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Competitive Hydrogenation of Butadiene and Butene on Palladium and Platinum Catalysts

In a recent study (*1*) of the selective hydrogenation of butadiene to butenes, the reactivity of palladium (in the form of single crystals and of supported catalysts) was compared with that of platinum. As shown in Table 1, the reactivity of single-crystal faces with (111) orientation is comparable to that of SiO_2-supported catalysts.

The argument put forward to explain the comparatively lower activity of platinum was its lower hydrogen coverage under a given pressure, in the presence of the hydrocarbons, arising from a heat of adsorption smaller than that on palladium (respectively 67 and 85 kJ/mol) (*2, 3*). Concerning its poorer selectivity toward butenes, the reason invoked was a similar heat of adsorption for butadiene and butenes: the olefinic intermediate compound remains partly on the surface and the reaction proceeds to butane.

A powerful kinetic method which is able to provide direct evidence for this different adsorption of dienes and butenes would be the competitive hydrogenation of these two molecules. However, to distinguish between the ethylenic hydrocarbon formed during the reaction and the molecules already present in the reactants, the experiments were performed according to the sequence: competitive hydrogenation of a butadiene–propene mixture followed by the hydrogenation of a 1-butene–propene mixture.

The principle of this method is well known (*4*) and it has been applied recently to the benzene–toluene pair to establish a correlation between the ratio of their adsorption coefficients and the electronic structure of different metal-supported catalysts (*5*).

It has been assumed that the reaction obeys a Langmuir–Hinshelwood mechanism, with the two hydrocarbons and hydrogen competing for the same sites on an energetically uniform surface. If hydrogen is adsorbed dissociatively, the hydrogenation rate of butadiene is given by

$$R_b(p) = k_b A_b P_b f(H_2)/(1 + A_b P_b + A_p P_p + A_H^{1/2} P_H^{1/2}) \quad (1)$$

and similarly for the rate of hydrogenation of propene

$$R_p(b) = k_p A_p P_p f(H_2)/(1 + A_b P_b + A_p P_p + A_H^{1/2} P_H^{1/2}), \quad (2)$$

where k, A, and P are the rate constants, adsorption coefficients, and partial pressures, respectively, and the subscripts b and p stand for butadiene and propene, respectively.

$R_b(p)$ is the hydrogenation rate of C_4H_6 with the C_4H_6 pressure kept constant while the C_3H_6 pressure is varied, and inversely for $R_p(b)$.

The competitive hydrogenations are performed under a large and constant hydrogen pressure, P_{H_2} (say 10 kPa), and a low hydrocarbon (HC) pressure (0.2 to 1 kPa). Therefore $f(H_2)$, which is the dependence of the rates with respect to H_2, can be considered as constant under these conditions. This factor is in any case eliminated when only the ratio of the rates is considered.

Thus the ratio of the hydrogenation rates is a linear function of the ratio of the partial pressures:

$$R_b/R_p = (k_b A_b / k_p A_p)(P_b/P_p). \quad (3)$$

From the slope of the plot of R_b/R_p vs P_b/P_p, one determines $k_b A_b / k_p A_p$.

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TABLE 1

Comparison of the Reactivity of Pd and Pt in the Hydrogenation of Butadiene to Butenes at 300 K (from Ref. (*1*))

Samples	Turnover[a] frequency (s^{-1})	Selectivity[b] (%)	Order with respect to	
			H_2	C_4H_6
Pd (111)	0.15	1	1	0
Pd (110)	1.2	1	1	0
Pd/SiO_2	0.2	0.9	1	0
Pt (111)	0.01	0.55	1	0
Pt/SiO_2	0.015	0.6	1	0

[a] $P_{H_2} = 0.7$ kPa, $P_{C_4H_6} = 0.2$ kPa.

[b] Selectivity for hydrogenation of C_4H_6 to butenes.

Moreover, the hydrogenation rate of C_4H_6 in the absence of C_3H_6 is simply expressed by $R_b(0) = k_b f(H_2)$, since the order of the reaction with respect to the hydrocarbon has been found to be zero. Thus, two experiments, namely hydrogenation of butadiene at (I) zero propene pressure, and (II) with a P_p/P_b ratio varied in a large enough range, lead to the determination of A_b/A_p:

$$R_b(0)/R_b(p) = 1 + (A_p/A_b)P_p/P_b. \quad (4)$$

As shown by Moro-oka and Ozaki (*6*), Eq. (4) is an approximation, valid only if the AP products are large with respect to 1 and the hydrogen coverage low. An experimental verification is thus necessary.

If expressions (3) and (4) are obeyed, they lead to the determination of k_b/k_p and of A_b/A_p.

If the same set of experiments is now completed with a propene–butene mixture, a simple combination between k_b/k_p and k_p/k_{be} on the one hand (be stands for butene), and between A_b/A_p and A_p/A_{be} on the other, leads to k_b/k_{be} and A_b/A_{be} for the butadiene–butene pair.

The hydrogenation reactions were studied on the Pt/SiO_2 and Pd/SiO_2 catalysts mentioned in Ref. (*1*); the Pt/SiO_2 sample is the well-known Eurocat catalyst (EuroPt 1) (*7*) and the Pd/SiO_2 was prepared by ionic exchange of $Pd(NH_3)_4(OH)_2$ on Aerosil 200, followed by a calcination in air at 670 K and a reduction in hydrogen at 600 K. The Pd and Pt loadings are respectively 2.05 and 6%.

The metal dispersion, which is similar in both cases (approximately 60%), was measured by small-angle X-ray scattering. All the particles have a diameter between 1.5 and 2.5 nm.

The catalytic reaction was carried out in a flow reactor at 300 K. A Brooks flow gauge allowed the pressures of the reactants to be varied from 0.1 to 100 kPa.

Results for the butadiene–propene pair are shown in Figs. 1 and 2. The linear variation of R_b/R_p versus P_b/P_p observed in Fig. 1 on (a) palladium and (b) platinum, shows that Eq. (3) is well verified; this confirms that the assumptions on which these kinetics are based are sound.

A linear variation of $R_b(0)/R_b(p)$ vs P_p/P_b is also observed in Fig. 2 and confirms the validity of Eq. (4).

The same linear relations were found for the butene–propene pair and are shown in Figs. 3 and 4. The numerical values derived from these plots are shown in Table 2 and the final parameters for the butadiene–butene hydrogenation, inferred from the two sets of measurements are given in Table 3.

In the first two rows of Tables 2 and 3, the values measured with Pd/SiO_2 catalyst at the early stage of the reaction and those measured after 3 h, when the rate is stabilized, are compared. The ratio of the rate constants does not vary but the ratio of the adsorption constants undergoes a fourfold increase in favor of the butadiene, when a stable activity is reached. This phenomenon is perfectly in line with the observed variation of selectivity for the formation of butenes which increases from 0.6 to 0.9, while the rate of conversion decreases by a factor of 4. The presence of carbonaceous species and perhaps of some interstitial carbon is probably the reason for this variation

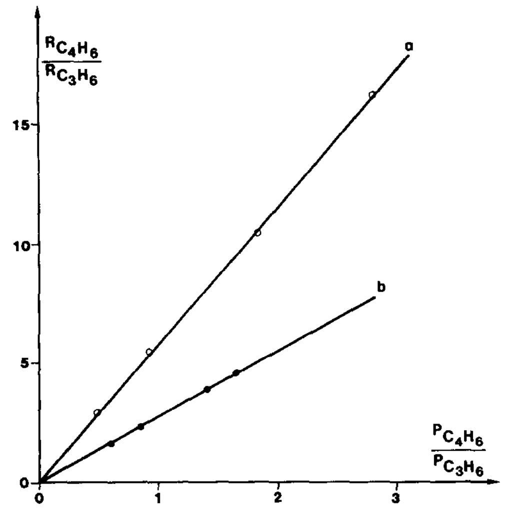

FIG. 1. Variation of the ratio of hydrogenation rates with the ratio of the pressures for the butadiene–propene pair on (a) Pd/SiO_2, (b) Pt/SiO_2.

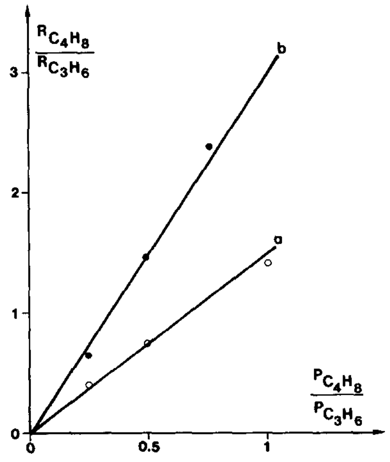

FIG. 3. Variation of the hydrogenation rates versus the ratio of the partial pressures for the butene–propene mixture on (a) Pd/SiO_2, (b) Pt/SiO_2.

of adsorption constant (probably a decrease in adsorption constant of the alkene).

Indeed, from an Auger electron spectroscopy experiment performed on a single crystal after the reaction (*1*), it was concluded that approximately one monolayer of carbon remains on the surface after evacuation. Also, the formation of bulk carbide has been observed by Stachurski (*8*) by X-ray diffraction, when a similar sample was kept at 373 K under acetylene.

This phenomenon was also observed at

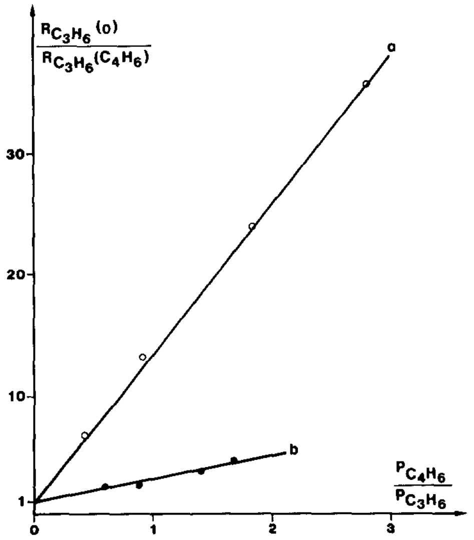

FIG. 2. Experimental verification of the validity of Eq. (4) in the case of the butadiene–propene mixture. (a) Pd/SiO_2, (b) Pt/SiO_2.

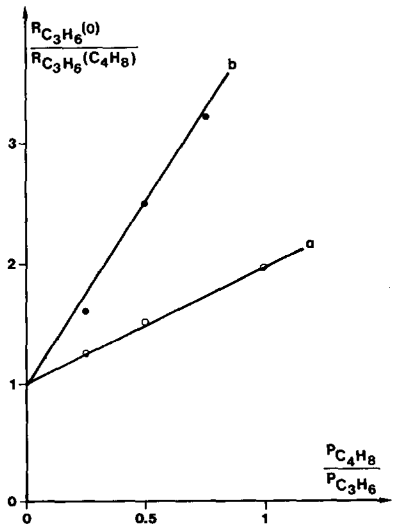

FIG. 4. Verification of the validity of Eq. (4) for the butene–propene hydrogenation on (a) Pd/SiO_2 and (b) Pt/SiO_2.

TABLE 2

Competitive Hydrogenation of Butadiene–Propene and Butene–Propene on Silica-Supported Pd and Pt Catalysts

Samples	A_b/A_p	A_{be}/A_p	k_b/k_p	k_{be}/k_p	R_b/R_p	R_{be}/R_p
Pd/SiO$_2$						
Fresh	3.5	1.2	0.4	1.58	1.4	1.9
Stabilized	12	1	0.5	1.5	5.8	1.5
Pt/SiO$_2$	1.9	2	1.2	1.5	2.2	3

TABLE 3

Competitive Hydrogenation of Butadiene–Butene

Samples	A_b/A_{be}	k_b/k_{be}	R_b/R_{be}
Pd/SiO$_2$			
Fresh	2.9	0.25	0.75
Stabilized	12	0.33	3.9
Pt/SiO$_2$	0.95	0.8	0.75

the same temperature under C_2H_4 (*9*). We have checked on our samples that after a preliminary conversion of acetylene at 300 K, the metal is deactivated and fully selective for the conversion of butadiene to butenes, even at the early stage of the reaction.

Comparing rows 2 and 3 of Table 3, one notes that the ratio of the adsorption constants for butadiene and butene is 12 times larger on "stabilized" palladium than on platinum; even with a ratio of the rate constants slightly larger for Pt, we have the confirmation that the reason for the *selectivity of palladium* (after stabilization of the catalyst) can be attributed unambiguously to its *capacity of adsorbing a diene more strongly than an alkene molecule.*

This also confirms the validity of the rake scheme first postulated by Bond and coworkers (*10*).

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