ON HYDROGENATION AND DEHYDROGENATION CATALYSTS. XIII.*
HYDROGENATION OF OCTINES WITH HYDROGEN SORBED ON A NICKEL CATALYST

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Investigations have been performed on the hydrogenation of octines with hydrogen sorbed on a nonsulfidated or sulfidated surface of a nickel catalyst in the absence of molecular hydrogen. Desorption characteristics of the hydrogen bound to the catalyst have been determined. It has been demonstrated that octane is formed at the very beginning of the contact between the test substance and the surface of the nickel catalyst. A mechanism has been proposed and discussed.

In earlier papers[1,2] of this Series observations have been mentioned on the formation of a considerable amount (about 20—30% by weight) of octane immediately after the addition of octines into the hydrogenation vessel at the very beginning of the hydrogenation. The content of octane in the reaction mixture did not change in the subsequent stages of the hydrogenation of the triple bond. As shown by chromatographic analysis of samples withdrawn during the hydrogenation, the uptake of hydrogen for the hydrogenation of the triple bond (read on burettes) did not correspond to the amount required by the theory for the products. It is known from the literature that the hydrogen which is sorbed by metallic catalysts, is able to react to a lesser or greater extent with unsaturated organic compounds. This observation has been used by some authors[3,4] to determine the amount of hydrogen which is sorbed by hydrogenation catalysts. Such a reaction of the hydrogen bound to the surface of the catalyst may be also expected in the case of octines.

In the present paper, we wish to report measurements of the composition of the reaction mixture during the contact of octines with the nickel catalyst in the absence of the molecular hydrogen in the fluid phase. The experiments were performed at 30°C in the medium of n-heptane. The nickel catalyst was reactivated to a different reduction degree α or poisoned (sulfidated) with thiophene. Desorption characteristics of hydrogen were also determined after shaking the nickel catalyst (nonpoisoned or poisoned) with various test substances.

EXPERIMENTAL

Materials. The test substances were of the same quality as stated in the earlier papers[1,2]. Calcination and reduction of the catalyst[2] at 380—420°C afforded samples of the following re-

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duction degrees α: 0·34, 0·50, 0·58, and 0·78. All samples of the catalyst were stored in the passivated state. The passivation was performed by a controlled oxidation of the sorbed hydrogen. Prior to the experiments, the catalyst was freshly reactivated for one hour in the stream of hydrogen at 240—250°C and then moistened with n-heptane or partially poisoned (sulfidated) by the addition into a solution of thiophene in n-heptane.

Analytical methods. Determinations of the reduction degree α of the catalyst, of the amount of sulfur bound to the surface of the catalyst, of the hydrogen amount bound by particular samples of the catalyst, of the desorption characteristics of hydrogen, and of the composition of the reaction mixture were performed in the same manner as mentioned in earlier papers[1,2].

Apparatus and procedures. The experiments were performed in an apparatus for hydrogenation under atmospheric pressure as described in ref.[5]. Exactly 1·0 g of the reactivated catalyst was added in the stream of hydrogen into n-heptane or into a solution of thiophene in n-heptane

TABLE I

Composition (in % by weight) of Reaction Mixtures Obtained on Shaking the Isomeric Octines or 1-Octene with Nickel Catalysts of Various Reduction Degrees α for 60 min

Experiment	Components	$\alpha = 0.34$	$\alpha = 0.50$	$\alpha = 0.78$
1	n-octane	17·9	25·0	19·1
	1-octene	0	13·8	10·6
	1-octine	82·1	61·2	70·3
2	n-octane	15·5	11·1	8·6
	cis-2-octene	0	11·5	3·4
	trans-2-octene	0	0	2·3
	trans-3-octene	0	0	2·9
	2-octine	84·4	77·4	82·8
3	n-octane	14·9	21·4	18·8
	trans-3-octene	0	12·0	16·6
	3-octine	8·51	66·6	64·6
4	n-octane	8·3	19·8	16·1
	cis-4-octene	0	16·6	21·2
	4-octine	91·7	64·6	62·7
5	n-octane	12·7	11·8	11·6
	cis-2-octene	26·3	22·9	43·6
	trans-2-octene	14·3	14·0	29·8
	1-octene	46·3	51·3	15·0
6	n-octane	—	0	—
	1-octene	—	9·2	—
	1-octine	—	90·8	—
7	n-octane	—	0	—
	trans-3-octene	—	5·8	—
	3-octine	—	94·2	—

(of the known sulfur content). The catalyst was then ground and transferred into the hydrogenation vessel. Total amount of the solvent (n-heptane[2] in all experiments), 30 ml. The determination was performed at 30°C and under atmospheric pressure. The apparatus was flushed with hydrogen for 20 min. The catalyst was shaken for about 5 min, the hydrogen was replaced by nitrogen (30 min), and the shaking was then continued. In experiments 6 and 7, the apparatus was flushed with nitrogen only. The hydrogenation vessel was then charged with 5 mmol of the test substance (an octine isomer or 1-octene) and the content of the vessel was vigorously shaken (450—500 min^{-1}). The measurement lasted 1 h. During this time, 6 samples were withdrawn from the vessel for the chromatographic analysis by means of a hypodermic syringe (after 1, 3, 10, 20, 40, and 60 min of shaking). This measurement was then followed by determination of desorption characteristics of the hydrogen from particular samples of the catalyst. The reduction degree α of the catalyst was 0·34, 0·50, and 0·78. The sulfidation was performed with the sample possessing the reduction degree $\alpha = 0·58$; content of sulfur, 4·0 mg S/g of the catalyst and 9·75 mg S/g of the catalyst.

Hydrogen balance. Prior to the hydrogenation the catalyst was shaken in an inert atmosphere with 5 mmol of the test substance (an octine isomer or 1-octene). Total seven samples were withdrawn. The first sample was withdrawn after shaking in the absence of gaseous hydrogen. The following samples were taken in the course of hydrogenation at the same intervals as stated in an earlier paper[1]. Prior to the hydrogenation, the nitrogen was removed from the hydrogenation vessel with 175 ml of hydrogen.

RESULTS AND DISCUSSION

Composition of the reaction mixture obtained by shaking the nickel catalyst with the corresponding octine in the absence of molecular hydrogen is shown in Table I. This composition was attained practically in all cases after 1 min of shaking. It was thus confirmed that the hydrogenation products of the sorbed hydrogen arose in the first moments of the contact between the unsaturated test substance and the surface of the catalyst, *i.e.*, at the stage of the so called forming of the catalyst surface[4]. As it may be seen from Table I, the final composition of the reaction mixture depends somewhat on the reduction degree α of the catalyst. Thus *e.g.* (see experiment 2) when α is lower than 0·50, no olefin is formed; on the other hand, both the *cis*- and *trans*-2-octene is formed when α is higher than 0·50. Nickel catalysts of a higher reduction degree α may cause isomerisations as it may be seen from experiment 5 which was performed with the use of 1-octene as the test substance. Also in this case the final composition did not considerably differ from that shown after 1 min of contact.

Table II shows composition of the reaction mixtures obtained by shaking the test substance with a poisoned (sulfidated) catalyst. The higher is the degree of poisoning, the lower is the ability of the nickel catalyst to effect hydrogenations by means of the sorbed hydrogen. When the catalyst surface is fully sulfidated[2] (sulfur content, 9·75 mg S/g of the catalyst) no hydrogenation occurs with the sorbed hydrogen in spite of a certain activity of the catalyst in hydrogenations with molecular hydrogen[2].

Table III shows the uptake of molecular hydrogen in hydrogenations of 5 mmol of 3-octine pretreated with the sorbed hydrogen. Similar values were obtained in

TABLE II

Composition (in % by weight) of Reaction Mixtures Obtained on Shaking (for 60 min) the Isomeric Octines with Nonsulfidated and Sulfidated Nickel Catalysts (Reduction Degree $\alpha = 0.58$)

Experiment	Components	Nonsulfidated catalyst	Sulfidated catalyst	
			4·0 mg S/g cat.	9·75 mg S/g cat.
8	n-octane	20·5	7·0	0
	1-octene	13·3	5·6	0
	1-octine	66·2	87·4	100
9	n-octane	17·2	12·9	0
	cis-2-octene	12·0	6·4	0
	2-octine	70·8	80·7	100
10	n-octane	21·9	8·8	0
	trans-3-octene	14·3	5·9	0
	3-octine	64·8	85·3	100
11	n-octane	11·7	5·1	0
	cis-4-octene	7·0	4·2	0
	4-octine	81·3	90·7	100

TABLE III

Hydrogen Uptake (mmol) in Hydrogenations of 3-Octine (5 mmol) after a Previous Shaking with the Catalyst in an Inert Atmosphere

Calculated[a]	Molecular hydrogen uptake	Total hydrogen uptake
1·04	—	1·04[b]
1·30	0·35	1·39
2·51	1·48	2·52
3·50	2·50	3·54
5·80	4·50	5·54
5·56	4·50	5·54
5·76	4·70	5·74

[a] The calculated amount of hydrogen is based on composition of the reaction mixture after the hydrogenation; [b] the sample of the reaction mixture was withdrawn prior to the hydrogenation after shaking 3-octine with the catalyst in an inert atmosphere.

hydrogenations of the remaining isomeric octines. A portion of the test substance is thus hydrogenated with the sorbed hydrogen; consequently, the uptake of the molecular hydrogen is lower (read on burettes). The overall uptake of hydrogen corresponds to the theoretical value.

In the above experiments, we have also determined the amount of the hydrogen bound in samples of the catalyst and changes in desorption characteristics. Both the sulfidated and nonsulfidated samples contained $5-6$ ml H_2/g of the catalyst. After shaking in an inert atmosphere with the corresponding test substances, the catalyst samples contained unexpectedly a higher amount of the bound hydrogen in spite of the presence of octane and octene in the reaction mixture. This amount was $10-16$ ml H_2/g of the catalyst in the case of shaking with 1-octene and $20-35$ ml H_2/g of the catalyst with isomeric octines. On the other hand, catalyst samples from experiments 6 and 7 (Table I; the surface of the catalyst was not previously saturated with hydrogen in these experiments) contained only a half (or even less) of the hydrogen amount given above. The changes in desorption characteristics (temperature maxima; the % values relate to the total amount of the desorbed hydrogen) of hydrogen after shaking of the original nonsulfidated (*1*) or sulfidated (*7*) nickel catalyst
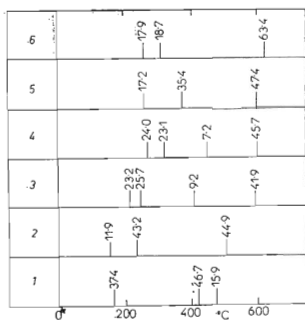

FIG. 1

Desorption Characteristics of Hydrogen after Shaking of the Nickel Catalyst with Various Test Substances

1 The original catalyst; reduction degree α = 0·58, *2* 1-octene, *3* 1-octine, *4* 2-octine, *5* 3-octine, *6* 4-octine.
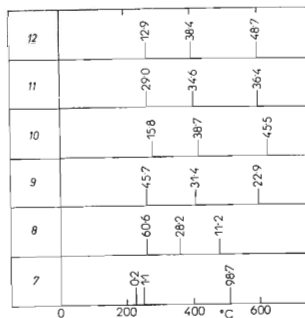

FIG. 2

Desorption Characteristics of Hydrogen after Shaking of the Sulfidated (Poisoned) Nickel Catalyst with Various Test Substances

7 The poisoned catalyst; reduction degree α = 0·58; sulfur content 4·0 mg S/g of the catalyst, *8* 1-octene, *9* 1-octine, *10* 2-octine, *11* 3-octine, *12* 4-octine.

with 1-octene or with one of the four isomeric octines are shown in Fig. 1 and 2. Noteworthy is the considerable change in desorption characteristics of hydrogen in comparison with the original catalyst samples *1* and *7*; this change is due to sorption of the corresponding test substance during the so called forming process[4] of the catalyst surface. Both types (*1* and *7*) of the catalyst show a very similar course of desorption curves when the same test substance is used. The same temperature (270 to 280°C) of the first maximum with samples 4−6 and 10−12 is characteristic. Some differences have been observed with catalyst samples shaken with 1-octine. As mentioned in earlier papers[1,2], the course of hydrogenation of 1-octine also differs from that of the remaining isomeric octines.

The assumption that the test substance reacts only with the chemisorbed hydrogen cannot explain the formation of octane and octenes. It has been observed that the amount of hydrogen corresponding to hydrogenation products of octines (octane and octenes) is after shaking with the catalyst many times higher than in the original catalyst sample. This finding might be due to the reversible adsorption of an additional hydrogen to the surface of the catalyst (*e.g.*, during the saturation of the catalyst surface with gaseous hydrogen). Only the chemisorbed or "dissolved" hydrogen is most probably determined by thermodesorption. The desorption curves are therefore characteristic for different preparations of the nickel catalyst[6]. The removal of the solvent prior to the thermodesorption measurement[7] is obviously accompanied by desorption of the reversibly sorbed hydrogen into the stream of the inert gas. In the hydrogenation vessel however, the catalyst is protected from the inert gas by a layer of the solvent; desorption of the reversibly sorbed hydrogen from the surface of the catalyst is therefore farly less probable in this case. The formation of octane from the octines or from 1-octene should depend on the ability of the catalyst surface to the activation of the hydrogen under the applied reaction conditions. The higher is the degree of poisoning, the lower is the activation. It has been demonstrated by experiments that the energy of the hydrogen–metal bond (as judged from temperature maxima) and the amount of hydrogen bound to the surface of the catalyst are highly influenced by sorption of the test substances. In future investigations on relations between the activity and "forms" of the hydrogen bound to the hydrogenation catalyst, the sorption of substrates must be therefore taken into account. Concerning the mechanism of the triple bond hydrogenation, the earlier observations[1,2] have been confirmed, namely, that octane is obtained during the so called "forming process" of the catalyst surface[4] and that the true hydrogenation of the triple bond proceeds in two steps.

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