ON HYDROGENATION AND DEHYDROGENATION CATALYSTS. XI.*
INFLUENCE OF THE DEGREE OF REDUCTION ON THE ACTIVITY AND SELECTIVITY OF NICKEL CATALYSTS IN HYDROGENATIONS OF ALKINES

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The influence of the degree of reduction on the activity and selectivity of the nickel carrier catalyst in hydrogenations of octines was studied. The maximum activity was observed at the reduction degree of $\alpha = 0.6$. The degree of reduction exerts no influence on the selectivity in hydrogenations of the triple bond to the double bond. On the other hand, the rate and selectivity of hydrogenations is affected by the structure of octines.

The properties of metallic hydrogenation catalysts depend on the preparative procedure, especially, on the prereduction (temperature, time). As shown in an earlier paper[1], the most active nickel catalysts in hydrogenations of a double bond, a carbonyl group, and a nitro group in the liquid phase in a polar medium are those which had been prereduced to the reduction degree of about $\alpha = 0.6$. Moreover, it has been observed that desorption of hydrogen from the catalyst depends on the reduction degree and that there may exist a relation between the activity and the amount of hydrogen which is desorbed at a certain temperature[2,3].

In the present paper, we have investigated the influence of the degree of reduction on the activity and selectivity of the nickel catalyst in hydrogenations of the triple bond to the double bond. Hydrogenations were performed at the atmospheric pressure and 30°C in nonpolar (n-heptane) and polar (absolute ethanol) media. Isomeric octines were used as test substances. The influence of passivation and reactivation of the nickel catalyst on the activity and selectivity was also studied. The desorption characteristics of the bound hydrogen were determined in all samples.

EXPERIMENTAL

Materials. The reagents used in analytical determinations were of the A. R. or *puriss.* grade. The 1-, 2-, 3-, and 4-octines were purchased from Koch-Light Laboratories and were redistilled before use. The following solvents were used: n-heptane (*puriss.*) was dried and rectified on a 20 TP

column; the purest ethanol (ČSN 66 0825) was absolutized as usual. The purity of all substances and solvents was checked by chromatography. Hydrogen and nitrogen were catalytically purified (removal of a small amount of oxygen) and dried over molecular sieves (Calsit 5).

Catalyst. The nickel catalyst was obtained by heating basic nickel carbonate on kieselguhr at $400-420°C$ in the stream of nitrogen. Composition of the catalyst: 54·6% NiO, 35·2% of kieselguhr, about 3% of graphite, and 7·2% of water (moisture). The catalyst was reduced at $360-380°C$. The different degree of reduction was attained by the use of different times (from 15 min to 24 h). When the reduction was finished, the catalyst was cooled to room temperature and added under hydrogen into the solvent. The catalyst was stored in a closed vessel in the atmosphere of hydrogen to prevent gradual passivation by the air oxygen[3]. Passivation of the nickel catalyst of the reduction degree $\alpha = 0.41$ was effected by a controlled oxidation of the sorbed hydrogen with oxygen[4]. The reactivation was effected with hydrogen at $240-250°C$ (the time of heating at this temperature was varied from 20 min to 8 h). The reactivated catalyst was stored under the solvent and in the atmosphere of hydrogen as above. The degree of reduction α (*i.e.*, the ratio of the nickel metal to the total nickel content in the catalyst) and the amount of hydrogen sorbed by the particular samples of the nickel catalyst was determined by procedures and in apparatus reported in the earlier paper[4].

Composition of the reaction mixture in the course of the hydrogenation of octines in excess n-heptane or absolute ethanol was determined chromatographically on a Chrom II apparatus (Laboratory Apparatus, Prague) with flame ionisation detection; capillary column, 50 m length, 0·1 mm diameter, moistened with Tridox. Conditions: temperature 100°C, nitrogen pressure 0·3 kp/cm^2, hydrogen flow 70 ml/min, one-microliter samples[5].

Apparatus and procedure. The activity and selectivity was determined in the earlier described apparatus[6]. The hydrogenation was performed at 30°C under kinetic conditions which were determined by experiments. The amount of the test substance (substrate) was 5 mmol and the amount of the solvent 30 ml. The test substances were added into the hydrogenation vessel in one portion. Hydrogenation of the triple bond occured at a constant rate under the conditions given. When a certain amount of hydrogen was taken up (usually $30-50$ ml of hydrogen), the shaking was interrupred, a sample was withdrawn by means of a hypodermic syringe and sealed into an ampoule. When the hydrogenation was finished, the composition of samples was determined by chromatography. The activity was expressed in ml of H_2 per min g of the total nickel. The amount of nickel was determined electroanalytically after accomplishment of the hydrogenation[6].

RESULTS AND DISCUSSION

The course of hydrogenations of the isomeric octines was different. Thus with 1-octine when about 1 mol of H_2 was taken up per 1 mol of 1-octine, the hydrogenation of the double bond occured at a higher rate up to the consumption of 1·5 mol of H_2 per 1 mol of 1-octine and then the rate rapidly decreased (Fig. 1). In contrast to 1-octine, the hydrogenation of 2-, 3-, and 4-octine practically stopped after conversion of the triple to the double bond (Figs 1—3). These observations are in accordance with those of Sokolskaja and coworkers[7] which investigated hydrogenation of higher acetylenes over Raney nickel in polar media and also in the presence of an electrolyte.

The influence of the degree of reduction α on the activity and selectivity of the
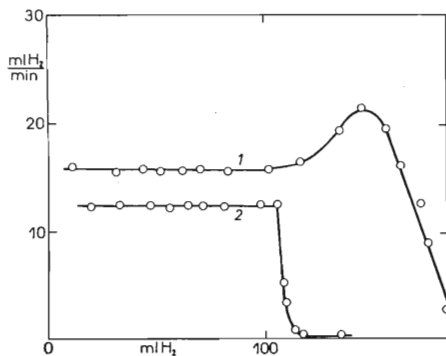
Fig. 1

Dependence of the Reaction Rate on the Total Hydrogen Uptake in Hydrogenations of 1-Octine *1* and 3-Octine *2*
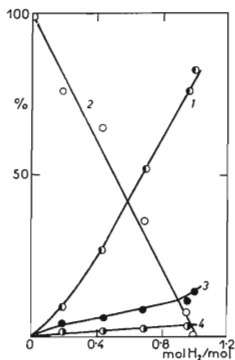

Fig. 2

Dependence of the Composition (in % by weight) of the Reaction Mixture on the Uptake of Hydrogen in the Hydrogenation of 3-Octine. ○ 3-Octine, ◑ *cis*-3-octene, ◐ *trans*-3-octene, ● octane.
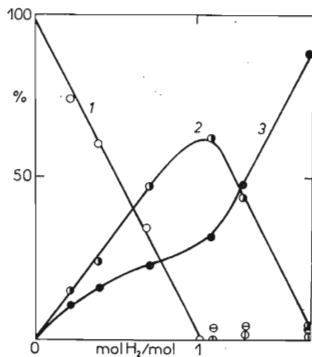

Fig. 3

Dependence of the Composition (in % by weight) of the Reaction Mixture on the Uptake of Hydrogen in the Hydrogenation of 1-Octine

○ 1-Octine, ◑ 1-octene, ● octane, ⊖ *trans*-2-octene, ◎ *cis*-2-octene.
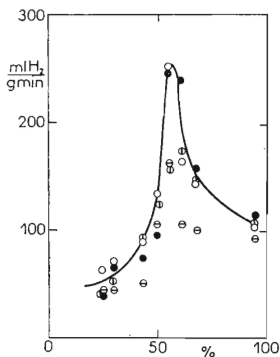
FIG. 4

Dependence of the Activity on the Degree of Reduction of the Nickel Catalyst
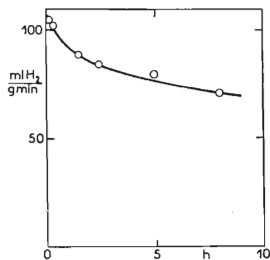
○ 1-Octine, ⊖ 2-octine, ● 3-octine, ⊕ 4-octine

FIG. 5

Dependence of the Activity of the Nickel Catalyst on the Time of Reactivation in the Hydrogenation of 1-Octine

nickel catalyst was determined in the range $\alpha = 0.23 - 0.95$ (Fig. 4). It may be seen that the degree of reduction α exerts a marked influence on the activity of the nickel catalyst. The highest activity in hydrogenations of the triple bond of all isomeric octines is shown by catalyst samples of a relatively narrow range of the degree of reduction ($\alpha = 0.5 - 0.6$). Similar results were obtained with the use of absolute ethanol as solvent. There has been also observed that the highest activity in hydrogenations of acetone, nitrobenzene, and dibutyl maleate in polar media is shown by nickel catalysts possessing the degree of reduction α equal to about 0·6. The ob-

TABLE I

Selectivity S of the Nickel Catalyst in Hydrogenations of Isomeric Octines

Solvent	1-Octine	2-Octine	3-Octine	4-Octine
n-Heptane	0·68	0·77	0·78	0·78
Absolute ethanol	0·69	0·92	0·92	0·91

served dependence thus appears of a general validity for this type of catalyst. The activity of catalysts of the degree of reduction α = 0·6 was somewhat dependent on the structure of the octine. Thus the activity was somewhat higher with octines the triple bond of which was situated at an odd carbon atom than with those possessing the triple bond at an even carbon atom.

Hydrogenations of octines afforded the corresponding octene as the principal product. The *cis*-isomer predominated in hydrogenations of 2-octine and 4-octine while the *trans*-isomer was the predominant product in the hydrogenation of 3-octine in accordance with results reported in the earlier paper[7]. Whenever a migration of the double bond occurred (hydrogenation of 1-octine and 2-octine), then the double bond shifted to the middle part of the chain. In view of the relatively low content of isomeric alkenes, the selectivity (S) was expressed as

$$S = \sum \% \text{ (by weight) of alkenes} / \sum \% \text{ (by weight) of alkenes + alkane}$$

under the uptake of 1 mol of H_2 per 1 mol of the alkine. It has been found that the selectivity does not depend on the reduction degree α of the catalyst. It depends merely on the structure of the octine or, to a lesser extent, on the solvent. The selectivity values are shown in Table I.

In the preparation of an industrial nickel catalyst, the problems of passivation, reactivation, and the required period of time are of great importance. The reactivation was performed in accordance with the earlier paper[4] in a stream of hydrogen at the optimum temperature of 240−250°C. As it may be seen from Fig. 5, the original activity is restored after the reactivation time of max. 1 h. When the reactivation is longer, a slight decrease of activity is observed. After 8 hours of reactivation, this decrease was about 30%. Concerning the selectivity, identical values are shown by the reactivated and the freshly reduced catalyst.
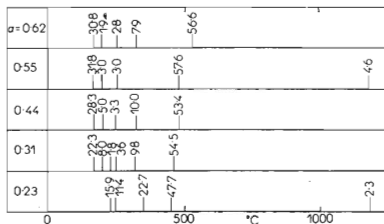

FIG. 6

Characteristics of Hydrogen Desorption from the Nickel Catalyst

Fig. 6 shows that portion (in %) of the total hydrogen which is desorbed from the catalyst moistened with n-heptane at temperature maxima given. Regardless the reduction degree α, the amount of the desorbed hydrogen varied in the range of $5-6$ ml of H_2 per 1 gram of the catalyst. Similar to the earlier paper[4], there may be observed some dependence between the desorption characteristics of hydrogen and the degree of reduction of the catalyst. There is some correlation between the activity of samples of various reduction degrees and the amount of hydrogen which is desorbed at max. 200°C. A linear dependence of the activity on the amount of the desorbed hydrogen cannot be, however, observed.

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