

## The Structure and Activity of Supported Metal Catalysts

### V. Variables in the Preparation of Platinum/Silica Catalysts

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A systematic study was made of the variables involved in preparing Pt-silica catalysts either by impregnation with chloroplatinic acid or by adsorption of platinum ammine from solution. A model of the impregnation process is suggested which is used to explain the variation of Pt area and crystallite size with Pt content; the number of Pt crystallites is discussed in terms of the porosity of the silica and an empirical correlation established between Pt area and the surface area of silica gels from different sources. The adsorption of  $\text{Pt}(\text{NH}_3)_4^{2+}$  from solution is related to the number of available exchange sites on silicas with different areas; the (mean) Pt crystallite size is constant over a 40-fold variation in Pt content and a size-controlling mechanism is proposed.

The reduction temperature needed to remove chlorine from impregnated silica causes sintering to an extent dependent on Pt content; the temperature for subsequent  $\text{H}_2$  desorption to give maximum specific adsorptive capacity was established. The reduction of adsorption-type catalysts is compared with previous work. Controlled firing in air unreduced catalysts provides an attractive method for producing series of catalysts with different mean crystallite size, from 15 Å upwards in adsorption-type catalysts. Crystallite growth in unreduced impregnated-type catalysts depends on various factors including silica area, gaseous environment, temperature and time of heat treatment: a growth mechanism involving vapor transport of volatile chlorides is described. Optimum conditions for drying impregnated catalysts to preserve Pt area were established.

#### INTRODUCTION

Major themes in the study of supported metal catalysts include methods for improving and measuring metal dispersion, the effect of metal crystallite size and nature of the support on specific activity, and the role of metal location within the support in relation to catalyst poisoning or diffusion control of reaction rates. Also individual studies of kinetics and mechanisms using various metal/support combinations are reported, as well as adsorption studies using infrared spectroscopy and other techniques. It is known that different methods for preparing supported metal catalysts and changes in the details of the method affect the metal dispersion and catalyst activity. Therefore it would

appear that a systematic examination of the variables involved in preparing some of these catalysts would be an aid to further progress in the standardization of methods of catalyst preparation. For example, a method might be described for providing a series of catalysts each with a particular mean crystallite size in the range 15–70 Å for use in studying crystallite size effects. Some methods used for varying crystallite size can introduce additional problems (1).

The platinum-silica system is a rather idealized one but appears particularly suitable for systematic study. Techniques for catalyst characterization, e.g., electron microscopy, selective chemisorption, have been successfully applied to it (2); de-

tailed descriptions of catalyst preparation have been given (3) and some of the variables affecting crystallite size and growth have been examined (3-5). The present work relates to platinum-silica catalysts made either by impregnation with chloroplatinic acid or by adsorption of the ammine from solution and examines the effect of support area, metal content, reduction conditions, heat-treatment, drying etc. on metal dispersion and other properties. As far as possible, mechanisms by which these changes in metal dispersion come about have been suggested.

## EXPERIMENTAL

### *Catalyst Preparation*

Impregnated-type catalysts were prepared by wetting completely, a known weight of the silica support with the appropriate quantity of chloroplatinic acid solution to give the required Pt content. The water was boiled off, stirring continuously, and the catalyst dried at 120°C for 16 hr (unless otherwise stated) in an air oven. Samples (~2 ml) were reduced by purging with hydrogen (diffused through a silver-palladium membrane) at room temperature and then the sample tube was transferred into an electric furnace already at the required temperature, e.g., 210°C. The hydrogen flow, 100 ml/min, was maintained for the period of reduction and the reduced catalysts were cooled to room temperature in hydrogen.

Adsorption-type catalysts were prepared (3) by adding the silica support to a well-stirred solution of "platinum ammine"; contact time, 3 min. The ammine solution was produced by adding an excess of ammonium hydroxide solution to a solution of chloroplatinic acid and heating to 80-90°C for 20 minutes. For example, a 2.5% Pt catalyst was prepared by adding an 18-times excess of 0.88 ammonium hydroxide, diluted 1 vol:3 vol water, to chloroplatinic acid solution, also diluted 1:3. After filtering and washing (at least 50 ml water/g catalyst), the catalyst was dried for 3 hr at 60°C in an air oven. The standard reduction procedure was to purge with pure hy-

drogen at room temperature for 2 hr, raise the temperature to 300°C over 2 hr and maintain at 300°C for a further 2 hr, in a flow of hydrogen, 100 ml/min. Catalysts were cooled to room temperature in hydrogen. In experiments where the unreduced catalysts were fired in air, samples contained in open porcelain crucibles were placed in an air oven *already at the required temperature*.

### *Catalyst Characterization*

Measurements were carried out on catalysts in the reduced state. Platinum contents were determined by X-ray fluorescence analysis. The mean crystallite size was derived from X-ray line-broadening as described in Ref. (6) which also gives details of the method used to estimate the amount of platinum present in crystallites of >50 Å and included in the mean size determination. The Pt area per gram catalyst was calculated from these X-ray data assuming that the crystallites were regular cubes with five faces exposed and that the mean size of the platinum undetected by X-ray diffraction was 25 Å.

Platinum areas were also measured by gas chemisorption using carbon monoxide or hydrogen (using a modified BET-type apparatus). One gram samples of catalyst were reduced and then outgassed at 350°C for 4 hr, and the gas adsorbed at 25°C and pressures up to ~5 Torr. The monolayer volume was obtained by extrapolating the linear portion of the corrected isotherm to zero pressure. As in previous work, it was assumed that 15% CO was "bridge-bonded" in Pt-silica catalysts; combined X-ray line-broadening and electron microscopy observations (6) supported this view for small crystallite sizes. Recently (7) a series of ammine adsorption catalysts gave a mean H atom-CO ratio of 1.13. A surface platinum atom area of 8.9 Å<sup>2</sup> was used in calculating Pt areas from adsorption measurements.

The silica gels used came from three different sources; Davison, usually grade 70 (sometimes grades 12 or 950), "Sorbsil," types M60, U30 and R50 (Crosfield Chemicals) and "Porasil" types A, B, C, and D

(Waters Associates, Ltd., manufactured by Pechiney-Saint-Gobain). Surface areas of the batches actually used were measured by a flow method using nitrogen as adsorbate and pore volumes by  $\text{CCl}_4$  absorption.

## RESULTS AND DISCUSSION

### *Support Area and Pt Content*

**Impregnated-type.** Where there is no interaction between the platinum salt and the silica (as in the case of chloroplatinic acid with Pt in the anion), then the size and distribution of the platinum crystallites ultimately produced is affected by the physical structure (porosity, surface area) of the support. The following model of the impregnation process is suggested: towards the latter stages of impregnation, the removal of water concentrates the impregnating solution to the point where crystallization of the metal salt begins, providing a nucleus in those pores still containing solution. Further drying crystallizes out the platinum salt in an amount depending on the volume of solution in the pore at the onset of crystallization. Presumably, the size of the platinum crystallite formed by reduction is simply related to the amount of salt deposited in the pore. If a very dilute platinum salt solution is used initially to wet the silica, then concentration has to proceed to the point where many pores are empty before crystallization begins and the number of platinum crystallites is substantially less than the number of pores in the silica. Increasing the strength of the impregnating solution will increase the number of pores containing a crystallite until the number of crystallites may equal the number of pores. Therefore, up to a certain Pt content, the number of crystallites will increase, the mean crystallite size will vary slowly, and the Pt area will be approximately proportional to the Pt content. Beyond this Pt content, the number of crystallites will remain constant if any tendency to nucleate more than one salt deposit in each pore is cancelled out during drying or in the early stages of the reduction process. Hence, the platinum

crystallites will increase in size and the Pt area will be proportional to (Pt content)<sup>2/3</sup> (6). It would also seem to follow that the crystallite size distribution should reflect the pore size distribution of the silica and should be rather broad.

Table 1 shows the mean crystallite size and number of crystallites,  $N$ , calculated from the Pt surface area data and Pt content (6), with new values at Pt contents

TABLE 1  
MEAN SIZE AND NUMBER OF PT CRYSTALLITES  
(IMPREGNATED-TYPE ON DAVISON "70" SILICA)

Pt content (%)	Mean crystallite size (Å)	No. of crystallites per g catalyst ( $\times 10^{16}$ )
0.15	39 <sup>a</sup>	0.11 <sup>a</sup>
0.29	30 <sup>a</sup>	0.47 <sup>a</sup>
0.63	32 <sup>a</sup>	0.90 <sup>a</sup>
1.06	38	0.92
1.24	35	1.3
2.57	42	1.6
3.10	36	3.1
4.20	35	4.6
4.90	40	3.6
5.40	39	4.2
8.50	56	2.3
10.20	54	3.0
11.50	60	2.5

<sup>a</sup> From CO chemisorption; otherwise from X-ray data.

where  $N$  is becoming constant. In support of the above ideas, the number of crystallites increased with Pt content (to ~3% Pt), then remained approximately constant while the mean crystallite size increased. Further, Fig. 1 shows the initial linear increase of Pt area with increasing Pt content expected. Beyond ~3% Pt, the rate at which the Pt area increased was appropriate to the expected two-thirds power relationship. Also a characteristic of impregnated Pt-silica catalysts is the wide range of crystallite sizes observed in electron micrographs (6, 8). For example, in a 3% Pt catalyst, sizes ranging 10–110 Å were observed.

The number of crystallites shown in Table 1 increased to  $\sim 3 \times 10^{16}$ /g catalyst

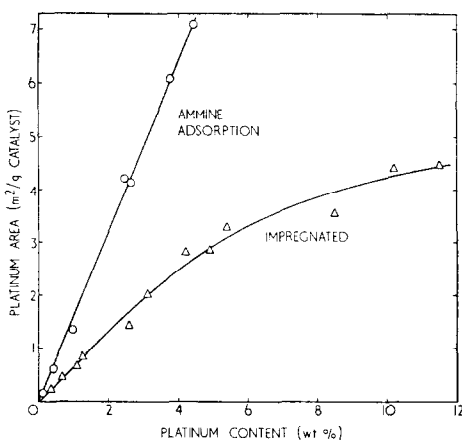


FIG. 1. Variation of Pt area in impregnated- and ammine adsorption-type catalysts with Pt content.

and, as discussed previously (6), this number is consistent with the number of pores in the silica used,  $4 \times 10^{17}$ /g catalyst. It is not to be expected, however, that there will be an exact correspondence between the number of crystallites, derived from a mean crystallite size, and the number of pores derived from support area without reference to the pore size distribution or the shape of the pores. If the silica gel is constructed from close-packed spheres, then complex pore shapes occur depending on the type of packing (simple cubic, rhombohedral, etc.), which might, if sufficiently large, nucleate more than one crys-

tallite. Alternatively, the effective number of pores may be decreased: in the example given above, the porosity of the support was 57% which is greater than the porosity of the "most open" cubic packing and suggests a certain amount of "voidage" within the granules, eliminating pores. Other uncertainties include the accessibility of the smallest pores to platinum salt and the interconnection of the pore system.

For various forms of close-packing, the number of pores is equal to the number of ultimate silica particles, which can be calculated approximately from the support area. It can be shown that the platinum crystallite size will decrease, i.e., the dispersion improves, as the support area is increased but this simple relationship is unlikely to apply for the reasons given above. Therefore an empirical approach was adopted to the question of how dispersion is affected by the porosity of the support, i.e., catalysts were prepared using silicas from different sources of supply, with widely different surface areas/pore volumes and a correlation sought between Pt crystallite size and surface area of the support.

Table 2 records the surface areas of the actual batches of silica gel used for catalyst preparation and nominal pore diameters expressed as the diameter of the sphere

TABLE 2  
EFFECT OF SUPPORT ON CRYSTALLITE SIZE (2.7% PT-SILICA IMPREGNATED CATALYSTS)

Type	Support			Mean crystallite size		(No. of pores) <sup>1</sup> / (No. of crystallites)
	Surface area (m <sup>2</sup> /g)	Pore volume (ml/g cat.)	Nominal pore diameter (Å)	X-ray data (Å)	CO ads (Å)	
"A"	423	0.74	74	30	24 ± 4	38
"B"	193	1.04	180	37	52 ± 2	38
"C"	92	0.65	325	60	58 ± 4	6
"D"	35	0.20	576	80	82 ± 11	1
"M60"	588	0.45	44	—	28	165
"U30"	483	0.70	63	—	19	29
"R50"	277	0.45	95	—	23	10
"12"	798	0.33	30	32	—	607
"70"	267	1.0	128	32	36	31

equal in volume to the mean pore volume (obtained from the total pore volume and number of pores). Measurements of CO chemisorption on the first four catalysts in the table were made by two independent methods, by a static volumetric technique and using a vacuum microbalance. Except for the second catalyst, crystallite sizes from X-ray data were in satisfactory agreement and the X-ray value was used for the catalyst on Davison "12" silica where the CO chemisorption measurement was unsatisfactory.

It can be seen from Table 2 that the correspondence between the number of crystallites and the apparent number of pores is only moderately satisfactory. When the nominal pore diameter is small, e.g., in Crosfield "M60" and Davison "12", then large numbers of pores remained unused. However, Fig. 2 shows that there is a satisfactory empirical correlation between Pt crystallite size and the surface areas of silicas from different sources. There is also some suggestion of a minimum crystallite size where a large silica area is associated with an adequate pore diameter. Finally, it might be noted that changing the silica support provides a method of varying the mean crystallite size in the critical 20–70 Å range, without recourse to sintering or varying reduction conditions, metal con-

tent etc., although the differences in porosity may be undesirable.

**Adsorption-type.** The adsorption of Pt  $(\text{NH}_3)_4^{2+}$  from dilute  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  solutions by silica gel has been discussed in terms of exchange with surface  $\text{H}^+$  ions and it has been demonstrated that the amount of platinum taken up can be controlled through adjustment of the pH (5). In the present work, the ammine was prepared in solution by heating chloroplatinic acid with excess ammonium hydroxide and silica gel contacted with this solution, pH 10. Adopting this standard method of preparation, up to 7% Pt could be adsorbed on Davison "70" silica gel, leaving platinum ammine remaining in the solution. The marked dependence of the degree of dispersion on the conditions of washing used in preparing these catalysts has already been described (3), and this excess ammine is a factor.

Table 3 relates to the uptake of platinum from solution and shows that most of the platinum complex was adsorbed by silica gels with surface areas of 200–800  $\text{m}^2/\text{g}$ . The platinum content of the solution used would have enabled catalysts with up to ~2.7% Pt to have been produced; lower area silica gels (Porasils "C" and "D") could not adsorb all the platinum ammine available in solution. If the exchange capacity relates directly to the number of

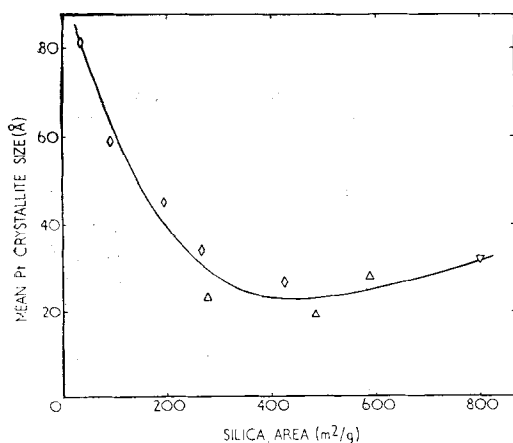


FIG. 2. Correlation of mean Pt crystallite size in impregnated-type catalysts (2.7% Pt) with area of silica supports from different sources; sizes from CO chemisorption,  $\Delta$ ; from X-ray data,  $\nabla$ ; average of both measurements,  $\diamond$ .

TABLE 3  
EFFECT OF SUPPORT ON Pt ADSORPTION  
FROM SOLUTION<sup>a</sup>

Support Type	Support			
	Surface area ( $\text{m}^2/\text{g}$ )	Pt content (%)	Mean size <sup>b</sup> (Å)	No. of crystallites/g catalyst ( $\times 10^{17}$ )
"12"	798	2.68	14	4.6
"M60"	588	2.42	13	5.3
"A"	423	2.66	15	3.8
"B"	193	2.42	16	2.7
"C"	92	2.00	17	1.9
"D"	35	1.10	17	1.0

<sup>a</sup> Maximum possible ~2.7% Pt, from conc. of solution used.

<sup>b</sup> From CO chemisorption.

surface hydroxyl groups on the silica gel (taken as 4.6/100 Å<sup>2</sup>) then on the Porasil "C" catalyst there is one Pt atom for every 7 hydroxyl groups. Where the number of available Pt atoms is apparently in considerable excess (compared with the observed exchange capacity), i.e., for Porasil "D" (Table 3) and in the example cited above for Davison "70", then there is one Pt atom for about every 5 hydroxyl groups. If each Pt atom has been deposited on the silica surface through the agency of the doubly-charged Pt(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> ion and if steric effects also occur, the involvement of about 5 hydroxyl groups seems reasonable.

Table 4 shows the Pt area, mean crystallite size and number of crystallites, in adsorption-type catalysts prepared on Davison "70" silica gel using various

TABLE 4  
VARIATION IN PLATINUM CONTENT (ADSORPTION-TYPE ON DAVISON "70" SILICA)

Pt content (%)	H <sub>2</sub> adsorption (cc/g)	Pt area (m. <sup>2</sup> /g catalyst)	Mean size (Å)	No. of crystallites/g catalyst (×10 <sup>17</sup> )
0.10	0.033	0.16	15	0.14
0.40	0.126	0.60	16	0.47
0.94	0.28	1.34	16	1.0
2.45	0.879	4.21	14	4.3
2.64	0.863	4.13	15	3.7
3.78	1.267	6.07	15	5.4
4.45	1.474	7.06	15	6.3

amounts of platinum up to ~4.5%, i.e., rather less than the maximum possible uptake. A noticeable feature of the results is the almost complete constancy of the mean crystallite size although the Pt-content varied more than 40-fold. Increase in the Pt content was accommodated solely by an increase in the number of crystallites as observed previously (9), and it follows that the Pt area is directly proportional to the Pt content, Fig. 1. The crystallites are substantially smaller than observed in impregnated-type catalysts and also, unlike these catalysts, the size is virtually independent of either support area or Pt content.

Nevertheless, the platinum present is far from being atomically dispersed and the mechanism leading to a constant mean crystallite size of ~15 Å (Table 4) might be discussed. It is assumed that, initially, Pt(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> ions are distributed over the silica surface but aggregation occurs in drying/reduction and the factor controlling the size at 15 Å is sought. Various arguments can be advanced against the idea that aggregation stops because all the platinum in each pore has been collected together. Instead it is proposed that the platinum aggregate develops from a nucleus which grows from platinum complexes within a given area of the surface determined by their mobility.

If initially the Pt (NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> ions were equally spaced out over the entire silica surface, this would mean that in the catalyst with (say) only 0.10% Pt, the ions would have traversed greater distances to form the aggregates which become 15 Å-size crystallites. This seems unlikely and therefore it is believed that the exchange sites on the silica surface are fully utilized as the solution containing Pt(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> ions penetrates into the pore system. If the solution is dilute, exchange sites on the less accessible silica surface remain unused. Thus, in the subsequent aggregation of platinum surface species, the low Pt content catalysts produce crystallites of the same size as those formed when much larger amounts of platinum are present.

It follows that the method of contacting and the contact time involved in preparing adsorption-type catalysts will give rise to differences in the extent of metal distribution and, of course, this forms part of the "art" of catalyst manufacture. The rate of adsorption of metal ions from solution compared with rates of diffusion etc. is relevant to this problem. The mean crystallite size reported in the present work must be taken as relating specifically to the method of preparation described. It has been shown previously for the Pt-silica system (3) that increasing the duration of contact between silica gel and solution from 3 min to 2 days always leads to a marked increase in the degree of Pt dispersion.

### Hydrogen Reduction

**Impregnated-type.** The metal salt impregnating the support usually has to be reduced to the metallic state, before the catalyst is ready for use, and a stream of gaseous hydrogen can be employed (as an alternative to wet reduction methods). It is necessary to establish the minimum temperature required for complete reduction and whether higher reduction temperatures could cause crystallite growth accompanied by a loss in metal area.

For catalysts prepared by impregnating silica gel with chloroplatinic acid, the reduction process can be followed by measuring the rate of HCl evolution. Reduction tests were carried out at 100 ml H<sub>2</sub>/min and 760 Torr using a 2 ml catalyst charge (below 80 ml H<sub>2</sub>/min, the rate of reduction is dependent on the H<sub>2</sub> flow rate). Figure 3 shows (open symbols) percentage of total chlorine evolved from a 2.5% Pt-silica catalyst at 22°C (undried catalyst) and at 80° and 210°C (previously dried at 120°C). Reduction is almost complete, 98.2%, after 2 hr at 210°C. In confirmation, the analyzed chlorine-content of a 3.3% Pt catalyst after the same reduction treatment was 0.10% Cl<sub>2</sub>, (corrected for Cl content of the silica) corresponding to 95.8% reduction, compared

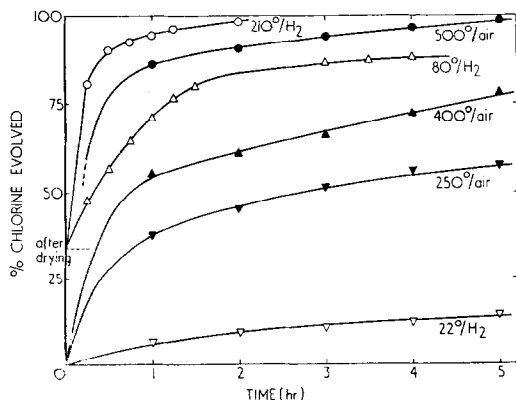


FIG. 3. Chlorine evolution from silica impregnated with chloroplatinic acid (Pt content 2.5%): undried and heated in H<sub>2</sub> at 22°C or, after drying, heated in H<sub>2</sub> at 80 or 210°C, open symbols; undried and heated in air at 250, 400 or 500°C, solid symbols.

with 0.004% Cl<sub>2</sub>, i.e., 99.8% reduction, after 2 hr at 500°C.

Table 5 shows the effect of reduction temperature on the Pt area, i.e., the extent to which crystallite growth has occurred during catalyst reduction. The Pt area was calculated from the crystallite size and the per cent Pt detected by X-ray

TABLE 5  
EFFECT OF REDUCTION TEMPERATURE  
ON PT AREA<sup>a</sup> (IMPREGNATED-TYPE)

Reduction temperature (°C)	Pt area (m <sup>2</sup> /g cat.) from X-ray data		
	1% Pt-SiO <sub>2</sub>	3% Pt-SiO <sub>2</sub>	10% Pt-SiO <sub>2</sub>
80	0.58	2.32	4.85
140	—	2.04	4.57
210	0.66	2.01	3.80
300	0.58	1.86	3.82
500	0.55	1.87	3.14
Maximum loss in area <sup>b</sup>	5%	20%	35%

<sup>a</sup> "Absolute" area of Pt crystallites, irrespective of adsorptive capacity.

<sup>b</sup> Compared with area after 80°C reduction.

diffraction. Thus, while a higher reduction temperature may produce a "cleaner" surface with more adsorptive capacity per cm<sup>2</sup> (see below), the actual total area of the platinum is decreased. This loss of area is of little significance in catalysts with small Pt contents, but with 10% Pt about one-third of the potential area was lost when the reduction temperature was raised from 80° to 500°C.

As shown in the next section, subjecting the *unreduced* chloroplatinic acid on the silica support to heat leads to aggregation and hence a loss of Pt area. Therefore, while the *reduced* catalyst is very much less affected by heat treatment, the start of the reduction process is a sensitive stage in catalyst preparation, requiring some attention to detail.

With regard to specific adsorptive capacity, it was reported previously (7) for impregnated Pt-silica catalysts reduced at

210°C, that "absolute" Pt areas derived from X-ray data agree with Pt areas obtained from hydrogen chemisorption, if the Pt (surface)/H atom ratio is  $\sim 1$ . However, Table 5 shows that the reduction temperature might usefully be increased depending on the Pt content.

In the present work, hydrogen was removed from the Pt surface after reduction by outgassing at 350°C for 4 hr, prior to chemisorption experiments. No significant differences in capacity for CO chemisorption were observed for outgassing treatments varying between 350°C for 1 hr and 500°C for 14.5 hr, for a catalyst with 12.5% Pt. Adams *et al.* (2) report for a 2.5% Pt-silica catalyst that hydrogen chemisorption increased with increasing evacuation temperature up to 250°C (for 1 hr), then remained constant up to 800°C.

**Adsorption-type.** Measurements of the rate of NH<sub>3</sub> evolution from the platinum ammine complex adsorbed on silica provided some indication of the extent of reduction achieved under different conditions. It was clear, at temperatures up to 210°C, that adsorption-type catalysts are less easily reduced than the impregnated-type, presumably reflecting their stability or strength of bonding to the surface of the support. At temperatures of 300°C and above, reduction was very rapid and apparently complete (no further NH<sub>3</sub> evolved) after 5 minutes.

Poltorak *et al.* (3) describe two reduction methods: Method 1 was described above under "Catalyst Preparation"; in Method 2, the catalyst was heated in air to 130°C, evacuated, the temperature raised to 300°C for 1 hr and then 0.1–1.0 Torr H<sub>2</sub> admitted for a further 1 hr period. Observed Pt dispersions expressed as (*H* atoms adsorbed)/(total Pt atoms) were 0.65 and 0.88 (Method 1) compared with 1.11 and 1.34 (Method 2) for catalysts with 2% Pt prepared with contact times of 3 min and 2 days, respectively. Ratios  $> 1$ , (at 1 Torr H<sub>2</sub> pressure and 20°C) were ascribed to the adsorption of molecular H<sub>2</sub> with an upper limit of  $\sim 1.3$  at maximum dispersion. In the present work, using reduction Method 1 (contact time

3 min) ratios of  $\sim 0.55$ – $0.6$  were usual, depending on the Pt content, in agreement with the above value of 0.65.

#### *Heat Treatment of Unreduced Catalysts*

Crystallite growth occurs when Pt-silica catalysts prepared either by impregnation with chloroplatinic acid or by adsorption of platinum ammine are heated (before reduction) in air to a sufficiently high temperature. Hence controlled firing in air of the unreduced catalyst provides an attractive method for producing a series of catalysts with different mean crystallite sizes.

**Impregnated-type.** It was shown previously (Fig. 1 and Table 1 in Ref. (4) for a nominal 2.5% catalyst, that the apparent crystallite size and fraction of total Pt detected by X-ray diffraction was increased at all firing temperatures above the (air) drying temperature, 120°C. Platinum areas calculated from X-ray data and from CO adsorption were in agreement; the mean crystallite sizes derived are shown in Fig. 4 for comparison with present observations on firing adsorption-type catalysts.

When alumina or charcoal supports were used, heat treatment of the unreduced salt caused very little Pt crystallite growth, perhaps as a consequence of its limited mobility on alumina and the vast area of the charcoal support. Again, it is not to be expected that Pt-silica catalysts, prepared by impregnating different grades of silica, will show the same response to firing temperature exhibited in Fig. 4 for Davison "70" silica, e.g., less crystallite growth occurred on the "950" grade (4). Table 6 shows the reduction in the Pt area, brought about by firing in air at 300°C for 5 hours, of catalysts supported on Porasil, grades "A"–"D", with (silica) areas ranging from 35–423 m<sup>2</sup>/g.

Again, the loss of Pt area, or crystallite growth, was increased by a reduction in the area of the silica support.

While a variation in crystallite size may be brought about by firing the unreduced catalyst in air, alternative environments (e.g., N<sub>2</sub>, Ar, vacuum), do not necessarily have an equivalent effect and prior H<sub>2</sub> re-



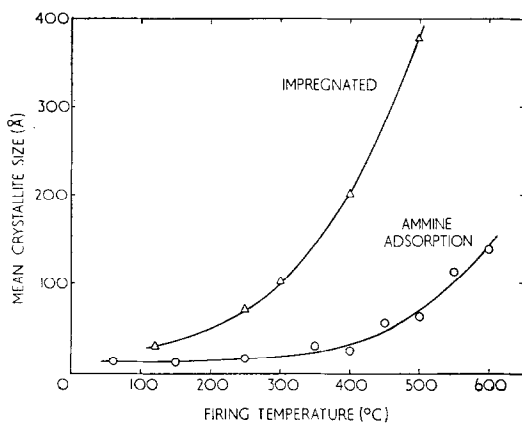


FIG. 4. Platinum crystallite growth due to firing impregnated- and ammine adsorption-type catalysts in air before the reduction stage.

duction to the metal before firing has a marked effect on the extent of crystallite growth. For example, a 3.05% Pt-silica catalyst adsorbed 0.55-ml CO/g catalyst when given the standard reduction at 210°C, another sample adsorbed 0.08 ml CO when the reduction was followed by heating in air at 600°C and a further sample adsorbed <0.01-ml CO if heating at 600°C preceded reduction. Also the loss of Pt from the catalyst which accompanies high temperature firing (in air at 600°C) was greatest (Pt content, 1.92% compared with 2.85%) when the firing stage preceded the reduction stage, rather than followed it.

Crystallite growth caused by heat treatment in air appears to reach a limiting

value after a certain period. For example, the mean crystallite size derived from CO chemisorption in a sample with 2.5% Pt, heated to 200°C in air before reduction, increased from 29 to 50 Å after 2 hr heating but only to 58 Å after 8 hours. (In terms of volume of Pt aggregated, the difference is less pronounced.)

The above observations (viz, inhibition of crystallite growth in air by prior hydrogen reduction, the loss of Pt at higher temperatures from the unreduced catalysts and the limitation of growth at a given temperature) suggest that the mechanism of crystallite growth in impregnated Pt-silica catalysts involves the volatile platinum chlorides. On drying at 120°C the chloroplatinic acid loses two molecules of HCl leaving the tetrachloride, PtCl<sub>4</sub>, on the support (see next section). Figure 3 shows the evolution of chlorine with time when a 2.5% Pt-silica catalyst was heated in a stream of air (solid symbols). The rapid initial decomposition rates followed by much slower rates resembles the pattern of crystallite growth observed. Essentially complete decomposition after 5 hr heating in air required a temperature of at least 500°C.

It is proposed that PtCl<sub>4</sub>, which has a measurable vapor pressure at 250°C (10), dissociates in the vapor phase when heated, evolving chlorine and depositing the lower chloride on the crystals of the Pt salt remaining on the support; larger crystals tend to grow and smaller ones to vaporize and disappear completely.

Calculation of the chlorine produced by dissociation of PtCl<sub>4</sub> at 250°C agreed well with the amount measured over 5 hr during the air treatment of a catalyst at this temperature. A steady-state is reached when all the higher chloride has dissociated unless the temperature is sufficiently high to produce a significant vapor pressure of the lower chloride which is less volatile. Crystallite growth slows down and will stop if no more platinum chloride can be vaporized. At higher temperatures growth by vapor-phase transport involves the successively lower chlorides until at 500°C and above the salt can dissociate completely

TABLE 6  
REDUCTION IN Pt AREA<sup>a</sup> BY FIRING Pt-  
PORASIL CATALYSTS AT 300°C  
(IMPREGNATED-TYPE)

Support	Support area (m <sup>2</sup> /g)	Platinum area (m <sup>2</sup> /g cat.)		% loss in Pt area
		Dried, 120°C	Fired, 300°C	
Porasil "A"	423	2.14	1.75	18
"B"	193	1.73	1.21	30
"C"	92	1.05	0.62	41
"D"	35	0.79	0.34	57

<sup>a</sup> Calculated from X-ray data.

depositing Pt metal (oxide?) crystallites. Prior reduction in hydrogen rapidly leads to the release of the metal and crystallite growth is minimized when the catalyst is subsequently fired in air, because the growth mechanism involving the chlorides is not available.

**Adsorption-type.** The platinum is highly dispersed over the silica support in catalysts prepared by ammine adsorption and so these catalysts are particularly useful in studying crystallite size effects. Although the crystallite size is suitably small it is less readily varied by the usual methods, but a well-controlled increase in size can be brought about by firing the unreduced catalyst in air (Fig. 4). Mean crystallite sizes shown for adsorption-type catalysts were derived from CO chemisorption data. Unreduced catalysts were fired for periods of 5 hr. Adsorption-type catalysts were more resistant to crystallite growth than the impregnated-type prepared on the same silica and the interesting 15–70 Å size range can be prepared by varying the firing temperature appropriately up to 500°C (for this particular silica and Pt content). Electron micrographs reproduced previously (1) show the even crystallite distribution in both unfired and fired adsorption-type catalysts.

The dissociation of the adsorbed ammine on firing in air is more complex than the

dissociation of chloroplatinic acid-platinum chlorides supported on silica. For present purposes it is sufficient to note that ammonia was evolved above 350°C, at which temperature crystallite growth was significant (Fig. 4). Presumably the ammine bonding to the surface must break down before growth, involving some more mobile surface species, occurs. Hence (unreduced) adsorption-type catalysts are more resistant to crystallite growth than the impregnated-type where the volatile chloride crystals deposited on the support readily grow by a mechanism involving vapor transport. As would then be expected, Pt was not lost from unreduced adsorption-type catalysts at firing temperatures up to 600°C.

#### Drying Conditions

Experiments on crystallite growth caused by heating unreduced catalysts in air (preceding section) suggested that milder drying conditions than the standard 120°C might be adopted to improve platinum dispersion in impregnated-type catalysts. Table 7 records the loss in weight on drying and the subsequent loss in weight when the catalyst was reduced (at 210°C). The expected weight loss on drying was 57% due to removal of water from the chloroplatinic acid solution, the water of

TABLE 7  
DRYING CONDITIONS (~3% Pt, IMPREGNATED-TYPE)

Drying conditions			X-ray data			
Temp. (°C)	Time (hr)	Atmos.	Drying loss (wt %)	Reduction loss (wt %)	Crystallite size (Å)	Fraction of total Pt detected
—	—	—	—	54.6	95	0.67 <sup>a</sup>
40	2	air	41.3	5.0	85	1.00
40	19	air	55.1	3.0	50	0.74
60	19	air	56.2	2.2	55	0.74
80	19	air	57.0	1.8	45	0.71
100	19	air	57.2	1.6	40	0.79
120	19	air	57.3	1.5	40	0.66
60	19	vacuum	57.3	1.8	45	0.68
120	19	vacuum	57.7	1.5	55	0.63

<sup>a</sup> Pt lost, Pt content 2.19%.

crystallization and the loss of two molecules of HCl. Reduction of  $\text{PtCl}_4$  to the metal would give an additional weight loss of 1.5%. A much greater loss in weight on reduction than 1.5% indicates that the catalyst had been incompletely dried; a temperature of 120°C in air or vacuum appears satisfactory for drying the catalysts.

Further, X-ray data on crystallite size show that drying in air at 120°C results in the least crystallite growth and none may have occurred. In contrast, reduction of the undried catalyst caused a severe loss of platinum with crystallite growth and incompletely dried catalysts, e.g., catalysts dried at 40°C for 2 hr, also contained large crystallites. In the initial stages of reduction these latter catalysts must have been heated at 210°C in the presence of water vapor as well as hydrogen. Now, as previously emphasized, the start of the reduction process is a particularly sensitive stage in catalyst preparation; rapid reduction of the chloride is required before the temperature used, 210°C, causes some crystallite growth. It is proposed that water vapor inhibits the hydrogen reduction process so that undried or incompletely dried catalysts have larger crystallites than catalysts which have been well-dried before reduction. The above observations also suggest that when impregnated Pt-silica catalysts are stored in the unreduced state, they should be thoroughly dried before reduction.

Adsorption-type catalysts were incompletely dried by the procedure adopted (60°C for 3 hr) as shown by large weight losses at the reduction stage. However, as noted above, heating in air for 5 hr at 300°C before reduction had no significant effect on the crystallite size (Fig. 4). Therefore, in contrast to the impregnated-type, the presence of water vapor during the initial stage of reduction does not promote crystallite growth in adsorption-type catalysts.

#### CONCLUSIONS

A number of methods can be used to provide series of Pt-silica catalysts each with

a particular mean size in the range of interest for studying crystallite size effects.

In principle, impregnated-type catalysts are more readily controlled in the initial stages of preparation; but, using chloroplatinic acid, crystallite growth occurs during reduction depending on the metal content, temperature, etc., and the exact procedure adopted. Providing the porosity of the support does not become a variable in the reaction studied, altering the specific area of the impregnated silica could be another useful method of controlling mean crystallite size. For example, using a high area silica an impregnated catalyst with crystallites of 19 Å mean size and Pt area of 3.3 m<sup>2</sup>/g was prepared containing 2.7% Pt.

An alternative method of reducing the mean size in impregnated catalysts is to decrease the Pt content. However, crystallites were still 30 Å-size when Pt was deposited on a silica of moderate area although the Pt content had been decreased to ~0.3% and the Pt area had fallen to 0.2 m<sup>2</sup>/g catalyst. It was shown previously that the use of very small metal areas can confuse the study of crystallite size effects (1). The residual chlorine content of the impregnated catalysts after different reduction treatments was noted and its effect on some catalytic reactions may be considerable. Although the methods used may suggest that most of the chlorine or water had been removed by certain reduction or drying treatments, more sensitive methods of detection might show that small amounts remain adsorbed.

Ammonia adsorption produces high Pt dispersions; the mean crystallite size is rather insensitive to Pt content and support area but catalysts with mean sizes from 15 Å upwards can be prepared by heat treatment (in air) before reduction. The amount of Pt adsorbed can be altered by pH (5) and by varying the surface area of the silica. Possibly the actual mode and time of contacting support and ammonia solution would be the main problem in preparing "standard" catalysts in different laboratories.

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