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The Structure and Activity of Supported Metal Catalysts

I. Crystallite Size and Specific Activity for Benzene Hydrogenation of Platinum/Silica Catalysts

T. A. DORLING AND R. L. MOSS

From the Warren Spring Laboratory, Stevenage, England

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The crystallite size of platinum supported on silica was increased by firing in air at temperatures up to 800°C. The mean crystallite size was obtained from X-ray line-broadening measurements and the amount of finely divided platinum, not detectable by X-ray diffraction, was also determined. Metal areas calculated from crystallite size data, taking into account the smaller crystallites, were in agreement with areas obtained from CO chemisorption, assuming that 15% was adsorbed in the bridged structure. The specific activity for benzene hydrogenation (rate per unit metal area) for a number of catalysts, fired below 400°C and containing varying amounts of finely divided platinum, was essentially constant; catalysts fired at 400° and 500°C, containing predominantly the larger crystallites, had a smaller specific activity and those fired at 600° and 800°C were inactive.

INTRODUCTION

The object of this study was to examine the interrelation of crystallite size, metal area, and catalytic activity of silica-supported platinum catalysts. It has been reported (*1*) that 2.5% Pt/silica catalysts, after reduction at 210°C have a narrow crystallite size distribution so that the mean crystallite sizes obtained from X-ray line-broadening, H_2 chemisorption, and electron microscope observation are in agreement. It would appear, however, that moderate heat treatments in air to produce catalysts with different mean crystallite sizes will also increase the range of sizes in a given catalyst. For example, in the case of Pt/alumina catalysts there is evidence (*2, 3, 4*) that, after heating, the catalyst may contain finely divided material as well as crystallites larger than 50 Å, which are the only ones observed by X-ray diffraction. Consequently, the actual platinum area may be substantially larger than the area calculated from an X-ray determination of the mean crystallite size. In the present work, the usefulness of the X-ray technique for estimating crystallite sizes, and hence metal areas, was extended by measuring the amounts of platinum present in the larger crystallites, which were compared with X-ray fluorescence analyses of total platinum content.

The loss of activity accompanying crystallite growth in Pt/alumina catalysts has been reported on various occasions, e.g., for cyclohexane dehydrogenation (*4*) and for the isomerization of *n*-paraffins (*5*), but there are few quantitative correlations of activity with metal area for series of supported catalysts having different mean crystallite sizes. The structure and activity of metal/silica catalysts has been reviewed (*6*) and recently it has been shown (*7*) that the specific activity of Ni/silica catalysts for the hydrogenolysis of ethane was essentially constant through a ×3 reduction in surface area. In the present work, the rate of C_6H_6 hydrogenation *per unit metal area* was measured for a number of Pt/silica catalysts; at the start of one series a major proportion of the platinum was in crystallites of less than 50 Å while at the other

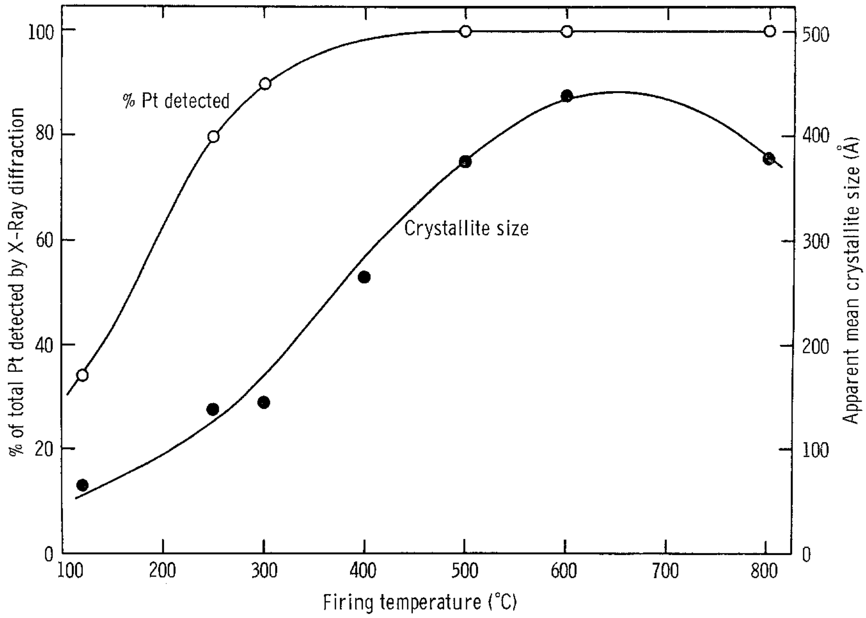

FIG. 1. Effect of firing temperature on crystallite size and percentage total platinum detectable by X-ray diffraction in 2.5% (nominal) Pt/grade 70 silica catalysts.

extreme the catalysts contained mostly crystallites of approximately 400-Å size.

EXPERIMENTAL

The catalysts were prepared by impregnating Davison grade 70 or 950 silica gel with the requisite volume of a 0.1 *M* solution of chloroplatinic acid; the water was boiled off and the catalyst dried at 120°C for 16 hr in an air oven. Before making X-ray measurements, the catalysts were reduced in a stream of hydrogen for 2 hr at 210°C. The total surface area of each catalyst was measured by a flow method (*8*) using nitrogen as adsorbate; the area of the metal on the support, by chemisorbing CO at 25°C, either from a stream of helium (*9*) or conventionally by gas dosing; and the total pore volume, by the absorption of CCl_4 vapor (*10*).

The activity of the catalysts for the hydrogenation of benzene was determined in a flow system at atmospheric pressure; a tubular reactor was used, 15 cm long and 0.5 cm diameter, thermostatted to ±0.1°C. Reaction mixtures were prepared by passing 100 ml/min of pure H_2 through a saturator at 0°C containing benzene, freed from dissolved air, to give a 3% C_6H_6 vapor content. Stopcocks with Neoprene diaphragms, glass joints with PTFE "sleeves," etc., were used throughout to eliminate possible contamination by vacuum grease. The reactant and product gas streams were sampled directly by means of a Perkin-Elmer valve combination and analyzed by vapor-phase chromatography. Before measuring rates of hydrogenation, the catalyst (standard charge, 2 cc) was reduced in pure hydrogen at, usually, 210°C for 2 hr.

RESULTS AND DISCUSSION

Crystallite Size

In order to examine the effect of crystallite size on catalytic activity, series of catalysts were prepared in which the crystallite size was changed by firing in air for 5 hr at temperatures of up to 800°C. Figure 1 shows the mean crystallite sizes observed in one such series (Pt/grade 70 silica) from the broadening of the (111), (200), (220),

TABLE 1
CRYSTALLITE SIZE, METAL AREA, AND CATALYTIC ACTIVITY (PT/GRADE 70 SILICA)

Firing temperature (°C)	Pt content (%)	CO chemisorp. flow method (cc/g)	Metal area (m^2/g)	Calc. area from X-ray data (m^2/g)	Catalyst charge (g)	Benzene converted at 25°C	
						%	Molecules/cm^{2}Pt/sec
120°	2.75	0.75	2.06	2.02	0.875	52.0	4.5×10^{13}
250°	2.30	0.27	0.74	0.75	0.797	16.6	4.2×10^{13}
300°	2.03	0.17	0.47	0.49	0.842	11.3	4.2×10^{13}
400°	2.56	0.11	0.30	0.26	0.845	4.7	3.2×10^{13}
500°	2.09	0.01	0.03	0.13	0.835	1.9	2.7×10^{13}
600°	1.95	0.01	0.03	0.10	0.822	Inactive	
800°	1.85	0.02	0.06	0.11	0.901	Inactive	

and (311) X-ray reflections using a counter-diffractometer; these individual values did not differ from the mean beyond the limits set by experimental error. A maximum in the observed crystallite size occurred at 600°C and was ascribed to the loss of platinum during firing (cf. Table 1, column 2).

Attempts to correlate metal areas calculated from crystallite size and areas measured by CO chemisorption indicated that, in some catalysts, substantial amounts of platinum must be present as crystallites sufficiently small ($<$50 Å) not to be included in the X-ray estimation of crystallite size. Evidence for this was obtained by determining the relative amount of platinum, detectable by X-ray diffraction, in catalysts fired over a range of temperature using magnesium oxide as an internal standard. The total platinum content of each catalyst was determined by X-ray fluorescence analysis and, assuming that all the platinum in the catalyst fired at 800°C was detected by X-ray diffraction, then the per cent platinum in crystallites larger than 50 Å was obtained for the other catalysts in the series (Fig. 1). It would appear that, below a firing temperature of 400°C, an increasing part of the platinum, e.g., approximately 60% in the sample which was subjected only to drying at 120°C and reduction, was highly dispersed.

Surface Areas and Catalytic Activity

Table 1 records surface area results for the catalysts supported on grade 70 silica, i.e., the area of the platinum itself obtained by CO chemisorption and by calculation from crystallite size. It has been found from infrared studies (*11*) that on silica-supported platinum, up to 15% of CO is adsorbed in the bridged structure. On this basis the volumes of CO chemisorbed were converted into areas of platinum metal per gram *of catalyst*, taking the cross-sectional area of a platinum atom as 8.9 Å^2, i.e., 1.12×10^{15} sites/cm^2 (*2*, *12*) (column 4, Table 1). There was no CO adsorption on the support alone, although this need not imply the absence of a cooperative effect with adsorption occurring on the support in the vicinity of the platinum.

The platinum crystallites were envisaged as being regular cubes with five faces exposed to adsorbing gases, and hence, the metal area of an amount of catalyst containing 1 g of platinum is given by $5 \times 10^4/rd$ in (meters)^2 where r is the edge length of the cube in angstrom units and d is the density of platinum. It is clear that the presence of finely divided platinum in crystallites smaller than 50 Å in catalysts fired below 400°C (Fig. 1) leads to an underestimation of metal area by this method of calculation, if only the observed crystallite size is used. Reasonable agreement with areas derived from CO chemisorption could be obtained, however, if a mean crystallite size of 25 Å was taken for this finely divided platinum and the area of this material also included (column 5, Table 1).

The activity of these Pt/grade 70 silica catalysts for the vapor-phase hydrogenation of benzene is shown in Table 1. Catalysts fired at temperatures between 120° and 400°C during preparation were sufficiently active to permit the reaction to be studied in the range 15–80°C and the activity at 25°C assessed directly. The activity of the catalyst fired at 500°C, was obtained by extrapolating the Arrhenius plot in the range 100–220°C. Catalysts fired at 600° and 800°C were too inactive for a determination of the rate of C_6H_6 hydrogenation at any temperature. The silica support by itself was inactive. The activity of the catalysts in terms of molecules of benzene converted per cm^2 platinum per second was found, using the metal areas recorded in column 5, Table 1. At one end of this series, 60% total platinum was present in crystallites smaller than 50 Å in size and at the other extreme, apparently all of the platinum was in crystallites of approximately 400 Å. Accompanying this crystal growth, the total pore volume, V, was initially constant at $\sim$0.43 cc/g catalyst, falling eventually to 0.35 and 0.30 cc/g in catalysts fired at 600° and 800°C, respectively. Samples of silica gel subjected to temperatures up to 800°C showed a similar reduction in total pore volume. The mean surface area, S, was 215 m^2/g, yielding an average pore radius, $\bar{r}$, of approximately 40 Å, using $\bar{r} = 2V/S$. Although the rates per unit area were constant for catalysts fired below 400°C, the per cent conversion varied considerably, suggesting that the availability of benzene was not rate-limiting. Calculation of Wheeler's quantity, h (*13*) at $<\sqrt{2}$ also indicated that the benzene concentration was >0 up to the end of the pore and for zero order reaction in benzene the rate should be unaffected by diffusion.

TABLE 2
ACTIVITY OF Pt/GRADE 950 SILICA CATALYSTS

Firing temperature (°C)	Crystallite size (A)	Metal area (static method) (m^2/g)	Benzene converted at 25°C	
			% per g catalyst	Molecules/cm^{2}Pt/sec
120°	45	2.00	36.9	2.8×10^{13}
250°	220	1.32	23.4	2.7×10^{13}
300°	210	1.52	32.3	3.2×10^{13}
400°	360	3.00	27.9	1.4×10^{13}
500°	640	1.53	13.0	1.3×10^{13}
600°	980	0.20	Inactive	
800°	890	0.04	Inactive	

Table 2 shows in shortened form the results of a similar investigation of crystallite size, CO chemisorption, catalytic activity, etc., made on 2.5% (nominal) platinum catalysts supported in this case, on grade 950 silica. The total surface area of these catalysts fired at temperatures up to 600°C was 330 m^2/g, decreasing sharply to 250 m^2/g after firing to 800°C, with again a reduction in pore volume from approximately 0.36 to 0.15 cc/g.

Both series of results support the same conclusions:

(*i*) The activity for C_6H_6 hydrogenation per unit metal area of catalysts fired below 400°C, containing varying amounts of highly dispersed platinum (crystallites of $<$50 Å size) was essentially constant, although the crystallite size and the size distribution varied substantially.

(*ii*) Catalysts fired at 400° and 500°C, containing predominantly the larger crystallites detectable by X-ray diffraction ($>$50 Å size), had a smaller specific activity.

(*iii*) Catalysts fired at 600° and 800°C were inactive; it would seem that the small metal area could not be compensated for by increase in reaction temperature. This inactivity cannot be ascribed conclusively to a direct crystallite size effect. The eventual divergence of metal surface areas calculated from X-ray and CO chemisorption data suggests the inaccessibility of the platinum surface to gas adsorption and reaction.

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