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The Retention of Hydrogen by Supported Metal Catalysts

There are many reports extant of the use of flow systems and microcatalytic reactors for the study of the hydrogenation of unsaturated hydrocarbons *(1, 2, 3)*. In most of these studies helium has been used as the carrier gas, and the normal procedure has been to reduce the catalyst in hydrogen at an elevated temperature (⩾200°C), followed by treatment in a stream of helium at the reduction temperature. The object of the latter is presumably to remove adsorbed hydrogen from the catalyst surface *(2)*.

Using alumina-supported palladium, rhodium, and platinum catalysts and a microcatalytic reactor technique, we have investigated the extent to which hydrogen is retained in a reactive form after treatment of the catalyst in helium: this has formed part of a program of investigation of the adsorption, retention, and self-hydrogenation of hydrocarbons on supported metal catalysts. The procedure which we adopted was (i) reduction of the catalyst in a stream of hydrogen at 200°C for 1 hr, (ii) flowing helium over the catalyst at 200°C for a minimum of 1 hr (longer times did not make any significant difference to the subsequent behavior), and finally (iii) cooling the catalyst in a stream of helium to the required temperature. Following this treatment, 0.5 ml (NTP) volumes of ethylene or higher olefins were injected into the helium gas stream immediately above the catalyst and the eluant from the reactor was monitored by gas chromatography. Two types of behavior were observed: (i) a fraction of the olefin was irreversibly adsorbed on the catalyst and (ii) the eluant gas contained saturated hydrocarbon. With both rhodium and palladium catalysts, the only hydrocarbon eluted following the first injection of ethylene was ethane. Several injections were necessary before ethylene was the sole product. With platinum, the ethane yield from the first injection was substantially less than with either rhodium or palladium.

To investigate further the mode of ethane production, i.e., whether by self-hydrogenation of ethylene—a common phenomenon on metal catalysts *(4)*—or by reaction with surface hydrogen not removed in the helium pretreatment, experiments were carried out with tritiated hydrogen. The catalysts were reduced as described previously and were then treated with helium at 200°C for various times as shown in Table 1. Two milliliters of tritiated hydrogen (total activity $20\ \mu c \equiv 1.6 \times 10^7$ disintegrations) was injected into the helium stream. The activity of the reactor eluant was monitored using a flow proportional counter *(5)*. The time taken for the activity of the eluant to fall to the background

TABLE 1
DESORPTION OF 'HYDROGEN' BY HELIUM TREATMENT AT 200°C

Wt. of catalyst, 0.5 g; total HT activity injected, 20 μc

Catalyst	Time of He treatment before HT injection (min)	Total HT count in eluant ($\times 10^3$)	Time to reach background
Rh-A	10	70.5	4 min
Rh-B	23	62.0	6 min
Pd-A	11	235.0	>11 hr
Pd-B	15	252.0	5½ hr
Pt-A	20	47.0	10 min

level varied from metal to metal as shown in Table 1. Once the background level had been attained it was assumed that all the desorbable "hydrogen" had been removed from the surface and an 0.5 ml (NTP) sample of ethylene was injected into the gas stream. The composition and activity of the reactor eluant were monitored using a radiochromatograph (*5*) and the results are summarized in Table 2.

TABLE 2
ELUANT ANALYSIS FOLLOWING FIRST INJECTION OF ETHYLENE TO TRITIATED SURFACE AT 200°C

Volume of C_2H_4 injected, 0.5 ml (NTP)

Catalyst	C_2H_6 yield (ml)	C_2H_4 yield (ml)	Total activity (counts $\times 10^{-3}$)		Specific activity (counts/ml $\times 10^{-5}$)	
			C_2H_6	C_2H_4	C_2H_6	C_2H_4
Rh-A	0.23	0.01	150	2	6.5	2.0
Rh-B	0.26	0.0	128	—	5.0	—
Pd-A	0.30	0.0	375	—	12.5	—
Pd-B	0.27	0.0	347	—	12.9	—
Pt-A	0.07	0.30	50	70	7.1	2.3

From these results we can draw the following conclusions:

(i) The helium pretreatment of the catalysts at the reduction temperature does not remove all of the *reactive* hydrogen from the surface.

(ii) The amount of reactive hydrogen on the Pt/Al_2O_3 catalyst is less than on the Pd/Al_2O_3 or Rh/Al_2O_3 catalysts, although the *total* amount of hydrogen retained on the platinum catalyst is similar to that on rhodium and greater than that on palladium.

(iii) The yields of ethane from the injection of 0.5 ml of ethylene are similar with palladium (0.3 ml) and rhodium (0.26 ml), although the specific activities are different (12.5×10^5 counts/ml with Pd and 5.0×10^5 counts/ml with rhodium). Thus the proportion of self-hydrogenation is appreciably less on Pd/Al_2O_3 than on Rh/Al_2O_3. Furthermore, since the ethane specific activities are similar over rhodium and platinum catalysts, although the ethane yields are markedly different, the relative proportions of self-hydrogenation must be similar over these two catalysts. This conclusion is consistent with the observation that the total amount of hydrocarbon recovered from palladium is greater than that from rhodium.

A full account of this work will appear in a later paper.

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