The Structure and Activity of Supported Metal Catalysts

IV. Ethylene Hydrogenation on Platinum/Silica Catalysts

T. A. DORLING, M. J. EASTLAKE, AND R. L. MOSS

From the Warren Spring Laboratory, Stevenage, England

The specific activity for ethylene hydrogenation was measured over Pt/silica catalysts in which the mean crystallite size was varied from 13 to ~200 Å. Catalysts were prepared by adsorption of the ammine or by impregnation with chloroplatinic acid, dried or fired in air, and reduced in hydrogen under various conditions. A detailed description of the catalysts was built up from measurements of CO chemisorption, X-ray line-broadening, and electron micrographs of ultramicrotome sections. It was found that an apparent effect of crystallite size on specific activity arose in low Pt content catalysts or catalysts fired at high temperature because of the poisoning or self-poisoning of the small Pt areas. A less obvious effect occurred in impregnation catalysts when the reduction temperature was varied, due to changes in the level of residual chlorine, which was shown to promote the catalytic reaction. Eliminating these apparent crystallite-size effects, the specific activity was constant over a series of catalysts where variation in the surface topography of the Pt crystallites is believed to be responsible for differences in the ease of ^{14}CO desorption. Comparison is made with the previously reported effect of crystal face on activity in ethylene hydrogenation.

INTRODUCTION

In recent years considerable efforts have been made to discover if the size of the metal crystallites in a supported metal catalyst can affect the specific catalytic activity. It does not seem unreasonable to expect that crystallite size should have an influence, e.g., if the crystallites are sufficiently small, the essential metallic properties may be different. Evidence cited includes changes in the X-ray absorption edge when hydrogen is adsorbed on 14-Å Pt crystallites supported on alumina (1). However, the term "crystallite-size effect" is probably more often used to describe the increase or decrease in catalytic activity which might arise from variations in the arrangement of atoms on the surface of the metal crystallites. Models representing crystallites of different size lead us to expect such variations and hence size measurements are used in an attempt to characterize the surface topography of the crystallites. Recently, it was proposed that

crystallite-size measurements could be supplemented by using the infrared-active nitrogen adsorption as diagnostic of the occurrence of B_5 sites (areas of 110 and 113 plane) on the crystallite surface (2).

Crystallite-size effects have been reported for some reactions, e.g., ethane hydrogenolysis (3) and neopentane isomerization/hydrogenolysis (4), but often the specific activity is constant. Now the most direct approach for examining the effect of surface structure on catalytic activity is the use of massive single crystals and a limited number of reactions have been studied; for instance, clear differences were observed when ethylene was hydrogenated over the various faces of a nickel single crystal (5). It therefore seemed of interest to look for a crystallite-size effect in supported metal catalysts using this test reaction. One essential difference between the two catalyst systems is the suppression of effects due to edge atoms when using a single crystal.

Further, it is now generally realized that crystallite-size effects in supported metal catalysts are likely to occur with the high dispersions often found in technical catalysts. The proportions of the various types of crystallographic site or surface atoms of different coordinations change most markedly in the crystallite-size range, <10 to ~70 Å. For example, in a regularly faceted 50-Å Pt crystallite, 85% of the surface atoms already have the properties of atoms in infinite ideal faces (6). If there are insufficient atoms to produce a perfect crystal face, this situation is deferred until larger crystallite sizes are reached. Therefore in the present work Pt/silica catalysts were prepared containing crystallites with a mean size which varied from ~15 to 75 Å. However, the methods adopted to change the crystallite size lead in themselves to other causes of variation in specific catalytic activity and such effects have been carefully studied.

EXPERIMENTAL

Catalyst preparation. "Impregnation"-type catalysts were prepared from Davison silica gel and solutions of chloroplatinic acid, boiling off the water while continuously stirring, and then drying at 120°C for 16 hr in an air oven. Catalysts were reduced in a stream of pure hydrogen under various conditions (see Results section). "Ammine-adsorption"-type catalysts were prepared by contacting the silica gel with a solution of platinum ammine for 3 min as described in ref. (7). These catalysts were dried at 60°C in air and reduced in flowing hydrogen (760 torr) for 2 hr at 20°C, followed by a temperature increase over 2 hr to 300°C and held at this temperature for a further 3 hr. Platinum contents were determined by X-ray fluorescence analysis of the reduced catalysts.

Catalyst activity measurements. The activities of the catalysts for ethylene hydrogenation were determined in a flow system at atmospheric pressure, passing pure hydrogen containing ~2.5% C_2H_4 at 100 ml/min over the catalyst contained in a glass U-tube. By a suitable combination of metal valves, both the reactant and product streams could be sampled directly for analysis by vapor-phase chromatography and conversions down to ~1% could be measured.

RESULTS

The platinum crystallite size in Pt/silica catalysts was varied in three ways:

(i) By using the ammine adsorption method to produce catalysts with very small crystallites.

(ii) By varying the Pt content from 0.1% to 11.5% in catalysts prepared by the impregnation method.

(iii) By firing some of these catalysts in air before reduction.

Mean crystallite sizes varied from 13 Å in type (i), through sizes of 30 to 75 Å for type (ii) and up to still larger sizes in type (iii) catalysts.

Catalyst Characterization

A detailed description of these Pt/silica catalysts was built up from the following measurements.

a. X-Ray line-broadening. The mean crystallite size was derived from X-ray line-broadening as described in ref. (8), which also gives details of the method used to estimate the amount of platinum present in crystallites of >50 Å size and included in the mean size determination (Table 1, columns 2 and 3). Using the previously stated assumptions about crystallite shape and the mean size of the highly dispersed platinum, i.e., crystallites <50 Å size, the total area of platinum per gram of catalyst was calculated (column 4).

b. CO chemisorption. Platinum could not be detected by X-ray diffraction in catalysts with low Pt contents nor in catalysts prepared by the ammine adsorption method. Hence platinum areas were measured by CO chemisorption at 25°C and pressures up to a few torr. From previous work (9) it was established that the assumption of 15% "bridge" bonding by CO leads to satisfactory agreement between Pt areas derived from CO chemisorption and from X-ray line-broadening in catalysts where mainly small crystallites are present.

TABLE 1
CHARACTERIZATION OF PLATINUM/SILICA CATALYSTS

Pt content (%)	Pt detected by X-ray diffraction			CO adsorption		Calculated mean crystallite size (Å)
	Crystallite size (Å)	Fraction of total Pt detected	Pt area (m²/g cat)	Volume (cc/g cat)	Area (15% bridged) (m²/g cat)	
2.45[a]	—	—	—	1.589	4.37	13
3.75[a,b]	—	—	—	1.075	2.96	30
0.14	—		—	0.034	0.09	39
0.27	—	—	—	0.074	0.21	30
0.63	—	—	—	0.169	0.46	32
1.24	85	0.43	0.82	0.287	0.79	35
3.0	60	0.42	2.12	0.800	2.20	33
3.4	65	0.59	2.01	—	—	40
6.9	70	0.55	4.17	—	—	39
8.5	75	0.83	3.55	—	—	56
10.0	90	0.79	4.02	—	—	58
10.2	80	0.80	4.29	—	—	56
11.5	70	0.91	4.46	—	—	60

[a] Prepared by ammine adsorption, other catalysts prepared by impregnation with chloroplatinic acid and reduced for 2 hr at 210°C.

[b] Fired in air at 350°C for 5 hr before reduction.

Platinum areas obtained from each type of measurement on catalysts containing 1.24% and 3% Pt (Table 1) illustrate this conclusion. Therefore it was assumed that Pt areas can be calculated on the same basis from CO adsorption on catalysts where X-ray line-broadening was not applicable. As further evidence, it has been shown (10) that the H atom/CO ratio for such catalysts is 1.13.

c. Electron microscopy. Electron micrographs (Fig. 1) of ultramicrotome sections of catalysts provided valuable confirmation of the very high Pt dispersion in type (i) catalysts indicated by CO chemisorption measurements. Figure 1(a) shows large numbers of extremely small crystallites of 10–20 Å size while in Fig. 1(b) it is evident that some crystalline growth has occurred as a result of heat-treatment.

Catalyst Life

A number of experiments were carried out using all three types of catalyst to examine the constancy of catalytic activity with time at a fixed temperature. A type (i) catalyst, Pt area = 4.4 m²/g catalyst, reduced at temperatures up to 300°C as described, was further reduced in the catalytic reactor at 80°C in a stream of hydrogen before activity testing. Shortly after this reduction (5 min), the ethylene hydrogenation rate (% converted) at −78°C was 7.6%, falling slowly to 5.9% over the next 30 min. The temperature was then raised to −75°C and the conversion only decreased from 7.6% to 6.9% in 30 min. The decrease at higher temperatures and conversions was also small: from 23.0% to 20.3% at −64°C over the same time interval.

A similar experiment was carried out with a type (ii) catalyst which had a relatively high Pt area (3.1 m²/g catalyst) in comparison with some of the other catalysts made by impregnation. At −78°C, the ethylene hydrogenation rate was initially 5.4% decreasing over the next 30 min to 3.5%. The catalyst was then vigorously re-reduced at 500°C for 2 hr and at −60°C the conversion fell from 21.7% to 16.9% over 30 min.

Experiments with a very low area type (ii) catalyst (0.06 m²/g catalyst) containing 0.1% Pt showed more rapid catalyst deterioration, perhaps accompanying the substantially higher temperature required to obtain a measurable rate of ethylene
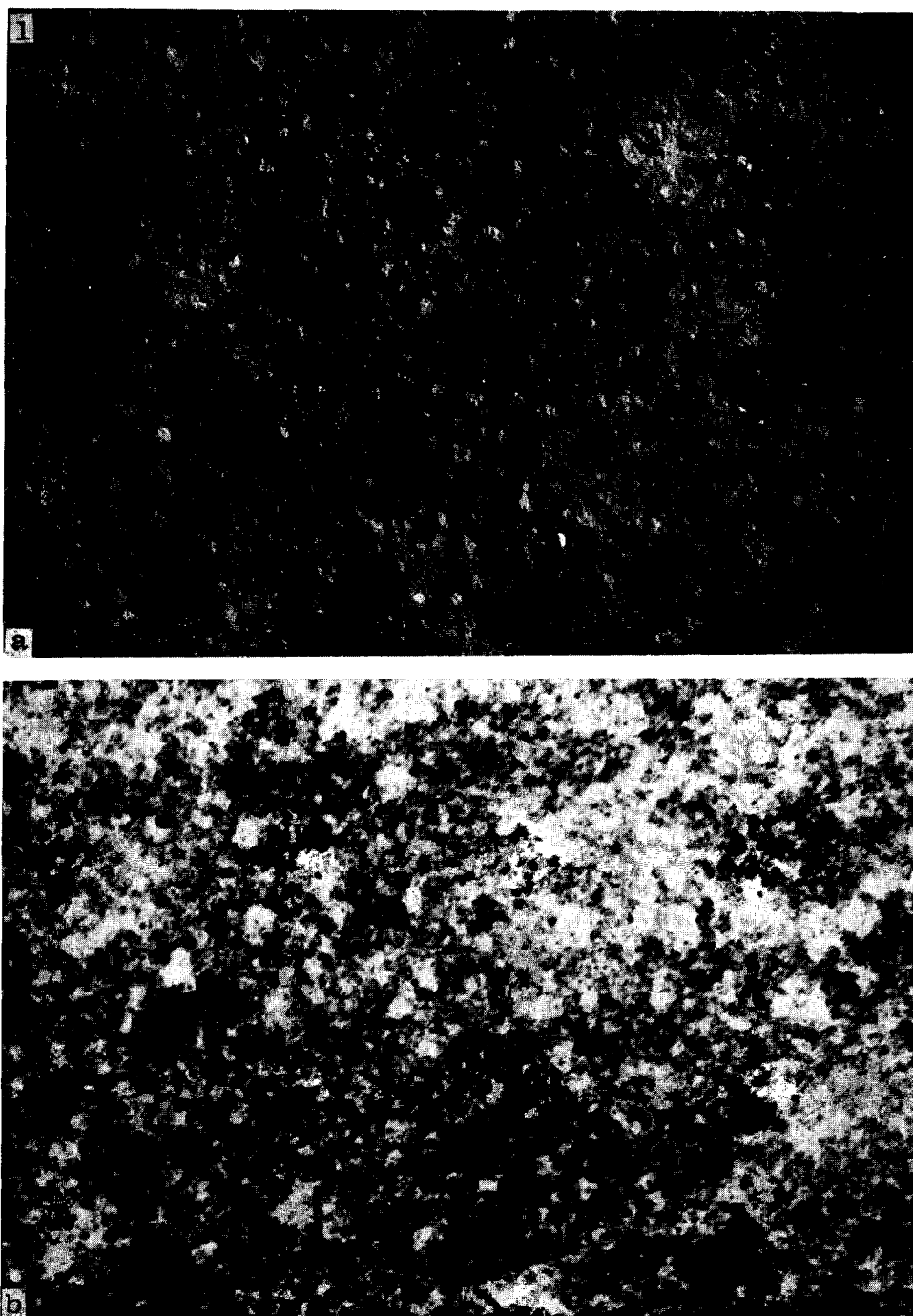
FIG. 1. Electron micrographs from ultramicrotome sections of reduced Pt/silica catalysts. Magnification 200,000×. (a) Ammine adsorption catalyst as prepared; platinum appears as pinpoint size dots evenly distributed over the entire area. (b) Same catalyst fired in air at 350°C for 5 hr.

hydrogenation. The conversion at $-35°C$ decreased from an initial 5.6% to 0.8% over 30 min. However, a mild reduction in H_2 (5 min at 60°C) restored much of the lost activity. Using another sample of this catalyst the following procedure for testing the activity was tried. The catalyst was reduced in the catalytic reactor at 210°C for 2 hr and the activity tested at $-45°C$; before raising to the next and subsequent higher temperatures, the catalyst was reduced at 80°C for 15 min. At each fixed temperature, the ethylene hydrogenation rate was measured after 2, 5, and 8 min.
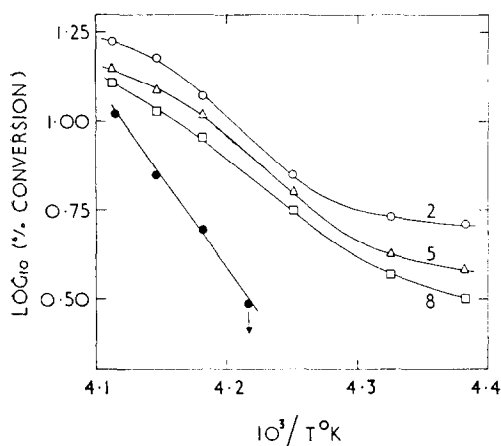

FIG. 2. Variation with increasing temperatures (open symbols) of % conversion 2, 5, and 8 min after reduction; pseudo-Arrhenius plot (filled circles) with decreasing temperatures.

The set of Arrhenius plots of variable slope shown in Fig. 2 was obtained.

The catalyst was reduced again at 210°C for 2 hr and data for an Arrhenius plot taken as rapidly as possible, starting at the highest temperature. This yielded a linear plot (Fig. 2) but holding at the lowest temperature ($-36°C$), the activity continued to decrease. A type (iii) catalyst with a low area, the result of heating in air before reduction, also showed a marked loss in activity at the temperature required to test its activity.

Variation in Reduction Temperature

Most experiments were carried out with catalysts reduced at 210°C and made by impregnation, type (ii) (see next section), where the platinum content was varied to change the crystallite size. Additional experiments are reported here on the effect of variation in reduction temperature on the specific activity of two catalysts of this type, containing 3.4% and 10.0% Pt.

Separate samples of the dried catalyst containing 3.4% Pt after the impregnation stage were reduced, in the first instance, for 2 hr at the temperatures recorded in Table 2, then again reduced at 80°C for ~1 hr after transfer to the catalytic reactor. The first catalyst in the series was reduced inside the catalytic reactor at 80°C for 2 hr. After measuring the rate of ethylene hydrogenation over a range of temperatures, the

TABLE 2

EFFECT OF REDUCTION TEMPERATURE ON CRYSTALLITE SIZE AND CATALYST ACTIVITY
(Pt/GRADE 70 SiO₂, IMPREGNATION TYPE)

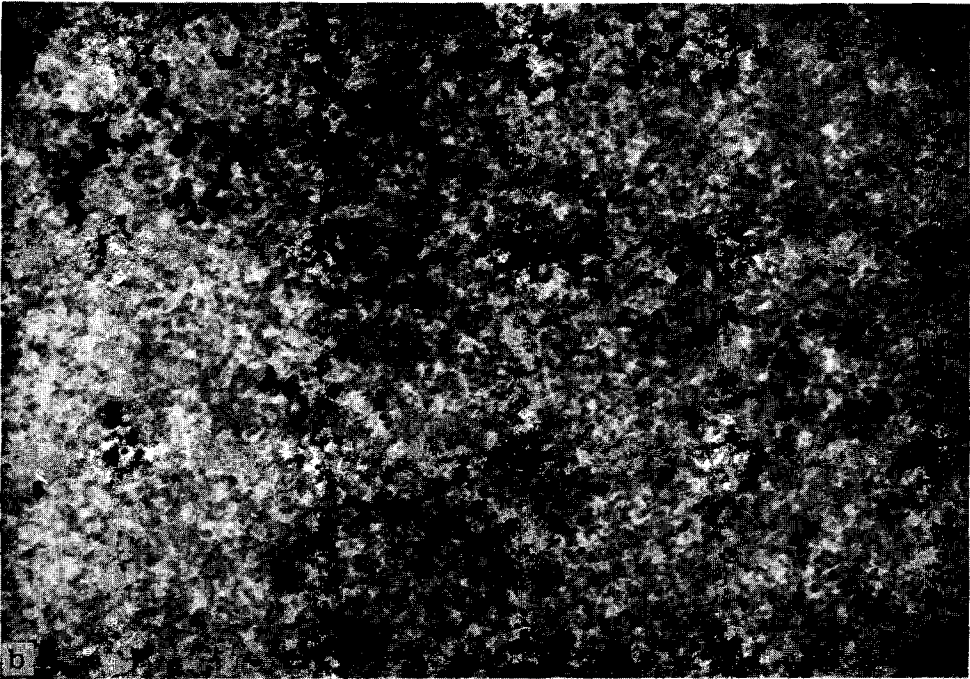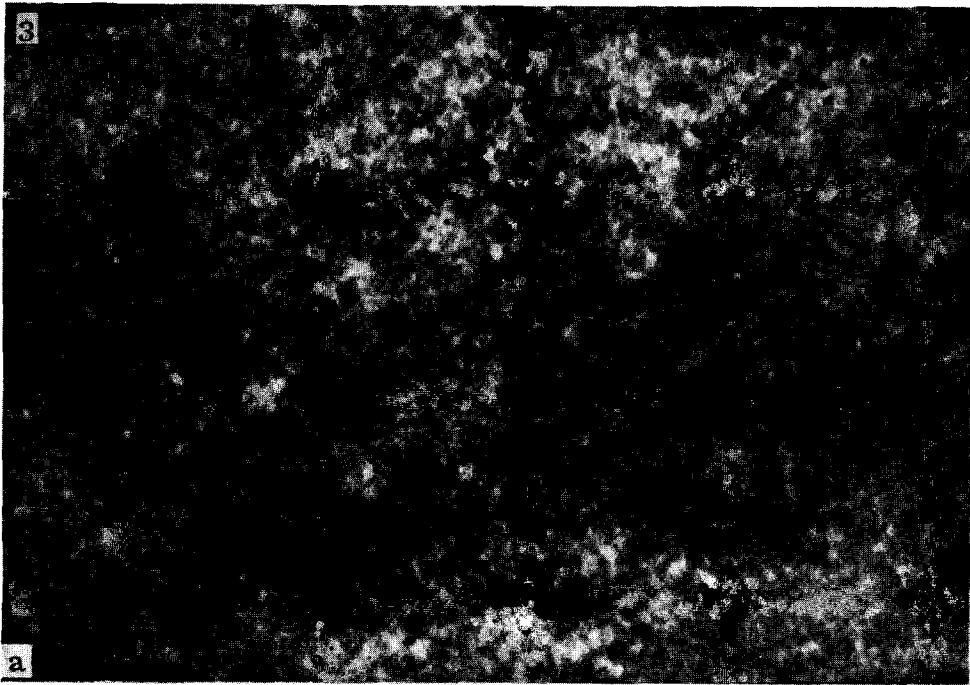| Pt content (%)	Reduction temp. (°C)	Crystallite size (Å)			Fraction detected by X-ray diffraction	Pt Area (m²/g cat)	Activation energy (kcal/mole)	Specific activity at −80°C (molecules/sec cm²) ×10⁻¹²
		(111)	(200)	(220)				
3.4	80°	55	—	—	0.50	2.30	8.2	19.6
	140°	60	—	—	0.54	2.16	9.0	12.7
	210°	65	—	—	0.59	2.01	9.7	7.4
	300°	80	—	—	0.55	1.97	9.7	2.9
	500°	75	—	—	0.52	2.15	9.6	1.7
10.0	80°	70	60	60	0.75	4.85	8.2	14.8
	140°	70	65	75	0.75	4.85	8.9	14.6
	210°	90	70	70	0.79	4.02	8.1	8.2
	300°	95	90	80	0.87	3.36	10.7	4.1
	500°	100	95	100	0.90	3.05	9.1	1.7

FIG. 3. Electron micrographs from ultramicrotome sections of reduced Pt/silica catalysts. Magnification 100,000×. (a) 10% Pt impregnation catalyst reduced at 140°C. (b) Same catalyst reduced at 500°C.
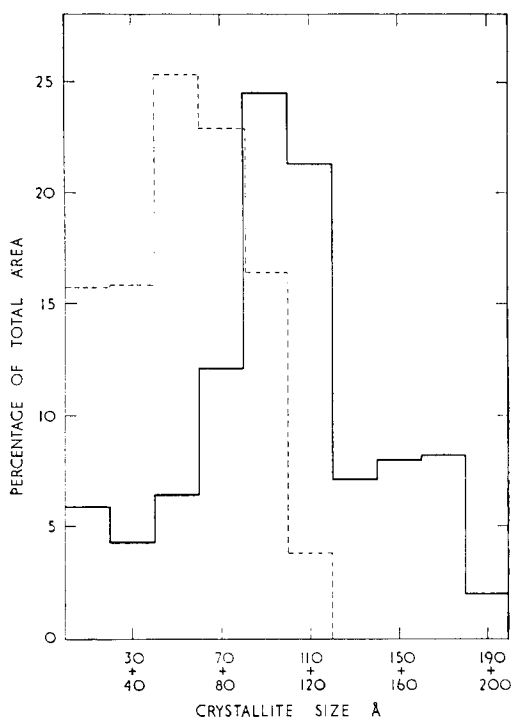
FIG. 4. Percent of total area due to crystallites of various sizes in electron micrographs shown as Fig. 3 (a) and (b); – – –, catalyst reduced at 140°C; ———, catalyst reduced at 500°C.

catalyst was discharged and the mean crystallite size and fraction of total platinum detectable by X-ray diffraction were determined. Separate dried samples containing 10% Pt were also reduced externally and given a further short reduction at 80°C after charging part of the sample into the catalytic reactor. X-Ray diffraction measurements were made on the remainder of each sample and a series of electron micrographs taken including Fig. 3(a) and (b).

Table 2 shows clearly that variation in reduction temperature had only a small effect on the crystallite size in the catalyst with 3.4% Pt. The effect is a little greater in the 10.0% Pt catalyst, the mean crystallite size increasing, with rising reduction temperature, from 70 to 100 Å and the fraction detected from 0.75 to 0.90. Electron micrographs (Fig. 3) confirmed this trend in the second series of catalysts with 10% Pt. The crystallite-size distributions in the

catalysts reduced at 140° and 500°C are compared in Fig. 4 in terms of the percentage of the total area due to crystallites of each size, i.e.,

$$\% \text{ area} = (N_i d_i^2 / \Sigma N_i d_i^2) \times 100$$

where there are N_i crystallites of diameter d_i. Figure 4 shows that increasing the reduction temperature caused only a modest upward displacement of the crystallite-size distribution, in agreement with the indications from X-ray diffraction measurements.

In contrast to this small effect on crystallite size, variation in reduction temperature had a marked effect on the specific activity. In both series of catalysts, the rate of ethylene hydrogenation per unit area of platinum decreased by a factor of about 10 as the reduction temperature was increased from 80° to 500°C. There was little change in activation energy and therefore no problem arose in comparing activities at a fixed temperature. The temperature chosen was common to each temperature range involved in the measurement of ethylene hydrogenation rates.

It was found also that an additional effect of increasing the reduction temperature was the more complete removal of the residual traces of chlorine from the catalyst. Thus, the weight percent chlorine remaining after reduction at 80°, 210°, and 500°C was 0.16, 0.13, and 0.034, respectively, compared with the silica "blank" of 0.029%. It was therefore of interest to attempt to restore the activity of one of the catalysts reduced at 500°C by treatment with chlorine. After exposure to chlorine gas at 250°C for 1 hr, followed by a short reduction (80°C for 5 min), the conversion at −80°C was 2.9% compared with the original conversion of 0.4%.

Specific Catalytic Activity

Ammine adsorption catalysts. A special reduction technique was applied to the catalysts (see Experimental) where temperatures up to 300°C were reached; Pt areas were then measured by CO chemisorption without further transfer in air. The platinum was found to occur as very small crystallites (mean size 13 Å) although
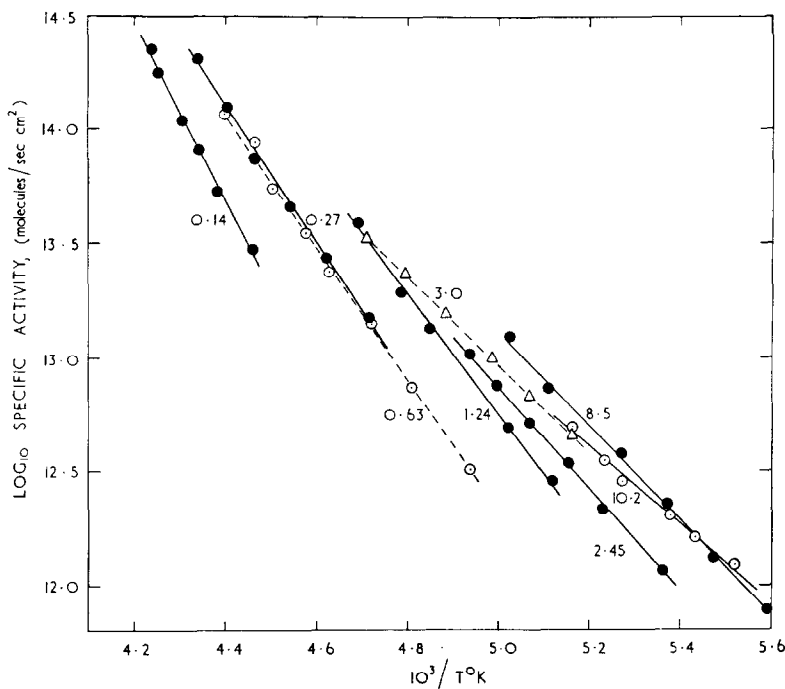
FIG. 5. Variation of logarithm of specific activity for C_2H_4 hydrogenation with reciprocal temperature for catalysts identified by Pt content (see Table 1).

reasonably large amounts of platinum were present. Hence a substantial platinum area was available for catalysis using the standard catalyst charge and, as reported above, little catalyst deterioration occurred after initial exposure to the reactant gases at the low temperatures required for measurable reaction rates.

Rates of ethylene hydrogenation (Fig. 5) were measured at temperatures between $-103°$ and $-67°C$ on a sample of catalyst (Table 1, 2.45% Pt), reduced again at 80°C after charging into the catalytic reactor. The activation energy was 10.5 kcal/mole and the specific activity at $-80°C$ was 3.0×10^{12} molecules/sec cm² Pt. Other ammine adsorption catalysts were fired in air before the first reduction to bring about crystallite growth. The specific activity of one such catalyst, fired at 350°C to give a mean crystallite size of 30 Å (Table 1, 3.75% Pt) was 1.8×10^{12} molecules/sec cm² Pt, with an activation energy of 11.0 kcal/mole.

Impregnation catalysts. Changes in crystallite size brought about by varying the platinum content lead to the production of some catalysts with very small platinum areas (Table 1). Thus, the standard charge, ~ 0.3 g, of catalysts with less than 1% Pt possessed platinum areas of less than 0.2 m². The deterioration of such catalysts in use is described above, but at higher platinum contents, and therefore larger platinum areas, deterioration was much reduced. However, a standard procedure for testing the activity of all these catalysts was adopted, viz., the rate of ethylene hydrogenation was first recorded at the highest temperature required to produce a conveniently measurable rate and then the temperature was reduced in steps over ~ 30 min to obtain data for Arrhenius plots (Fig. 5).

Table 3 summarizes results for impregnation catalysts containing more than 1% Pt, up to the highest concentration used, 11.5% Pt. The mean crystallite-size variation accompanying this change in platinum content was from 35 to 60 Å.

TABLE 3
SPECIFIC ACTIVITIES OF IMPREGNATION CATALYSTS FOR C_2H_4 HYDROGENATION

Pt content (%)	Reduced at 210°C			Reduced at 80°C	
	Temperature range (°C)	Activation energy (kcal/mole)	Specific activity at −80°C × 10^{-12} (molecules/sec cm²)	Activation energy (kcal/mole)	Specific activity at −80°C × 10^{-13} (molecules/sec cm²)
1.24	−60° to −78°	11.7	2.1	10.8	0.5
3.0	−61° to −86°	8.8	4.2	8.5	1.2
3.4	−67° to −96°	9.7	7.4[a]	8.2	2.2
6.9	−69° to −87°	10.6	3.0	—	—
8.5	−74° to −94°	9.6	5.7	9.6	2.3
10.0	−74° to −101°	7.0	8.2[a]	8.2	1.8
10.2	−80° to −101°	8.5	4.6	10.3	1.8
11.5	−67° to −93°	11.9	6.5	—	—

[a] Reduced externally at 210°C, then 80°C in catalytic reactor.

Before testing their activity, catalysts were reduced in the reactor at either 80° or 210°C for 2 hr. A similar temperature range for testing activity was used after each reduction and only the temperature range for catalysts reduced at 210°C is shown in the table. Also, because the platinum area was not seriously altered by change in reduction temperature from 80° to 210°C, areas obtained from catalysts reduced at 210°C were used throughout in calculating specific activities (Table 3, columns 4 and 6).

The specific activity of an impregnation catalyst fired at 600°C in air before reduction to induce crystallite growth was also measured. The mean crystallite size from the CO chemisorption determination of the Pt area was ~200 Å and the specific activity at −80°C (reducing at 80°C in the reactor) was 2.6×10^{12} molecules/sec cm² Pt. Catalysts fired at lower temperatures, 300–500°C, retained much more Pt area and showed the standard specific activity of 2×10^{13} molecules/sec cm² Pt for catalysts reduced at 80°C (Table 3).

DISCUSSION

In order to explore the effect of crystallite size on specific activity for ethylene hydrogenation thoroughly, many catalysts were employed differing in method of preparation, Pt content, reduction, or firing treatment. The conclusion which emerges from the analysis of these results, summarized in Table 4 and elaborated below, is

that the parameters which are varied to induce a variation in crystallite size can themselves produce changes in specific activity. It is only when these apparent crystallite-size effects are eliminated that a clear statement can be made about the existence or absence of an effect of crystallite size on specific activity.

The most obvious source of apparent crystallite-size effects arises from the use of catalysts with low metal areas which result either from small metal concentrations or from heat-treatment which produces very large crystallites. These catalysts are more susceptible to contamination and also require higher temperatures to produce measurable reaction rates, which may cause fragmentation of C_2H_4 and self-poisoning. Reference to the Arrhenius plots for catalysts containing less than 1% Pt (0.14%, 0.27%, and 0.63%), Fig. 5, shows them to be well displaced from the plots for other Pt/silica catalysts—an apparent crystallite-size effect.

Now the mean values of the specific activity at −80°C and the activation energy for the ammine adsorption and for the other impregnation catalysts, all with reasonably large Pt areas, were 4.6×10^{12} molecules/sec cm² Pt and 10.0 kcal/mole, respectively. Using these values, the calculated specific activity at −46°C is 2.3×10^{14} and at this temperature ($10^3/T°K = 4.4$) the *initial* specific activity of the 0.27% and 0.63% Pt catalysts is 1.3×10^{14} molecules/sec cm² Pt. This strongly sug-

TABLE 4
SUMMARY OF RESULTS

Catalyst	Mean crystallite size (Å)	Pt surface area (m²/g cat)	Reduction temp. (°C)	Specific activity at −80°C (molecules/sec cm²)	Remarks
Impregnation <1% Pt	30–40	0.1–0.5	210°	0.1–0.6×10^{12}	Low specific activity due to catalyst deterioration
Fired at 600°C	∼200	0.2	80°	3×10^{12}	
Impregnation 3.4% Pt	40	2	80°	20×10^{12}	Decreasing specific activity as Cl_2 removed by reduction
			210°	7×10^{12}	
			500°	2×10^{12}	
Impregnation 9.8% Pt	50–75	3–5	80°	15×10^{12}	
			210°	8×10^{12}	
			500°	2×10^{12}	
Impregnation 1%–11.5% Pt	30–60	0.8–4.5	80°	5–23×10^{12}	(See text)
			210°	2–8×10^{12} (random values)	Approx. constant specific activity
Ammine adsorption	13–30	3–4	300°	2–3×10^{12}	

gests that these low Pt area catalysts would exhibit the standard specific activity but for their deterioration in use, already described.

The characteristics associated with this effect were high activation energies in temperature-falling experiments and curved Arrhenius plots in temperature-rising experiments (Fig. 2). The "activation energy" for these catalysts with 0.14%, 0.27%, and 0.63% Pt was 16, 14, and 14 kcal/mole, respectively, compared with the accepted value of 8–10 kcal/mole. It is interesting to note that 16 kcal/mole was observed previously (11) in the temperature range 45–93°C over a very low area 0.05% Pt/silica catalyst calcined at 583°C in air.

A less obvious source of apparent crystallite-size effects is the variation in specific activity accompanying changes in reduction conditions (Table 2). When the reduction temperature was increased from 80°C through to 500°C, the mean crystallite size in the ∼10% Pt catalyst increased from ∼50 Å (75% Pt in size 70 Å) to ∼75 Å (89% Pt in size 100 Å) and was accompanied by approximately a 10-fold decrease in specific activity. However, the same variation was observed in the specific activity of 3.4% Pt catalysts although there was little variation in crystallite size

with increasing reduction temperature. This appears to rule out a direct crystallite-size effect and the low reduction temperatures required to produce differences in specific activity seems to eliminate ideas about thermal smoothing of the crystallite surfaces.

Instead, it is believed that efficiency in removing the last traces of chlorine from the chloroplatinic acid deposited on the silica gel is an important factor in determining catalyst activity. The subsidiary experiments, in which after vigorously reducing the catalyst at 500°C the activity was restored by a chlorine treatment, provide substantial support for this explanation. A more extensive study of the effect of chlorine in hydrogenation reactions will be reported later.

A further consequence of promotion by trace amounts of chlorine is the extent to which the effect is related to the crystallite size. The specific activity (at −80°C) of impregnation catalysts reduced at only 80°C increased from 0.5×10^{13} to 2.3×10^{13} molecules/sec cm² Pt with increasing crystallite size and this probably resulted from the more complete chlorine removal from the catalysts with low Pt contents and small crystallites.

In contrast, the specific activity of

catalysts reduced at 210°C varied *randomly* between 2×10^{12} and 8×10^{12} molecules/sec cm^2 Pt (Table 3). Further, the specific activities of other catalysts from which chlorine had been almost completely eliminated [type (i) and type (ii) reduced at 300° and 500°C] had the same specific activity although the crystallite size varied appreciably. Hence, when the complicating effects of low metal area and chlorine promotion are avoided, a "crystallite-size" effect is absent for ethylene hydrogenation over platinum crystallites between 13 and 75 Å size supported on silica.

This absence of a true crystallite-size effect for a reaction which was catalyzed at different rates on the faces of a nickel single crystal (5) is *not* seen as a consequence of any lack of variation in the surface topography as the crystallite size is varied. When the desorption of ^{14}CO from some of these Pt/silica catalysts used in the present work was studied (12), clear differences were found. These results on ^{14}CO desorption could be explained quantitatively in terms of the fractions of the Pt surface composed of edge and plane atoms occurring on incomplete cubooctahedra of varying size.

Instead, it is believed that the essential differences between the two systems, i.e., Ni single crystals and supported Pt, lies in the relative stabilities of the ethylene molecule on these surfaces and the very different metal areas and reaction temperatures involved. Ideas about the formation of acetylenic residues from ethylene and self-hydrogenation are well established, with nickel more susceptible than platinum. For example, pretreatment with ethylene reduced the rate of ethylene hydrogenation on Ni films to 40% while platinum had 95% of the standard activity (13) and in confirmation only 6%–8% of ethylene

—^{14}C preadsorbed on Pt (supported on alumina) remained after the reaction of a $C_2H_4 + H_2$ mixture (14). In the present work, where sufficiently large Pt areas were used to permit very low reaction temperatures, fragmentation of the ethylene should not be dominant. Hence the hydrogenating activity was measured rather than the tendency of different crystallographic planes and sites to become blocked by carbon-containing residues.

Therefore it is concluded that a true crystallite-size effect is absent for ethylene hydrogenation over Pt/silica catalysts but apparent effects can be produced by methods commonly adopted to vary the crystallite size.

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