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The Structure and Activity of Supported Metal Catalysts

VII. CO Poisoning and Metal Location in Palladium-Charcoal Catalysts

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1% Pd-charcoal catalysts capable of catalyzing ethylene hydrogenation in the gas phase at very low temperatures were poisoned by CO concentrations of 0.5–2.5 ppm in the reactant stream. Preparations of these catalysts, containing widely distributed Pd crystallites, were less susceptible to poisoning than preparations where the crystallites were located at the charcoal granule edges as shown by electron microscopy. Correlations were found between the time required for catalysts to be rendered inactive for ethylene hydrogenation by 0.75 ppm CO and the known activities of these catalysts for the liquid-phase hydrogenation of methylbutenol or nitrobenzene. These correlations arise because the liquid-phase hydrogenation rates are diffusion-limited, and like the CO poisoning times are dependent upon the location of the Pd crystallites within the charcoal support.

INTRODUCTION

When describing the physical characteristics of supported metal catalysts, considerable emphasis is placed on the extent to which the metal has been dispersed, whereas often the *location* of the metal within the support is equally or more important. For example, metal location has to be considered where diffusion of reactants or products is likely to be rate-controlling or where the reactants or reactant medium contains a poison. Electron microscopy is a useful method for observing where the metal has been placed with respect to the edge or interior of the support granule. It only provides, however, a subjective impression instead of a quantitative description and it is difficult to apply to some low metal-content, high-dispersion catalysts. Accordingly, work is described which followed from the observation that different Pd/charcoal catalysts had variable lifetimes for the hydrogenation of ethylene, where a connection was established with metal location.

EXPERIMENTAL

Catalysts

The catalysts used were charcoal-based and contained 1% Pd by weight. Catalyst G1 was prepared by slurrying 5 g charcoal with 50 g water, boiling for a few minutes and then adding 0.02 *M* $PdCl_2$ solution (in HCl) with constant stirring before filtering and drying in a vacuum desiccator. Catalyst H1 was prepared according to method B in Ref. (*1*) involving pretreatment of the charcoal with 10% HNO_3 before addition of the $PdCl_2$ solution. The catalyst was reduced with alkaline formaldehyde solution, filtered, washed, and dried as before. The palladium areas measured by CO chemisorption (*2*) were 1.62 and 2.37 m^2/g catalyst, respectively.

Other 1% Pd/charcoal catalysts were supplied by Johnson Matthey and Co. and were research grades of standard types. An extensive examination of the structure of these catalysts was reported previously (*2*). Palladium areas, again measured by

CO chemisorption and following the same catalyst designations, were: types A1, B1, B2, and C1, 0.60–0.75 m^2/g catalyst; type D1, E1, and E3, 1.35–1.50 m^2/g catalyst; type F3, 2.15 m^2/g catalyst.

Experimental Methods

The catalyst charge consisted of 0.1 g catalyst mixed with 0.2 g ballotini and was subjected *in situ* to the same pretreatment given to samples when their metal surface area was measured. Air was removed from the catalyst charge by purging with helium; the catalyst was then reduced with 100 ml/min hydrogen at 25°C for 2 hr, the hydrogen pumped out, the temperature raised to 100°C and the catalyst evacuated overnight. Catalyst G1, which had not been reduced at the preparation stage, was reduced (also *in situ*) at 100°C before activity measurements. The activities of the catalysts for ethylene hydrogenation were determined in a flow system at atmospheric pressure, passing pure hydrogen containing 5% ethylene at 100 ml/min over the catalyst contained in a glass U tube surrounded by a cold bath (ethanol–liquid nitrogen). By a suitable combination of valves, both the reactant and product stream could be sampled directly for analysis by vapor phase chromatography. Hydrogen was purified by diffusion through a silver–palladium membrane and Phillips research-grade ethylene was used, except where otherwise stated (i.e., in initial experiments). The CO poison was introduced into the ethylene–hydrogen reactant stream at ppm levels by the addition of helium containing 10 ppm CO (Hilger IRD).

Catalysts were examined by electron microscopy in the form of thin sections cut on an ultramicrotome. The sample was prepared for cutting by setting it in the end of a block of "Araldite" resin. The electron microscope used had a rated best-line resolution of 4.5 Å; with the present samples, the typical point resolution would be 10 Å.

RESULTS AND DISCUSSION

It was found in preliminary experiments with technical-grade ethylene that the rate of ethylene hydrogenation at a bath temperature of −115°C over types A1 and C1 Pd/charcoal catalysts decreased sharply after a short time had elapsed. In contrast, the rate of ethylene hydrogenation, using the same ethylene supply, remained constant over a much longer period when type B1 catalysts were used. When the ethylene supply was changed to a high-purity research grade, then the activity loss was not observed for types A1 and C1. It is not surprising that catalysts can be poisoned by impure ethylene; but of particular interest is the markedly greater resistance to poisoning exhibited by type B1 catalysts, although the metal areas of these three catalyst types, containing 1% Pd, were approximately equal. Eventually, it was discovered that CO, added to the reactant stream (prepared from research-grade ethylene) to give a concentration of CO at the ppm level reproduced the poisoning phenomena. This is illustrated by Fig. 1 which shows clearly that the type B1 catalyst is again more resistant to poisoning than the type C1 (both operated at a bath temperature of −115°C).

Now, it was observed previously (*2*)

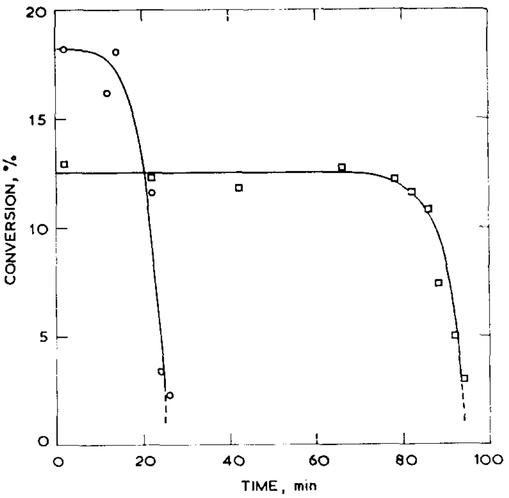

FIG. 1. Variation of hydrogenation rate with time using research-grade C_2H_4 containing 0.5 ppm CO over 1% Pd–charcoal catalysts; type B1, □; type C1, ○ (expressed as percent C_2H_4 converted per 100 mg catalyst).

TABLE 1
EFFECT OF CO CONCENTRATION AND TEMPERATURE (1% Pd/CHARCOAL)

Expt no.	CO concentration (ppm)	Catalyst type	Temperature (°C)	Initial C_2H_4 conversion (100-mg charge) (%)	Life (min)
1	2.5	C1	−86	10.9	52
2	2.5	C1	−86	8.1	54
3	2.5	C1	−75	15.3	30
4	2.5	C1	−75	7.5	24
5	2.5	B1	−86	9.0	43
6	2.5	B1	−86	8.5	42
7	2.5	B1	−86	7.2	52
8	2.5	B1	−75	21.2	42
9	0.75	C1	−75	3.7	47
10	0.75	B1	−75	4.5	80

from electron micrographs of ultramicrotome sections, that type B1 catalysts, with 10% Pd, contained metal crystallites in a reasonably even distribution over the charcoal support, whereas type C1 catalysts with 10% Pd were in marked contrast. In these type C1 catalysts, the palladium was concentrated in certain areas which could often be associated with the outside of the charcoal granule; compare Figs. 2(a) and 2(b) in Ref. (*2*). It would seem that the varying response with respect to poisoning might arise from such differences in metal *location* and it would therefore be worthwhile to establish a method for deriving a reliable "index" of poison resistance.

Measurement of Poison Resistance

The effect was further investigated using the same pure ethylene supply to which 2.5 ppm CO had been added (Table 1, Expts 1–8). In these experiments, most of the discrimination between types B1 and C1 with respect to CO poison resistance, has been lost, especially at a bath temperature of −86°C. At −75°C (Expts 3 or 4 and 8), catalyst B1 had a slightly longer "life" than catalyst C1. These new operating bath temperatures, i.e., −86 and −75°C, rather than −115°C, which are a consequence of catalyst aging, are not the main reason for the loss of discrimination. When the poison concentration was reduced from 2.5 to 0.75 ppm CO, then the discrimination between the two types of catalyst (Expts 9 and 10) is more apparent. Nevertheless, it seemed that discrimination between catalysts with respect to CO poisoning would be somewhat dependent upon the temperature which it is necessary to adopt to obtain a convenient rate of ethylene conversion for measurement, e.g., widely different temperatures might have to be adopted. Accordingly alternative methods of conducting these CO poisoning experiments were sought and one such method is described in the next section. Although rather unconventional as a method of measuring reaction rates, it was found to give reproducible and substantial differences between the various types of catalyst with respect to CO poison resistance.

Before describing this method, it is of interest to consider the ability of CO to bring about the almost total deactivation of the catalyst for ethylene hydrogenation at these very low temperatures. Assuming that all the CO molecules supplied are taken up by the palladium surface in type C1 catalysts (where the palladium is readily accessible), then the upper limit of the coverage causing deactivation is between 10 and 45%, depending on the reaction temperature. This could mean that a substantial fraction of the surface is inactive before CO was admitted either because the reaction takes place on 'active sites' or because exposure to the ethylene–

hydrogen mixture has covered the surface with inactive residues. Certainly, it is known from tracer studies (*3*) with [^{14}C]-ethylene that Pd/alumina catalysts retain 60–70% of the ethylene preadsorbed during subsequent ethylene hydrogenation.

The alternative method of conducting the CO poisoning experiments was as follows: The reaction was started in the absence of CO at a low temperature, say, −75°C, and the bath temperature raised gradually until the conversion of ethylene to ethane was ~30%. Usually, at this point, the conversion increased spontaneously to 100% as a consequence of the heat of reaction liberated to the catalyst. The manner in which this condition is attained will, of course, depend on the catalyst, the amount charged and the shape of the catalyst bed. A thermocouple inside the bed showed that temperature 'spikes' accompany the spontaneous increase in conversion to 100% before the temperature settles down to a value above the bath temperature. The reactant flow was upwards through the catalyst bed and total conversion would be established initially at the top of the bed. Next, the hot zone flashed down through the bed until only the lowest layer of catalyst was reacting.

The poison (0.75 ppm CO) was then added to the reactant stream and as the lowest layer of catalyst was deactivated by CO poisoning, the reaction zone moved upwards through the bed. A point is reached eventually when the uppermost layer of catalyst cannot catalyze 100% conversion. In this method of conducting the poisoning experiments, the time taken from the admission of CO until the conversion begins to fall away from 100% *cannot be meaningful.* Instead, the index of poison resistance is the time which elapses between the onset of observable poisoning (the decline from 100% conversion) and the attainment of only a low residual activity (the "CO poisoning time").

Figure 2 shows the poisoning of two samples of type B1 and two samples of type C1, 1% Pd/charcoal catalyst. The time which was required before the conversion began to fall from 100% is independent of catalyst type, illustrating the above statement that this time is not a reliable index of poison resistance. In contrast, the time taken from onset of observable poisoning to total activity collapse was reproducible, i.e., 40 or 42 minutes for type C1 samples and 146 or 156 minutes for type B1 samples, a ratio of 3.7. (It is interesting to note that the time required for poisoning in the first method of conducting the experiments, illustrated by Fig. 1, are in the same ratio for these two types of catalyst.) The accelerating rate of catalyst deactivation may be a consequence of a decrease in catalyst-bed temperature due to a lower input of reaction heat.

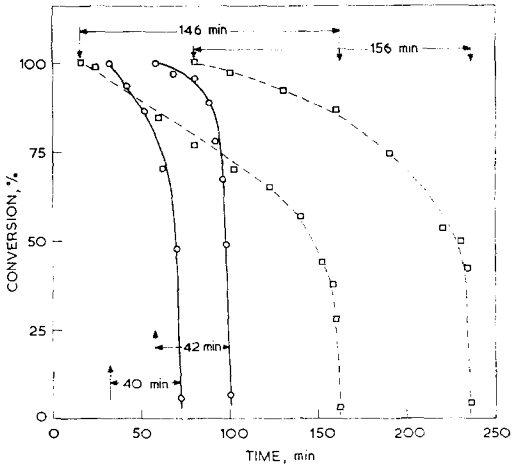

FIG. 2. Measurement of times required for onset of observable CO poisoning and the deactivation of 1% Pd–charcoal catalysts; type B1, □; type C1, ○; conversion expressed as percent C_2H_4 converted per 100 mg catalyst. Time indicated from onset to deactivation (the "CO poisoning time").

The explanation of the different CO poisoning times recorded in Fig. 2 for the two types of catalyst remains the same as that initially advanced. Type C1 has the metal located mainly at the edges of the charcoal support granule and therefore the palladium is less well "protected" in comparison with type B1 where the palladium crystallites are well distributed throughout the interior pore system of the charcoal granules. Confirmation was sought by measuring CO poisoning times for a variety of 1% Pd/charcoal catalysts which had

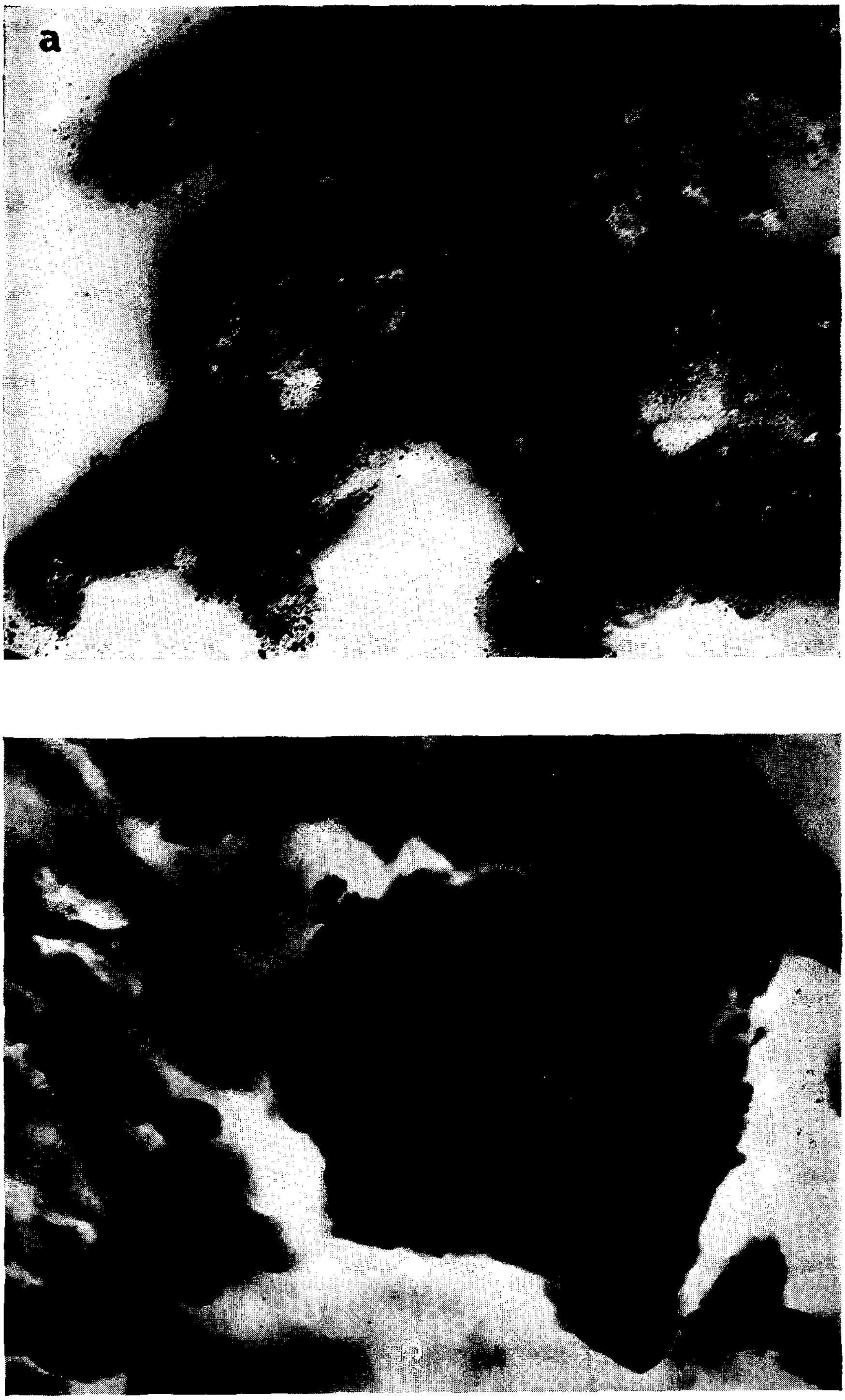

FIG. 3. Electron micrographs of ultramicrotome sections of 1% Pd-charcoal catalysts: (a) type F3 showing decoration of support granule edges with Pd crystallites; (b) type E3 showing obvious Pd concentration at support granule edges; ×100,000.

been examined in detail by electron microscopy. While results from the latter technique on metal *location* (as distinct from metal *dispersion,* i.e. crystallite size range) are subjective, it is believed that the electron micrographs shown or described are representative of the large number taken.

The electron micrographs of the catalysts listed in Table 2 show a gradation with respect to metal location downwards through the table. In catalysts G1 and H1, a very uniform distribution of palladium crystallites was evident while at the other extreme (Fig. 3(b)) there was an obvious concentration of the palladium at the edges of the charcoal support granule. Information on metal location is collected in Table 2 together with the observed CO poisoning times for these catalysts containing 1% Pd. Reference is also made in Table 2 to electron micrographs of catalyst types B1 and C1 containing 10% Pd which were shown in a previous publication (*2*), and represent near-extreme cases of metal location. It should be noted, however, that the CO poisoning times recorded in Table 2 were obtained using the 1% versions of these catalysts. The results presented in Table 2 show that the CO poisoning time decreases as the location of the palladium changes from the interior to the exterior of the charcoal support granules.

Correlation with Liquid-Phase Activity

Further confirmation of the view that the CO poisoning time is related to Pd location can be obtained by examining the behavior of these catalysts in diffusion-limited reactions. If a catalytic reaction is chosen which can be rapidly catalyzed by palladium metal in diffusion-free conditions then some form of palladium catalyst or reaction conditions might be found which would diminish the observed conversion because of the insufficient supply of reactants to the palladium surface (or diffusion of products from it). The use of a high-area charcoal support with a network of narrow pores might give rise to diffusion limitation of the rates measured over palladium supported on charcoal. Thus, type B1 catalysts, with the palladium crystallites distributed throughout the charcoal granule, would be most susceptible to diffusion-limited rates. Conversely, type C1 catalysts with the palladium concentrated at the support granule edges would be least susceptible. As a result, 1% Pd/charcoal catalysts (prepared on the same charcoal) should exhibit an inverse correlation be-

TABLE 2
METAL LOCATION AND CO POISONING (1% Pd/CHARCOAL CATALYSTS)

Catalyst	Metal location: Electron micrograph	Metal location: Description	CO poisoning[a] (min)
G1	—	Very uniform crystallite distribution; no Pd concentration at support granule edges	Very long[b]
H1	—		Very long[b]
B2	—	Uniform, but groups of small Pd crystallites occur [cf. also Ref. (*2*) Fig. 4a]	176
B1	cf. Ref. (*2*), Fig. 2a		151 ± 5
E1	—		137 ± 7
F3	Fig. 3(a)	Pd crystallites still fairly well distributed but support granule edges "decorated"	125
D1	—		108
A1	—		104 ± 4
C1	cf. Ref. (*2*), Fig. 2b	Obvious Pd concentration at support granule edges	38 ± 4
E3	Fig. 3(b)		32 ± 4

[a] Time elapsed, onset of observed poisoning to collapse of activity to residual level.

[b] Conversion still ~90%, 3–4 hr after onset of poisoning first observed.

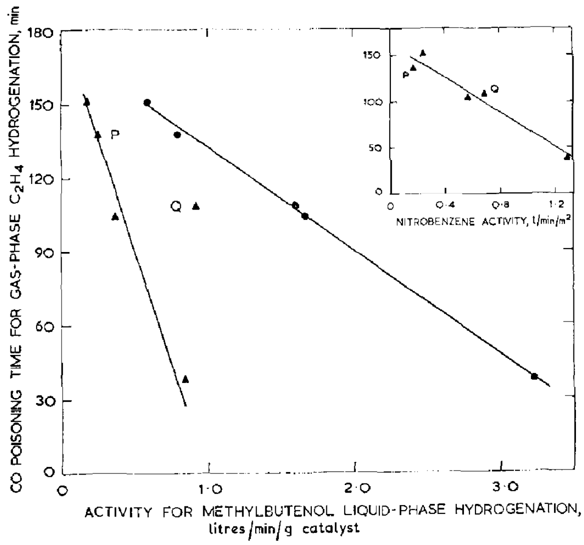

FIG. 4. Correlation of CO poisoning times with activity per unit weight of 1% Pd–charcoal catalysts for the liquid-phase hydrogenation of methylbutenol, ●, or nitrobenzene, ▲. Inset, correlation with activity per unit area (for nitrobenzene hydrogenation). Activities expressed as H_2 consumed.

tween CO poisoning time (if this correctly assesses metal location) and catalytic activity in a diffusion-limited situation.

Although the gas-phase hydrogenation of ethylene (in the absence of CO) could be carried out over Pd/charcoal catalysts at bath temperatures down to −115°C, no clear evidence of different specific activities was found using the various catalyst types. The specific activities of types A1, B1, and C1 with 1% Pd were 11.7, 12.9, and 9.5% ethylene converted per square meter of palladium at −115°C. Fortunately, we had made available to us information on the activities of these 1% Pd/charcoal catalysts in the liquid-phase hydrogenation of methylbutenol and nitrobenzene, both subject to diffusion limitation under the test condition adopted.

In general, there was a satisfactory correlation between CO poisoning times for gas-phase ethylene hydrogenation and the measured activities of the same series of catalysts for these liquid-phase test reactions. The shortest CO poisoning time was associated with the best catalyst performance in the hydrogenation of methylbutenol or nitrobenzene and conversely. Figure 4 (main part) shows CO poisoning times plotted against liquid-phase activities, where the latter are expressed *per unit weight* of catalyst. *It must be emphasised that the results recorded in Fig. 4 involved Pd/charcoal catalysts which had not only the same Pd content but also the same charcoal support, i.e., catalysts A1–E1.*

The methylbutenol reaction is faster than the nitrobenzene reaction by a factor of ~4 and it is particularly sensitive to diffusion limitation. Methylbutenol hydrogenation rates expressed per unit weight of catalyst show a particularly good correlation with CO poisoning times, although the catalysts had Pd areas differing by a factor of ~2. Catalysts G1 and H1 which had very long (unmeasured) CO poisoning times (Table 2) were rather inactive for this reaction, again fitting into the general picture. This result is most easily understood if we consider the methylbutenol reaction taking place mainly on palladium crystallites located at the charcoal granule edges. Although catalysts D1 and E1 have higher Pd areas, it would seem that they have a less effective Pd surface for methylbutenol hydrogenation because most of it is located some distance from the charcoal granule edges, reflected in longer poisoning times, than the most active C1 catalysts. (It is believed that CO poisoning times are reasonably independent of Pd area, in an identical location.) A correlation between CO poisoning time and methylbutenol hydrogenation rate, expressed per unit area of Pd surface, must fail.

In contrast, the intrinsically slower nitrobenzene reaction which is less sensitive to diffusion limitation, can effectively utilize more of the Pd surface. The palladium crystallites located some distance from the charcoal granule edges in catalyst D1 actively catalyze nitrobenzene hydrogenation (point Q on Fig. 4). Hence point Q falls off the plot of CO poisoning time versus activity for nitrobenzene hydrogenation, expressed *per unit weight*. Catalyst E1 has its extra Pd surface more inaccessibly located for this reaction and falls on the plot (point P). The enhanced activity of catalyst D1 (point Q) can be accommodated by expressing nitrobenzene hydrogenation rates *per unit area* (Fig. 4, inset). While point P is moved off this new plot (inset) to the left, the lesser sensitivity of the nitrobenzene reaction to Pd crystallite location means that a reasonable correlation is still observed.

CONCLUSIONS

The life of a Pd/charcoal catalyst for ethylene hydrogenation (in the presence of trace amounts of CO) seems to be dependent on the location of the palladium crystallites within the charcoal granules, as suggested by electron micrographs. Correlations were found between diffusion-limited hydrogenation rates in liquid-phase reactions and "CO poisoning times" for ethylene hydrogenation (in the gas phase). These liquid-phase hydrogenation rates were known to vary according to the degree of diffusion limitation imposed by the location of the palladium crystallites within the charcoal granules. Hence, the correlations observed confirm the view that CO poisoning times are dependent on metal location. The methods of measuring CO poisoning times using Pd/charcoal catalysts, described in the preceding sections, might form the basis of a technique for characterizing such catalysts with respect to metal location. However, the CO poisoning times observed are likely to be a consequence of the interaction of a number of variables including preparative method, metal content, and the pore-size distribution of the support.

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