancies are hardly significant they may possibly suggest that oxygen atoms cannot be bonded with all the Pt atoms because of steric hindrance due to the relative size of cages and agglomerates.

Carbon monoxide adsorption yields CO/Pt = 0.41 and 0.58 on two different samples giving H/Pt = 1. One cannot definitively interpret these values since, on the one hand, there may be steric hindrance in the cage, and on the other hand, a mixture of bridge-bonded and linearly bonded CO on platinum may take place. However, it emerges that the amounts of CO and O chemisorbed on agglomerates are almost similar, which is in agreement with the results and discussion of Wentrcek *et al.* (*19*).

B. Platinum Dispersion on PtY Zeolite Pretreated at 600°C

Location and Dispersion of Platinum Atoms

Crystal structure analysis of PtY zeolite pretreated at 600°C (sample I 600) has shown that almost all Pt^{2+} ions occupy SI′ sites in the sodalite cages. They are bonded to 3 O(3) framework oxygen with a 2.20 Å Pt–O distance (half way between 2.36 and 2.03 Å: distances calculated assuming ionic and covalent radius, respectively, for the atoms). Upon reduction at 300°C (I 600 R 300) most of the Pt atoms are found to occupy random positions throughout 2.5 Å radius spheres concentric with the sodalite cages. This is essentially the same behavior as $Pd^{(0)}$ atoms in PdY zeolite (*8*): reduced atoms have no electrostatic requirements to occupy cation sites any longer and are thus randomly distributed along the cage walls. However, 3 out of the 10 $Pt^{(0)}$ initially present in sodalite cages are found on SI′ (0.065) sites. The SI′ (0.065)–O (3) distance (2.54 Å) is intermediate between 2.20 Å distance found in the unreduced I 600 sample and the sum of the oxygen radius and platinum metallic radius (2.79 Å). These atoms on preferential SI′ (0.065) positions are actually reduced, as shown by hydrogen uptake measurements, but they are probably in slight interaction with the aluminosilicate framework via a partial electron transfer from the Pt atoms to electron acceptor sites of the zeolite. Lewis acid sites are actually formed during the 600°C pretreatment by dehydroxylation of silanol groups.

As only average population is determined from diffraction data, one is unable to assert whether the 10 Pt atoms occupying the sodalite cages are in two or three cages forming aggregates of 3–4 atoms or whether they are in maximum dispersion: six cages each containing 1 $Pt^{(0)}$ and two cages occupied by a couple of $Pt^{(0)}$. The following remarks sustain this last hypothesis:

i. Before reduction Pt^{2+} ions have probably the highest dispersion because electrostatic requirements prevent the overcrowding of sodalite cages by multivalent cations.

ii. After the 300°C reduction Pt atoms of 2.8 Å diameter remain in their own cages because they cannot pass through 2.2 Å apertures of the sodalite cage. When they can leave cages, they are likely to migrate along the large pore system (supercages) and subsequently agglomerate in it, instead of entering another sodalite cage.

iii. By heating above 300°C, Pt atoms are progressively removed without any structure damage. This may be expected for isolated atoms, whereas clusters of 4 atoms in sodalite cages would behave like agglomerates in supercages, namely they would be trapped until structure breakdown occurs. SAXS results indicate that most of the platinum atoms do not scatter in the usual range of angles (this is compatible with the model of atomically dispersed platinum discussed above). However, 30%

of Pt atoms would also form 6–8 Å particles which obviously cannot fit into the sodalite cages and must therefore be considered as agglomerates in supercages. This is inconsistent with crystal structure results indicating that most of the atoms are in sodalite cages. These discrepancies are probably due to difference in sample treatments. Only a very small amount of powder (10 mg) is used for X-ray diffraction measurements, whereas 200 mg are needed for SAXS data collection. Many trials have shown that the Pt^{2+} ion distribution in the sodalite cages and consequently the final platinum dispersion greatly depend upon the amount of powder treated as far as heavily Pt-loaded zeolites are concerned.

When the zeolite is evacuated at increasing temperature Pt atoms progressively migrate out of the sodalite cages to form crystallites and agglomerates. This is evidenced both by X-ray diffraction and SAXS results. X-Ray diffraction indicates that at 600°C (sample I 600 R 600) there are less Pt atoms randomly distributed in sodalite cages (site U) than at 300°C (sample I 600 R 300); simultaneously one observes the gradual formation of 20–30 Å crystallites, and at 800°C about 50% of the platinum is organized in crystallites. The interpretation of SAXS results (Table 2) is more complex. In sample I 600 R 300 a notable fraction of the platinum was not detected so that the diameter calculated from the metallic surface (21 Å) is larger than the diameter calculated from the distribution curve (9 Å). In sample I 600 R 800 the metallic area measured by SAXS is identical to that found for I 600 R 300 but the total amount of platinum is now detected; accordingly, the diameter calculated from the metallic area (20 Å) is nearly equal to the diameter corresponding to the maximum of the distribution curve (18 Å). Hence, X-ray diffraction and SAXS results suggest that formation and growth of agglomerates and crystallites occur between 300 and 800°C at the expense of isolated Pt atoms migrating from sodalite cages. These species leave the sodalite cages as soon as they acquire a sufficient energy to go through the 2.2 Å barrier giving access to the large pore system. This removal spreads over a wide temperature range (300–800°C) probably because Pt atoms are not all stabilized in the same manner in the cages.

The platinum dispersion after 900°C (sample I 600 R 900) evacuation is quite similar to that observed for I 300 R 900; platinum forms crystallites of 25–30 Å diameter occluded throughout the bulk of the destroyed zeolite crystals.

Hydrogen Chemisorption vs Platinum Dispersion

The PtY zeolite pretreated at 600°C (I 600 R 300) exhibits a very unusual behavior as far as hydrogen chemisorption is concerned: the chemisorption increases as the zeolite is heated at increasingly higher temperatures (Fig. 4). It looks as if the platinum dispersion, which is initially very poor, gradually improves upon heating the solid at temperature as high as 800°C. This interpretation is obviously misleading and inconsistent with the results reported above showing that Pt-agglomerates and Pt-crystallites are forming up to 800°C at the expense of isolated Pt atoms. One is led to conclude that atomically dispersed platinum in sodalite cages is not capable of chemisorbing hydrogen. This was already found for $Pd^{(0)}$ atoms encaged in sodalite units of PdY zeolite (*8*). Hence the whole pattern of results is consistent: hydrogen chemisorption increases when platinum agglomerates and platinum crystallites (which can chemisorb hydrogen) are forming at the expense of atomically dispersed platinum (which cannot chemisorb hydrogen). The H/Pt ratio never reaches unity because 20–30 Å crystallites (giving $H/Pt < 0.5$) are formed concurrently with platinum agglomerates (giving $H/Pt = 1$).

At 800°C H/Pt = 0.65, and this ratio fits with the 50% agglomerates–crystallites proportion roughly estimated by X-ray diffraction. The subsequent fall of H/Pt from 0.65 to 0.15 on heating at 900°C is due to the complete transformation of agglomerates according to the mechanism already discussed for the zeolite pretreated at 300°C.

The initial hydrogen chemisorption after 300°C evacuation (sample I 600 R 300) gives H/Pt = 0.25 (Fig. 4). This part of platinum chemisorbing hydrogen probably corresponds to the fraction of platinum characterized by SAXS as being agglomerates of 6–10 Å located in the supercages. Indeed, adsorption as well as SAXS measurements were performed on larger amounts of zeolite than for X-ray diffraction measurements so that some Pt^{2+} does not enter the sodalite cage during the 600°C pretreatment.

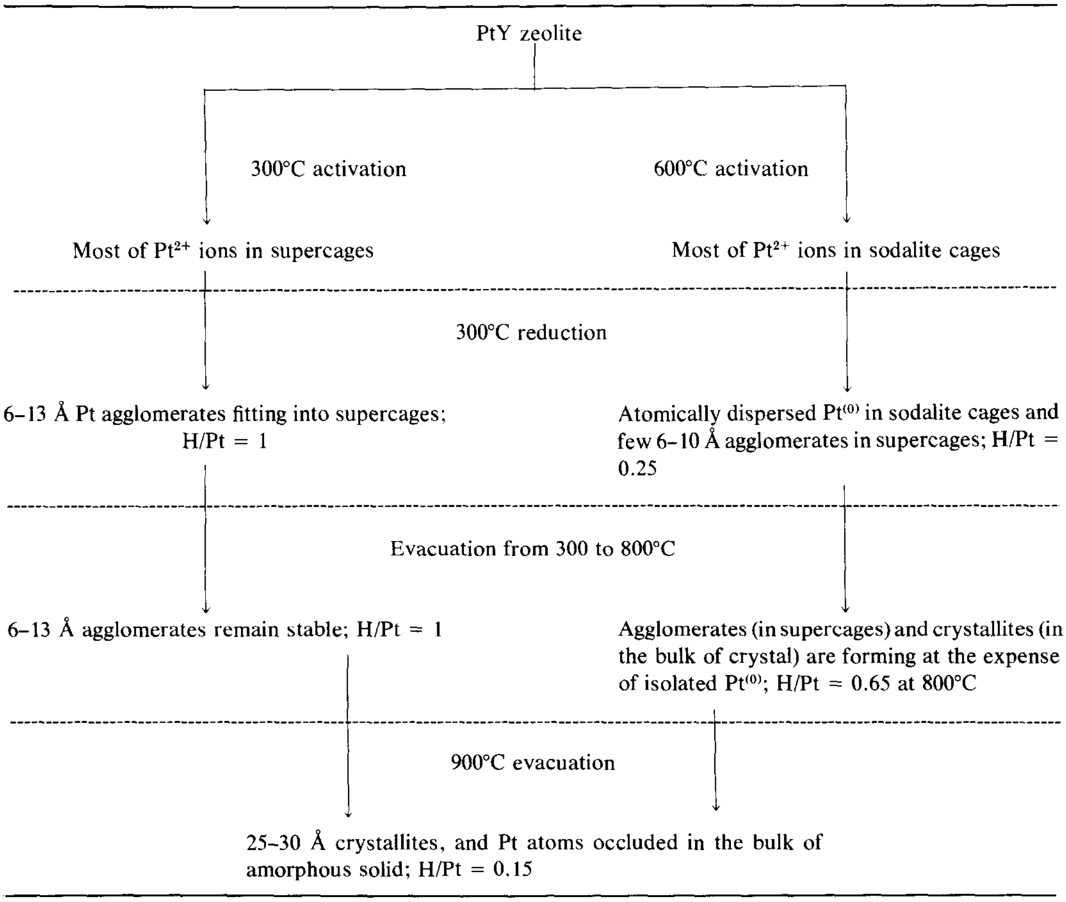
The question arises as to why the Pt atoms dispersed in sodalite cages do not chemisorb hydrogen. Three interpretations can be tentatively proposed:

i. At least 2 Pt atoms are required to dissociate molecular hydrogen since 1 Pt can only accept 1 H.

ii. Atomically dispersed platinum has lost its metallic properties including hydrogen chemisorption.

iii. Hydrogen chemisorption is inhibited because a partial electron transfer between Pt atoms and Lewis acid sites occurs. None of these interpretations can be ruled

TABLE 4



out in the present state of knowledge of this system. One may even add a fourth interpretation: molecular hydrogen cannot enter the sodalite cages and therefore cannot be activated by the platinum encaged there. As a matter of fact the kinetic diameter of H_2 molecule (2.89 Å) is larger than the six-membered oxygen ring (2.2 Å) giving access to the sodalite cage; however, the possibilities of sorption in zeolites can be forecast with certainty only if there is at least 1 Å difference between the respective diameters of the molecule and the cage aperture. Furthermore, one cannot decide from any simple experimental method whether or not molecular hydrogen enters the sodalite cage at room temperature; therefore, the fourth interpretation cannot be discarded.

CONCLUSION

This study has shown that platinum can be obtained in various well-defined states of dispersion in the zeolite matrix depending on the treatments applied to the samples. Table 4 summarizes these findings. The activation pretreatment does not place 100% of the Pt atoms in a given cage and therefore the final dispersion is not strictly homogeneous. In this respect the amount of treated powder and the exchange level in platinum play a major role. However, the results reported here nearly approach the ideal scheme where according to the pretreatment temperature all the Pt atoms would be either dispersed as agglomerates in supercages or atomically dispersed in sodalite cages. These two states of dispersion are of great fundamental and applied interest. Platinum agglomerates in zeolite supercages provide a unique model of high and homogeneous dispersion at the "frontier" of the metallic state. This work also shows that they have an unusually high thermal stability. It must be noticed that the agglomerates characterized in this work have a comparatively large size (6–13 Å); however, it is likely that smaller agglomerates could be obtained from PtY zeolite containing less platinum.

Platinum atoms isolated in sodalite cages are, a priori, of little interest as far as catalysis is concerned since these atoms are inaccessible to all molecules except small polar molecules such as H_2O or NH_3, and moreover they do not chemisorb hydrogen. However, atomic dispersion opens a new field for solid state investigations with the modern methods of physical chemistry, the first question to be cleared up being the lack of chemisorption properties of this system.

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