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Role of Hydrogen in Butene Isomerization Catalyzed by Supported and Unsupported Palladium*

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Experimental measurement of butene-1 isomerization in the presence of low concentrations of hydrogen have demonstrated that the rate is proportional to the square root of the hydrogen partial pressure. This dependency on $[H_2]^{1/2}$ has been found to apply to palladium supported on α-alumina as well as to palladium–metal microspheres. In addition, the distribution of butene-2 isomers during the initial portion of the isomerization is of equal magnitude. These observations give further support to the addition–abstraction mechanism of hydrogen as an essential step for double-bond migration and geometrical isomerization.

INTRODUCTION

A number of recent publications have dealt with the problem of olefin isomerization catalyzed by group VIII metals (*1–8*). In these studies, as well as in some work carried out in our laboratory (*9*), the role of hydrogen in double-bond migration and geometrical isomerization of olefins has been explored. The results of our studies on palladium metal and palladium–silver alloys have pointed to an addition–abstraction mechanism of hydrogen as an essential step in the isomerization process. As a matter of fact, on these catalysts the surface density of chemisorbed hydrogen during catalysis appeared to control the course of three types of related reaction involving olefins: isomerization, hydrogenation, and dehydrogenation (*9*). Moreover, in the dehydrogenation of butane by means of a Pd/Ag thimble, the surface could be made catalytically stereospecific by pretreatment of the catalyst with the isomer desired in the presence of low concentrations of hydrogen (*9, 10*). In the present study we turned our attention to a supported palladium catalyst. Alumina was selected as the support material. In addition we compared the catalytic properties of the supported Pd-catalyst with those of bulk Pd metal, in the form of microspheres.

EXPERIMENTAL DETAILS

Conventional impregnation techniques were employed for catalyst preparation. A measured aliquot of a solution containing metallic palladium dissolved in aqua regia was used to impregnate low-surface area 65% α-alumina carrier† (surface area 20 m^2/g, 50 μ diameter particles) to yield 2.2 wt % palladium relative to support. The impregnated material was dried in air at 125°C, then reduced in a stream of hydrogen (1 atm pressure) first at 400°C for 4 hours, then at 700°C for 4 hours. For blank runs involving only the alumina support without dispersed palladium, the α-alumina was subjected to the procedure just described including exposure to aqua regia. A catalyst sample was placed in the reactor, pretreated in situ with O_2 at 300°C for about 15 min, and then flushed in helium at the reaction temperature.

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† Kaiser Aluminum & Chemical Corp., Pleasanton, CA.

In the experimental work to be reported, the mass of catalyst employed was from 0.3 to 0.5 g. The powdered material was placed on top of a fritted glass disk contained in a vertically oriented Pyrex cylinder (~10 cc in volume) and surrounded by a temperature-controlled furnace. Helium at a volumetric flow rate of 1500 cc/min was used as a carrier gas. The reactants, butene and hydrogen, were admixed to the stream at the desired concentrations by means of calibrated flowmeters (Fig. 1). Before and after passage through the reactor, aliquots of the gas stream could be withdrawn through special sampling valves (Loenco model 1-208) and analyzed by gas chromatography (Hewlett–Packard, model 5750). A column (25 feet in length and 0.25 in. in diameter) containing BMEA* and operated at 25°C gave good separation of the three butene isomers.

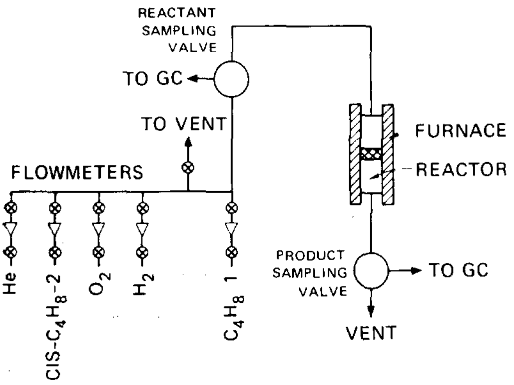

Fig. 1. Schematic diagram of apparatus (⊗ valve; △ flowmeter).

For measurement of the surface area of the catalyst, the chemisorption of CO was employed (*11*). About 0.5 g of supported catalyst was placed on the aluminum pan, which was suspended from the beam of the Cahn microbalance† by a quartz fiber. After degassing of the catalyst at 400°C for approximately 15 hours under vacuum, we cooled the sample to room temperature and introduced 25 Torr of CO into the system. (A molecular sieve trap was employed to remove traces of CO_2 from the CO supplied with a purity specification of 99.5% by volume.) After attainment of sorption equilibrium, the physisorbed CO was pumped off the sample at room temperature. The difference in mass between the physisorbed portion and the total mass adsorbed represented the quantity of chemisorbed CO. These measurements were repeated at successively higher CO pressures until the weight change due to chemisorption reached a limiting value. In calculating the metal surface area we assumed a value of 0.86×10^{15} surface sites for CO adsorption per cm^2 of palladium surface. Chemisorption of CO on the Al_2O_3 support was found to be small. By this procedure an average value of 0.44 m^2/g was measured for the surface area of the supported Pd-catalyst. For the Pd microspheres‡ the surface area was found to be 0.014 m^2/g as measured by the conventional BET technique (Krypton).

Experimental Results

The importance of hydrogen for isomerization activity of the Pd/Al_2O_3 catalyst is demonstrated by the results presented in Fig. 2. After the catalyst was subjected to pretreatment in oxygen and helium at

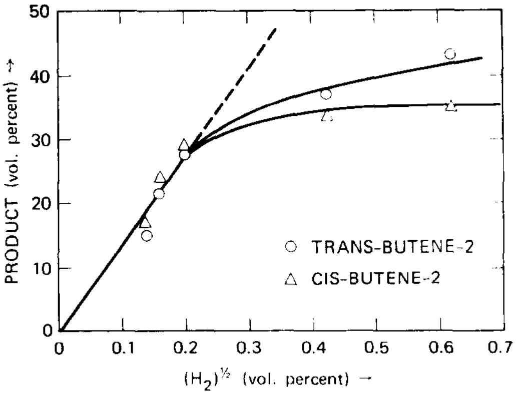

Fig. 2. Butene-1 isomerization catalyzed by Pd/Al_2O_3 at 100°C and various concentrations of molecular hydrogen (initial butene-1 = 0.5 vol %; carrier gas He; ○ *trans*-butene-2; △ *cis*-butene-2).

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* 80 w % [20 wt % bis-*o*-methyloxy-ethyl adipate on 60/80 Chromosorb W], 20 w % diethyl sebacate on 60/80 Chromosorb W].

† Cahn Instrument Company, Paramount, Ca.

‡ Obtained from Engelhard Industries, Inc., Newark, NJ.

300°C (cf. section on experimental details), it exhibits insignificant catalytic activity (<2 vol % conversion) when exposed to butene-1 (1-B) at 100°C. However, the addition of hydrogen to the reactant stream leads to effective isomerization with conversion to butene-2 (2-B) as high as 80 vol % under our experimental conditions. The product distribution in terms of the two geometric isomers of butene-2 indicates that the *cis-* and *trans-* forms are produced at about the same rate, far removed from the equilibrium ratio. This effect is due in part to the short contact time between reactant and catalyst at the high flow rates employed. A linear relationship is noted between the steady-state isomer concentration in the product stream and the square root of the hydrogen concentration up to about 50 vol % of olefin conversion. At higher hydrogen concentrations, the measureable formation of butane begins to cause deviations from this dependency on $[H_2]^{1/2}$.

Under similar conditions of pretreatment and reactant composition, the bare alumina support (without palladium) at 100°C exhibits no isomerization activity for butene-1 or *cis*-butene-2 even in the presence of added hydrogen (Table 1, Series A). To acquire some isomerization activity the reaction temperature needs to be raised to 300°C and the alumina support exposed to hydrogen pretreatment as demonstrated by the data listed in Table 1 (Series C and D).

In the butene-isomerization experiments in which Pd metal was employed in the form of metal microspheres, the metal particle diameters ranged from 44 to 53 microns (*9*). The pretreatment procedure was similar to that employed for Pd/Al_2O_3 i.e., exposure to oxygen (300°C) and flushing in helium (100°C). At a reaction temperature of 100°C, no isomerization activity was observable when butene-1 was passed over the catalyst. However, the addition of small concentrations of hydrogen to the reactant stream led to isomerization, as shown in Fig. 3. Again the formation of the *cis-* and *trans*-isomers of butene-2 exhibits the same dependency on the square root of the molecular hydrogen concentration as observed for the Pd/Al_2O_3 catalyst. In the reaction regime in which the isomerization activity varies linearly with $[H_2]^{1/2}$ we can compare the specific conversion rate of butene-1 for the two catalysts employed. At 10^{-2} vol % H_2 we

TABLE 1

Isomerization Activity of Alumina Support

(α-Alumina)

Series	Temp. (°C)	Reactants (Vol %)			Prod. Distrib. (Vol %)			Mass Catalyst (g)
		H_2[a]	1-B[b]	C-2-B[c]	1-B	C-2-B	t-2-B	
A	100	0.013	0.5	0	100	0	0	0.30
	100	0.026	0.5	0	100	0	0	
	100	0.10	0.5	0	100	0	0	
	100	0.20	0.5	0	100	0	0	
	100	0.38	0.5	0	100	0	0	
B	100	0	0	2.2	0	100	0	0.30
C[d]	325	0	0	0.3	2	88	10	0.50
D[e]	325	0	0	0.3	1	94	5	0.50

[a] Purity: (Matheson) 99.9%.

[b] Purity: (Phillips 66) 99 mole %.

[c] Purity: (Phillips 66) 99 mole %.

[d] Catalyst pretreated at 440°C in O_2 (1 atm), followed by He (1 atm); then flushed at 325°C in He.

[e] Catalyst pretreated at 440°C in O_2 (1 atm), followed by He (1 atm) and H_2; then flushed at 325°C in He.

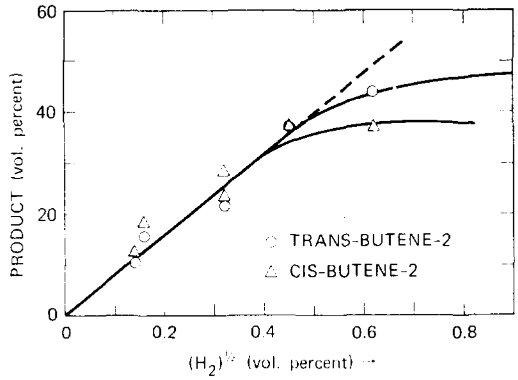


FIG. 3. Butene-1 isomerization catalyzed by Pd microsphere at 100°C and various concentrations of molecular hydrogen (initial butene-1 = 0.5 vol %; carrier gas He; ○ *trans*-butene-2; △ *cis*-butene-2).

calculate a value of 0.33×10^{-3} moles/m^2 min for the supported catalyst (Pd/Al_2O_3) and 1.9×10^{-3} moles/m^2 min for the Pd-microspheres. This six-fold difference in conversion rate is somewhat greater than the estimated experimental error. But it is indicative of the fact that the Al_2O_3 support is not contributing to the isomerization process under our experimental conditions.

DISCUSSION

The results obtained provide further evidence for the hydrogen addition-abstraction mechanism during olefin isomerization on Pd-catalysts. Also, they offer some insight into the rate-controlling step associated with the isomerization reaction involving a sorbed butyl radical as an intermediate. Based on the observed relationship between isomerization activity and gaseous hydrogen concentration, we may consider the following elementary steps in the isomerization process:

$$H_2(g) \rightleftarrows 2H(s) \qquad (1)$$

$$C_4H_8(g) + H(s) \rightleftarrows C_4H_9\cdot(s) \qquad (2)$$

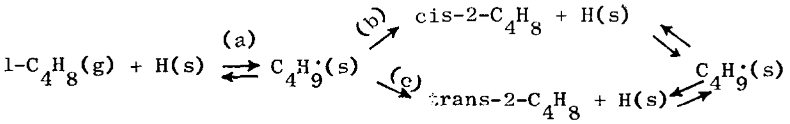
$$C_4H_9\cdot(s) \rightleftarrows C_4H_8^*(g) + H(s) \qquad (3)$$

where (s) represents sorbed species, (g) gaseous species, and $C_4H_8^*$ an isomer of C_4H_8. Since the chemisorption of hydrogen on a palladium surface (step 1) is known to be a nonactivated process, the subsequent reactions (step 2 or 3) may be rate-determining. For step 2 the reaction rate will be given by the term $k_2P_b\sigma_H$, where k_2 is the rate constant for the forward reaction, P_b the gas phase concentration of 1-butene, and σ_H the fractional surface coverage of chemisorbed hydrogen atoms. Step 3 describes the hydrogen abstraction–desorption reaction leading to the butene isomer $C_4H_8^*$. This process is expected to be faster than step 2 and to show like dependence on hydrogen at low surface coverages. The amount of chemisorbed hydrogen will be given by $\sigma_H \alpha P_{H_2}^{1/2}$, where P_{H_2} represents the partial pressure of molecular hydrogen. Thus the isomerization rate controlled by step 2 would be expected to be half-order in molecular hydrogen as observed experimentally. On the other hand, for the complete hydrogenation of an olefin to the alkane, it has been shown (*12*) that the reaction mechanism involves

$$\text{alkene} + 2H(s) \rightleftarrows \text{alkane} \qquad (4)$$

so that the rate is given by the term $k_4P_{\text{alkene}}\sigma_{H_2}$. Consequently, olefin hydrogenation becomes the predominant reaction at high surface densities of hydrogen and exhibits first-order dependency on molecular hydrogen (*12*).

As indicated, the availability of surface hydrogen and the formation of the sorbed butyl radical play an important role in isomerization and hydrogenation. According to the mechanism proposed above (step 2), the butyl radical forms by the interaction of a chemisorbed hydrogen atom with a butene molecule from the gas phase (Rideal-type mechanism) and is attached to the surface at a single palladium site. Because of unhindered rotation about each of the C–C bonds, the radical has lost all stereospecificity. Thus in the subsequent step (3) the return of a hydrogen atom from the radical to the surface will make equally probable the formation of *cis*- or *trans*-butene-2, as observed in our experiments. The nonequilibrium distribution offers further evidence for the butyl radical intermediate and the reaction sequence:



where the formation of the two isomers from the butyl radical (reactions b and c) occurs at similar rates and the equilibrium distribution of the butene-2 isomers is ultimately attained by subsequent interconversion of *cis*- and *trans*-butene-2.

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