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The Influence of the Substrate on the Behavior of Graphite-Supported Palladium Catalysts

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To investigate whether the properties of the metal are affected by the interaction between the metal and the substrate, palladium on graphite has been used as a catalyst for the hydroisomerization of 1-butene; the variable parameters of the reaction being studied as a function of whether (a) the palladium was "decorating" the graphite surface or (b) the palladium was randomly dispersed over the graphite surface. The results show that decoration of the graphite by the metal increases both the rates of hydrogenation and isomerization. Furthermore under reaction conditions the palladium is mobile on the substrate surface; this mobility results in an increase in the particle size of the palladium and a consequential loss in catalytic activity.

INTRODUCTION

In 1958, Bassett (*1*) showed that on alkali halide crystals the movement of gold particles was prevented by the presence of irregularities in the surface of the crystals. This lack of mobility gives rise to surface "decoration" in which the metal particles are concentrated at defects and surface steps of the crystal. This phenomenon of decoration is also shown by graphite with gold or silver particles (*2*), and it has been suggested (*3*) that the cessation of movement of the metal particles is associated with the formation of a metal–substrate interface, while mobility occurs on a layer of adsorbed gas.

EXPERIMENTAL

British Nuclear Grade A graphite was used as support. This was ground to a size of 30–60 mesh and then ultrasonically dispersed in water to give particles of approximately 10 μ in size which were suitable for electron microscopic studies. The graphite particles were loaded with approximately 1% w/w palladium by either of two methods: (a) Palladium was evaporated from a tungsten filament onto the graphite under a vacuum of 10^{-5} torr. (b) The graphite was dispersed in a solution of palladous chloride in dilute hydrochloric acid. The suspension was evaporated to dryness and the supported salt was reduced to the metal at 200°C by hydrogen until the evolution of hydrogen chloride ceased.

Samples of each catalyst were examined by transmission electron microscopy which showed that in both cases the palladium was randomly dispersed on the surface of the graphite. The presence of the palladium as metal was also confirmed by electron diffraction.

Decoration of the graphite by palladium was achieved by heating the catalyst to 300–500°C for 1 hr (Fig. 1). Below 300°C the palladium particles were immobile, while at temperatures above 350°C nucleation occurred resulting in the formation of very large ($>10^3$ Å) palladium particles.

The catalytic properties of the graphite-supported palladium for the hydroisomerization of 1-butene were examined using 100-mg samples of catalyst. Each sample of catalyst was activated in an atmosphere of hydrogen at 200°C for 1 hr. At this tem-

Fig. 1. (a) Decorted actalyst A (from $PdCl_2$); (b) decorated catalyst B (evaporated Pd).

perature the activation procedure did not induce any significant decoration of the graphite surface by palladium.

The activity of the various catalyst samples was examined using a 1:1 1-butene–hydrogen mixture at a total pressure of *100* ± 2 mm. Reactions were followed by the pressure fall observed on a mercury manometer and after the required conversion the reaction products were analyzed by gas chromatography. Rates of hydrogenation (r_h) and isomerization (r_i) were then calculated as described in a previous article (*4*).

Results and Discussion

A typical series of results for catalyst A (prepared from $PdCl_2$) and catalyst B (prepared by palladium evaporation) in both undecorated and decorated states is shown in Table 1. In each case the catalyst showed a progressively decreasing activity for a series of reactions. This was especially marked with the decorated catalyst B after four reactions at 43°C; both r_i and r_h were reduced by a factor of approximately 10.

The analysis of the reaction products showed that the (trans/cis) ratio in 2-

FIG. 2. Catalyst B-2 showing nucleation after reaction at 43°C.

butene was independent of (a) the method of catalyst preparation and (b) whether or not the palladium was decorating the graphite surface. A value of 1.6 ± 0.3 was observed at a constant (3.5%) conversion to *n*-butane.

From the results presented in Table 1 it can be seen that with catalyst A, decoration increases the rates of both hydrogenation and isomerization by a factor of approximately 5, while with catalyst B, decoration increases the rate of isomerization approximately 25 times. Catalyst B, prepared by evaporation of palladium onto the sub-

FIG. 3. Nucleation of catalyst B-2 after reaction at 43°C.

strate, was substantially less active than catalyst A, prepared from palladous chloride, for both hydrogenation and isomerization.

Electron microscopic examination of the catalyst samples after activation and before reaction showed that in catalyst A, the average particle size of the palladium was 65 ± 10 Å, and in catalyst B the average particle size was 140 ± 70 Å. The average density of palladium particles decorating the graphite surface was $4 \pm 0.4 \times 10^{6}$ cm^{-2} and $2.4 \pm 0.2 \times 10^{6}$ cm^{-2} for catalysts A-2 and B-2, respectively. Examination of

FIG. 4. Catalyst A-2 after reaction showing loss of decoration.

the catalysts after reaction showed that the decreasing catalytic activity of catalyst B-2 was due to loss of decoration caused by nucleation of the palladium particles (Fig. 2) and the eventual formation of particles approximately 1300 Å in diameter (Fig. 3), although the temperature was maintained at 43°C throughout the reaction series. With catalyst A after reaction (Fig. 4), the micrographs show that, as with catalyst B, some rearrangement of the palladium particles has taken place during reaction, resulting in the formation of polyhedral crystallites, but with *no significant* increase in particle size.

From these observations we can draw the following conclusions:

(1) The greater catalytic activity of

TABLE 1
ACTIVITIES OF DECORATED AND UNDEOCORATED PALLADIUM/GRAPHITE CATALYSTS

Catalyst	Temp. (°C)	r_i (mm^{-1} min^{-1})	r_h (mm^{-1} min^{-1})	(r_i/r_h)
A-1 (undecorated)	39°	5.0	0.15	33.3
A-2 (decorated)	39°	31.2	0.90	34.7
B-1 (undecorated)	43°	0.15	Negligible	—
B-2 (decorated)	43°	3.8	0.75	5.1

catalyst A than of catalyst B is a consequence of the smaller palladium crystallite size and a greater concentration of palladium particles decorating the graphite in A than in B.

(2) Decoration of the sample increases r_i and r_h equally, suggesting that the same type of surface site is involved in both reactions.

(3) Since decoration which involves the formation of a metal–substrate interface (*3*) across which electrons may flow, increases the catalytic activity, it would appear that one of the main functions of a catalyst support for favorable catalytic activity would be the ability to modify the electron content of the bonding orbitals of the metal in such a manner as to favor the formation of reaction intermediates. This conclusion is further substantiated by the observation that with catalyst A the particle sizes of the palladium on the decorated and undecorated samples were virtually identical. Further work is being carried out in an attempt to investigate further these phenomena.

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