

## ACTIVITY AND SELECTIVITY OF PALLADIUM CATALYSTS IN HYDROGENATION OF ISOMERIC *n*-OCTINES\*

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The activity and selectivity of palladium catalysts in hydrogenation of isomeric *n*-octines has been examined. Both the activity and selectivity was dependent on the triple bond position in the particular *n*-octine, on the polarity of the solvent and on the carrier. Similar to the nickel catalyst, the hydrogenation over a palladium catalyst has been demonstrated to obey a two-step mechanism.

The fair selectivity of nickel catalysts in hydrogenations of a triple bond to a double bond has been shown in an earlier paper<sup>1</sup>. The occurrence of a higher percentage of *n*-octane (10–20%) at the beginning of hydrogenations (particularly in the case of 1-octine) might be ascribed to the adaptation (the so called forming) of the surface of the nickel catalyst due to sorption of *n*-octines and not to involvement of an one-step hydrogenation mechanism. In hydrogenations of alkynes, palladium has been claimed to exhibit a higher selectivity than nickel<sup>2–5</sup>; also in this case, both the one-step and the two-step mechanism is admitted for the formation of the corresponding alkane.

In the present paper, we have examined the hydrogenation of isomeric *n*-octines in a both polar and nonpolar solvent over palladium applied to various carriers, with respect to the formation of *n*-octenes and *n*-octane. Hydrogenations were performed at 30°C under atmospheric pressure. Attention has been also paid to changes in desorption characteristics of the bound hydrogen.

### EXPERIMENTAL

*Materials.* For solvents, technical gases, and purity of test substances see the earlier paper<sup>1</sup>.

*Catalysts.* Three palladium catalysts have been used differing in the carrier and the content of the active metal, namely, Pd on kieselguhr (0.5% Pd), Pd on active charcoal (4% Pd), and Pd on silica (4.8% Pd) (prepared on a laboratory scale according to the patent literature<sup>6</sup>).

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*Composition of hydrogenation products* in the course of the experiment has been determined by chromatography<sup>7</sup> with the use of poly(ethylene glycol) 600 on Chezasorb II as the stationary phase. The hydrogen bound to catalysts has been determined in the same manner as in the earlier paper<sup>1</sup>.

*Apparatus and procedure.* The hydrogenation apparatus has been described in detail earlier<sup>8</sup>. The exactly weighed amount of the catalyst was flushed into the hydrogenation vessel by means of the solvent (30 ml in each experiment) and air was replaced by nitrogen. Nitrogen was then replaced by hydrogen and the catalyst was activated by shaking at 30°C for 20 min. The diffusion effects were shown to be excluded with the use of 0.3–0.5 g of the catalyst and 450 revolutions per min. The hydrogenations were always performed with 5 mmol of the test substance at 30°C and under atmospheric pressure. Hydrogenations of the triple bond proved to be reactions of the pseudozero order up to 90% conversions. The activity was defined as ml (H<sub>2</sub>)/min g (catalyst). The ability of hydrogen bound by the catalyst (palladium) to hydrogenate the triple bonds was tested with the use of silica as carrier, *i.e.*, on the Pd/SiO<sub>2</sub> catalyst. In each experiment, there was always used 0.6 g of the catalyst. Procedure and withdrawal of samples for the chromatographic determination of the content of reaction mixtures was the same as in an earlier paper<sup>1</sup>.

## RESULTS AND DISCUSSION

The course of hydrogenations of *n*-octines over the palladium catalysts was the same as over the nickel catalysts<sup>9</sup>. For the activity of the particular types of the palladium catalyst see Table I. The values given represent average of at least two measurements differing less than by 8%. It may be seen from Table I that the activity value depends on the structure of the particular octine, on the chemical nature of the solvent, and the carrier (when the concentration of palladium is the same). It is of interest that the triple bond of the remaining isomeric *n*-octines is hydrogenated over palladium at a higher rate than that of 1-octine, in contrast to the nickel catalyst<sup>9</sup>.

Table II shows the selectivity values expressed (by weight) as the ratio of the result-

TABLE I

Dependence of the Palladium Catalyst Activity [in ml H<sub>2</sub> per min g (catalyst)] in Hydrogenations of *n*-Octines on Solvents and Carriers

Test substance	Pd/kieselguhr		Pd/silica gel		Pd/act. charcoal
	absolute ethanol	<i>n</i> -heptane	absolute ethanol	<i>n</i> -heptane	<i>n</i> -heptane
1-Octine	21.5	28.0	14.6	27.9	116.0
2-Octine	19.3	36.6	46.9	73.7	37.2
3-Octine	22.3	72.7	101.5	117.0	146.5
4-Octine	46.7	80.7	94.5	118.5	124.3

TABLE II

Dependence of the Palladium Catalyst Selectivity  $S$  in the Triple Bond Hydrogenation of *n*-Octines on Solvents and Carriers;  $S = \text{mol of } n\text{-octane}/(\text{mol of } n\text{-octane} + \text{mol of } n\text{-octenes})$

Test substance	Pd/kieselguhr		Pd/silica gel		Pd/act. charcoal
	absolute ethanol	<i>n</i> -heptane	absolute ethanol	<i>n</i> -heptane	<i>n</i> -heptane
1-Octine	0.82	0.72	0.96	0.79	0.75
2-Octine	0.98	0.97	0.98	0.96	0.62
3-Octine	0.97	0.95	0.98	0.93	0.77
4-Octine	0.98	0.98	0.98	0.98	0.62

ing olefins to the sum of products. The selectivity value refers to the uptake of 1 mol  $\text{H}_2$  per 1 mol of the test substance. It has been confirmed that palladium catalysts exhibit a higher selectivity than the nickel catalysts on the same carriers<sup>9</sup>, except for the hydrogenation of 1-octine. In the case of the Pd/active charcoal catalyst, the selectivity value was the same as with the Ni/kieselguhr catalyst.

It has been also found that the solvent polarity may affect the occurrence of isomerisation reactions. Thus *e.g.*, the hydrogenation of 1-octine on the Pd/kieselguhr catalyst in absolute ethanol was accompanied by migration of the double bond from position 1 into position 2. With the uptake of 1.25 mol  $\text{H}_2$  per 1 mol of 1-octine,

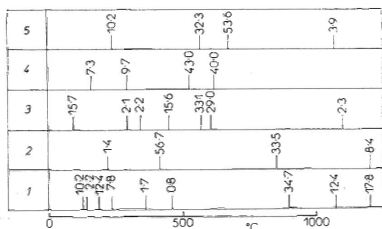


FIG. 1

#### Characteristics of Hydrogen Desorption from Palladium Catalysts

1 Pd/C (absolute ethanol as solvent), 2 Pd/C (*n*-heptane), 3 Pd/SiO<sub>2</sub> (absolute ethanol), 4 Pd/SiO<sub>2</sub> (*n*-heptane), 5 Pd/SiO<sub>2</sub> (pre-shaken with 1-octine; *n*-heptane as solvent).

the composition of the hydrogenation mixture was 14.8% of 1-octene, 23.1% of *cis*-2-octene, 13.8% of *trans*-2-octene, and 48.3% of *n*-octane. On the same catalyst but when *n*-heptane was used as solvent, the hydrogenation of 1-octene afforded a mixture of 1-octene and *n*-octane.

Owing to the low content of palladium in the Pd/kieselguhr catalyst, the present apparatus and procedure<sup>10</sup> do not allow to determine the amount of hydrogen due to the thermal desorption. With the remaining two catalysts, the following values were found in *n*-heptane (absolute ethanol) as solvent: 3.6 ml (8.5 ml) H<sub>2</sub> per 1 g of the Pd/SiO<sub>2</sub> catalyst and 17.3 ml (20.8 ml) H<sub>2</sub> per 1 g of the Pd/C catalyst. Fig. 1 shows the desorption characteristics of hydrogen from palladium catalysts; the data refer to percentage from the total amount of hydrogen which is desorbed at the temperature given. With the use of the same type of palladium catalysts and a polar solvent, the hydrogen is bound in more energetically different "forms" than in the case of a nonpolar solvent, as indicated by the number of temperature maxima in diagrams (Fig. 1). This finding is in a qualitative accordance with the earlier observations on the effect of solvents on desorption characteristics of hydrogen from Raney nickel<sup>11</sup>. When the same solvent is used, the desorption characteristics of hydrogen from palladium may depend on the nature of the carrier, cf. Fig. 1.

Similar to the earlier work<sup>1</sup>, we have also paid attention to the ability of the palladium-sorbed hydrogen to react in the absence of the molecular hydrogen with the test substances in *n*-heptane as solvent in the fluid phase. We have observed that the hydrogenation occurs only in that case when the palladium-catalyst surface had been previously saturated with hydrogen. With 1-octene as test substance, there was obtained about 10% of *n*-octane; the remaining isomeric *n*-octenes afforded only 3–4% of *n*-octane. Similar to the experiments with the nickel catalyst<sup>1</sup>, the whole amount of *n*-octane was formed immediately after the addition of the test substances into the hydrogenation apparatus and did not increase by shaking the test substance with the catalyst for one hour. Fig. 1 also shows the desorption characteristics of the Pd/SiO<sub>2</sub> catalyst pre-shaken for 60 min with 1-octene. Comparison with the original catalyst sample shows the similarity of both desorption characteristics except for a somewhat higher desorption temperature in the 600°C region in the case of the pre-shaken sample. In the cases stated, the predominant portion of hydrogen was desorbed at temperatures between 500 and 600°C while the "forms" of the less strongly bound hydrogen (desorbing up to 300°C) were less abundant in contrast to hydrogenations over the nickel catalysts. It has been observed earlier<sup>12</sup> in the case of the Ni/kieselguhr catalyst that any decrease of the bound hydrogen "form" desorbing at 175°C leads to a directly proportional decrease of activity in hydrogenations of alkynes to alkanes. The more difficult hydrogenation to *n*-octane over the palladium catalyst (than over the nickel catalysts) might be ascribed to these effects. It has been unequivocally established that also in the case of the palladium catalyst the *n*-octane is formed in the first moments of the contact between the unsaturated test substance

and the active component (catalyst) at the stage of the so called "forming" of the catalyst surface. Consequently, the one-step mechanism may be excluded in the subsequent course of the triple bond hydrogenation.

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