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Hydrogen Migration on Alumina/Palladium Catalysts for Benzene Hydrogenation*

KENNETH M. SANCIER

Solid State Catalysis Laboratory, Stanford Research Institute,
Menlo Park, California

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Benzene was hydrogenated in a slug reactor at 150°C with hydrogen passing continuously over a catalyst consisting of mixtures of alumina and of palladium supported on alumina. As the metal-supported catalyst was diluted with alumina, the percentage hydrogenation per milligram palladium in the catalyst increased and approached a limiting factor of improvement of about three for a dilution of 200/1 or more. To account for this dilution effect, a model is suggested whereby the catalyst granules form a close-packed array and intergranular hydrogen migration occurs through about three layers of the array. Assuming that only the geometric area of the alumina is active, we estimated that the migration distance of chemically reactive hydrogen is about 0.5 mm and the fractional surface coverage of the hydrogen on alumina is as much as 3×10^{-2}.

INTRODUCTION

A plethora of evidence supporting the concept of hydrogen migration on supported metal catalysts, as well as on supports without metal, has been generated from various types of kinetic measurements. These include hydrogen chemisorption (*1–6*) hydrogenation of olefins (*3, 7, 8*) reduction of inorganic compounds (*9–11*) dehydrogenation (*12–14*) isomerization (*15–16*) hydrogen isotope exchange (*17*) ortho-para hydrogen conversion (*18*), and ESR studies of hydrogen atoms produced by irradiation (*19, 20*). Although the preponderance of evidence supports hydrogen migration between the support and the supported metal, the catalytic effects of the support and the metal have not always been clearly separated. For example, some uncertainty arises in cases where catalyst pretreatments at high temperatures (*8, 16*) (e.g., about 500°C compared to 200°C used in this study) might permit supported metals such as platinum or palladium to migrate across the support surface, or in other cases where the catalysis might have occurred only on the supported metal (*15, 16*).

Very little is known about the mechanism of hydrogen migration or the nature of surface conditions of supports which favor the migration. However, it is almost certain that the supported metal chemisorbs hydrogen, which migrates on the support. Also, the fact that the presence of adsorbed water accelerates the hydrogen reduction of tungsten trioxide in the presence of platinum (*10*) suggests that the migrating hydrogen interacts with labile hydroxyl surface groups, a view supported by the infrared studies of the exchange of deuterium with the hydroxyl groups of silica (*1*) and alumina (*17*). Additional information is needed to understand the mechanisms of the migration, to optimize catalytic reactions that depend on the migration process, and to obtain an unequivocal interpretation of surface area measurements of supported metals that depend upon hydrogen sorption (*21, 22*).

In the present investigation, we examine

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the distance traversed by chemical reactive hydrogen from granules of alumina-supported palladium to granules of alumina, and the amount of hydrogen on the alumina available for catalytic hydrogenation. For this purpose, we have modified and extended the experimental technique used by Sinfelt and Lucchesi (*8*).

EXPERIMENTAL DETAILS

The catalytic hydrogenation of benzene was carried out in a catalytic microreactor with hydrogen as the carrier gas. The catalyst powder was placed on a medium glass frit of a heated glass cylindrical reactor (2-cm^3 volume). Hydrogen (Matheson, prepurified grade) flowed through the reactor at about 70 cm^3/min and entered the gas chromatograph. A secondary stream of hydrogen at about 5 cm^3/min was bubbled through benzene (Mallinckrodt, reagent grade) kept at room temperature, and 0.5-cm^3 aliquots of this gas were injected into the hydrogen carrier gas to the reactor. The benzene and cyclohexane leaving the catalyst were analyzed by a gas chromatograph with a silicone-710 column ($\frac{1}{4}$ in. × 10 ft) at 86°C.

The catalyst was pretreated in the reactor at 200°C for about 2 hr in hydrogen. Subsequently, hydrogenation activity was determined for several aliquots of benzene, after the temperature had been lowered to 150°C.

The catalyst was composed of the two components, alumina (Al_2O_3) and 2.2 wt % palladium supported on alumina (Pd/Al_2O_3), which were added separately in various proportions to the reactor, mixed by gently rolling the powders for several minutes until the powder appeared homogeneous, and tamped gently to form a column about 1.1-cm high. This method of mixing will result in less palladium transfer to alumina than more severe methods such as grinding (*8*) or pelletizing. The alumina (Kaiser Aluminum and Chem. Corp., with a surface area of 23 m^2/g, porosity of 61%, and alpha content of 65% with the remainder principally delta and theta) was milled and sieved, and the cut passed by mesh 115 and held on mesh 170 was used. To prepare Pd/Al_2O_3, the sieved alumina was impregnated with palladium chloride solution, evaporated to dryness, and heated at 400°C in flowing hydrogen for 4 hr.

RESULTS AND DISCUSSION

The distance of hydrogen migration across the support was determined from a series of hydrogenation measurements for various proportions of the two components of the catalyst, Pd/Al_2O_3 and Al_2O_3. The experimental conditions were chosen to minimize migration of Pd, either by mechanical or diffusive mass transfer, to the added Al_2O_3. For example, the powders comprising the catalyst were mixed by gentle tumbling in the reactor, and the pretreatment did not exceed 200°C. In order to provide a constant contact time, the total quantity of catalyst was maintained at 1000 mg with few exceptions.

The fraction of benzene converted to cyclohexane as a function of the composition of the catalyst is shown in Table 1. The percentage hydrogenation is calculated from the ratio of the amount of cyclohexane formed to the sum of benzene and cyclohexane in the gas leaving the reactor. The reproducibility indicated was determined by averaging the results of several consecutive runs with a given catalyst; the catalyst activity was found to be essentially unchanged for several catalysts examined after exposure to air for several days or to hydrogen flowing continuously over the catalyst at 150°C overnight. The alumina used did not exhibit detectable hydrogenation activity (Table 1).

As the Pd/Al_2O_3 was diluted the percentage hydrogenation decreased, but the percentage hydrogenation per mg Pd increased. This result suggests that only part of the hydrogenation occurs on the Pd and the rest occurs on the alumina. The role of alumina in promoting the hydrogenation reaction is illustrated by Fig. 1. Upon dilution the hydrogenation rate per mg Pd increased initially with a slope indicating an enhancement factor of about 8 for a dilution of 200, and ultimately approached an enhancement factor of 3 for a dilution of 200 or greater. This latter enhancement

TABLE 1
HYDROGENATION OF BENZENE TO CYCLOHEXANE OVER THE MIXED CATALYST, Pd/Al_2O_3 AND Al_2O_3, AT 150°C

Catalyst[a]				Hydrogenation	
Mass (mg)					
Pd/Al_2O_3	Al_2O_3	Pd	$\frac{\text{mg } Al_2O_3}{\text{mg } Pd/Al_2O_3}$	(vol %)	(vol %) per mg Pd
100	0	2.2	0	45 ± 2	21 ± 0.9
55	0	1.2	0	33 ± 0.9	27 ± 0.8
100	900	2.2	9	69 ± 1	31 ± 0.5
50	950	1.1	19	40 ± 2	37 ± 2
25	475	0.55	19	22 ± 1	40 ± 2
25	975	0.55	40	25 ± 0.4	46 ± 0.7
5	995	0.11	200	7.4 ± 0.5	67 ± 5
1.5	1000	0.033	670	2.2 ± 0.2	65 ± 5
0	1000	0	—	Nil	

[a] Pd/Al_2O_3 and Al_2O_3 were added separately, mixed, and pretreated at 200°C in H_2 for 2 hr.

factor implies that about 60% of the hydrogenation occurred on alumina.

The enhancement shown in Fig. 1 can be accounted for by considering that upon dilution each granule of the Pd/Al_2O_3 is surrounded by increasing numbers of granules of Al_2O_3. Ideally, such alumina granules may be considered to be uniform spheres which form hexagonal closepacked (hcp) structures. The dilutions required to form the successive hcp layers are indicated along the abscissa of Fig. 1 by Roman numerals, and according to this model enhancement occurs up to the third layer. If the enhanced hydrogenation of benzene involves hydrogen migration across the

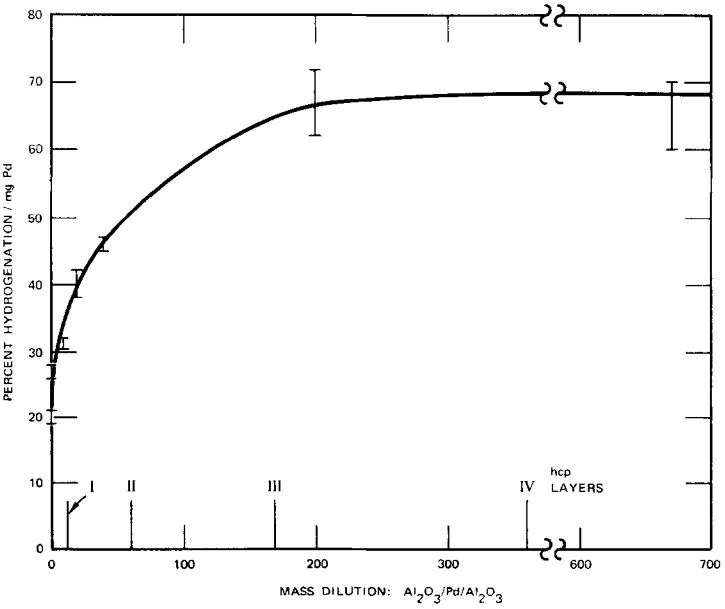

FIG. 1. Effect of diluting Pd/Al_2O_3 with Al_2O_3 on the percentage hydrogenation of benzene per mg Pd at 150°C. Roman numerals refer to the average number of hexagonal-close-packed (hcp) layers corresponding to the given dilutions.

alumina surface, the distance of migration is evidently limited to transport across about three layers, that is, across the surface of three granules. We may now obtain an order-of-magnitude estimate of the minimum migration distance by using the geometric area of the alumina granules (0.1 mm average diameter), and thus obtain a migration distance of $3(\pi D/2) \approx 0.5$ mm. To estimate the maximum migration distance we use the total surface area of the alumina, which for the three layers corresponds to a migration distance of about 20 mm. The actual migration distance is between these limits. It is surprising that the hydrogen migrates over such distances since migration must occur from one alumina granule to another where intergranular contact must be poor, at least in terms of contact area.

An estimate of the surface coverage of chemically active hydrogen may be made from information on the amount of benzene introduced per aliquot to the catalyst, the hydrogenation conversion, and the probable active surface area of alumina. For example, the aliquot of benzene contained about 2×10^{15} benzene molecules. As concluded above, about 60% of the observed conversion may be attributed to the diluent alumina. Then for the case of total hydrogenation of 69 vol % per aliquot, about 8×10^{14} benzene molecules will be hydrogenated. Since hydrogenation requires six hydrogen atoms per benzene molecule, the amount of reactive hydrogen atoms required is about 5×10^{15} atoms. Accordingly, the fractional surface coverage of reactive hydrogen atoms is estimated to be between about 10^{-5} and 10^{-2} depending upon the active alumina area assumed (the total surface area has about 10^{20} sites/g and the geometric surface area about 10^{17} sites/g). These values are in adequate agreement with reported values from different techniques. Namely, the fractional surface coverage of hydrogen chemisorbed on γ-Al_2O_3 has been reported (*4*) to be about 10^{-4} at 300°C, and in another study (*5*) it was about 10^{-2} at −52°C.

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