# ON HYDROGENATION AND DEHYDROGENATION CATALYSTS. XII.*
## POISONING OF THE NICKEL CARRIER CATALYST IN HYDROGENATIONS OF ALKINES

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The influence of the degree of sulfidation (poisoning) at the surface of a nickel catalyst by sulfur compounds was investigated. When the amount of sulfur bound to the catalyst increased, the activity monotonously decreased, but the selectivity remained unchanged. It may be therefore assumed that hydrogenation of both the triple and double bond occurs at the same active center and that the selectivity depends on the ratio of reaction rates in both steps. The sulfidation of the nickel catalyst surface results in an increased energy of the metal–hydrogen bond and in a lower ability of the surface to activate hydrogen.

In the technical praxis, the action of catalytical poisons may lead to a lower activity of the catalyst or to suppression of side reactions. In the latter case, the reaction rate decreases but a higher selectivity is obtained. In contrast to hydrogenations in the gas phase, there are very few reports on the influence of catalytic poisons on the course of hydrogenations in the liquid phase[1,2].

In the present paper, we have investigated the influence of the poisoning of the nickel catalyst by sulfur compounds on the activity and selectivity of this catalyst in hydrogenations in the liquid phase. The catalyst was poisoned by sulfur compounds of various structures such as thiophene, heptyl mercaptan, and diheptyl sulfide. The influence of the degree of poisoning on the activity and selectivity was investigated in hydrogenations of 1-, 2-, 3-, and 4-octine at 30°C and at atmospheric pressure with the use of n-heptane as solvent.

## EXPERIMENTAL

*Materials.* For the test substances, n-heptane, and hydrogen see the preceding paper[3]. Thiophene, heptyl mercaptan, and diheptyl sulfide were purchased from Koch-Light Laboratories,; England.

*Catalyst.* The nickel carrier catalyst (composition: 50·9% NiO, 28·9% Kieselgur, 3% graphite loss on calcination, 18·1%) was calcined and reduced at 380—420°C, and then passivated by controlled oxidation of the absorbed hydrogen with oxygen[4]. The degree of reduction of our catalyst

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was $\alpha = 0.58$. Prior to each measurement, an exactly weighed portion of the passivated catalyst was reactivated[3] at 240−250°C in the stream of hydrogen for one hour, the catalyst allowed to cool, and added under hydrogen into the solvent containing the particular sulfur compound.

*The degree of sulfidation of the nickel catalyst* (milligrams of sulfur per one gram of the catalyst) was determined as follows. An exactly weighed amount of the passivated catalyst was reactivated and added into an exactly measured volume of n-heptane containing the known amount of a sulfur compound (sulfur). The catalyst was ground and allowed to settle. The content of sulfur in the clear supernatant was then determined.

*The content of sulfur* in n-heptane before and after the sulfidation of the catalyst was determined titrimetrically[5]. The method consists in the reduction of the organically bound sulfur with Raney nickel and decomposition of the thus-formed nickel sulfide with hydrochloric acid. The liberated hydrogen sulfide is introduced into acetone containing aqueous sodium hydroxide and titrated with mercuric acetate with the use of Dithizone as indicator. The sensitivity of this method is $10^{-1}$ p.p.m. of S; accuracy, 3%.

*The amount of hydrogen* sorbed on the catalyst on the composition of the reaction mixture during the hydrogenation was determined by the same methods and in the same apparatus as reported earlier[3].

*Apparatus and procedures.* An exactly weighed amount (10 g) of the passivated catalyst is reactivated, ground in n-heptane containing the known amount of the sulfur compound, and added into a closed vessel equipped with two stopcocks. The suspension of the catalyst is kept under hydrogen at 30°C for 15 min (this time is sufficient to attain the equilibrium of absorption). The value of the sorbed sulfur (milligrams of S per one gram of the catalyst) was determined from the sulfur content in the n-heptane solution before and after the sulfidation of the catalyst.

*The activity was determined* by the same method and in the same apparatus as reported earlier[6]. There was used 0·2−0·4 g of the catalyst, 30 ml of the solvent, 5 mmol of the test substance (octines), the temperature of 30°C, 450 revolutions per min. In the course of hydrogenations, samples were withdrawn and analysed chromatographically. As shown by preliminary experiments, the reaction rate is the same when the hydrogenation is performed in pure n-heptane as solvent or in n-heptane containing the same amount of the sulfur compound as used in sulfidation of the catalyst. No desorption of the sulfur compound from the surface of the catalyst into the solvent was observed when pure n-heptane was used. For practical reasons, pure n-heptane was therefore used in all experiments reported in the present paper.

## RESULTS AND DISCUSSION

The course of the hydrogenation of isomeric octines over the poisoned (sulfidated) catalyst was similar to that over the unpoisoned catalyst[3] except for the lower activity in dependence on the degree of sulfidation (Table I).

The amount of sulfur bound at the surface of the catalyst increased with increasing concentration of the sulfur compound in n-heptane up to a certain value. Since the sulfur compound was quantitatively bound to the metallic surface of the nickel catalyst, the n-heptane over the catalyst did not contain even a trace of this sulfur compound. The maximum amount of the sulfur compound sorbed by the catalyst corresponded to 9−10 mg of S per one gram of the catalyst (thiophene or diheptyl

sulfide) and 14—15 g of S (heptyl mercaptan). The concentration of the sulfur compound in the solvent was then gradually increased, but no additional sulfur was bound to the catalyst. In the case of thiophene, the final concentration was about 6% by weight; this concentration would correspond to the sorption of about 30 mg of S per one gram of the catalyst. The observeation that the sorption of the sulfur compound by the catalyst is limited appears to indicate that the sorption occurs merely at the metallic surface of the nickel catalyst. This finding was used to calculate the magnitude of the catalyst surface. It was assumed that the maximum amount of thiophene bound to the surface of the catalyst is 9·7 mg of S per one gram of the catalyst

TABLE I

Dependence of Activity on the Degree of Sulfidation at the Surface of the Nickel Catalyst with Thiophene, Benzyl Mercaptan, and Diphenyl Sulfide in Hydrogenations of Isomeric Octines

| Sorbed sulfur (mg of S per 1 g of catalyst) | Catalyst activity, ml of $H_2$/min g of the catalyst | | | |
|---|---|---|---|---|
| | 1-octine | 2-octine | 3-octine | 4-octine |
| Poisoning with thiophene | | | | |
| 0 | 197·0 | 5·49 | 99·4 | 79·9 |
| 0·071 | 125·6 | 27·4 | 62·6 | 69·2 |
| 0·716 | 100·6 | 16·6 | 44·0 | 54·6 |
| 1·937 | 88·9 | 10·6 | 44·2 | 44·1 |
| 6·460 | 18·9 | 8·8 | 24·5 | 20·2 |
| 8·720 | 21·8 | 8·2 | 16·8 | 17·1 |
| 9·660 | 18·6 | 9·9 | 10·4 | 14·7 |
| 9·75 | 18·3 | 7·3 | 12·8 | 10·7 |
| Poisoning with heptyl mercaptan | | | | |
| 0 | 197·0 | 54·9 | 99·4 | 79·9 |
| 1·73 | 57·6 | 22·3 | 44·8 | 45·0 |
| 2·88 | 48·3 | 11·5 | 38·0 | 37·2 |
| 6·44 | 40·8 | 10·7 | 14·1 | 14·2 |
| 12·12 | 7·8 | 2·0 | 5·1 | 1·6 |
| 14·79 | 6·0 | 0·9 | 1·5 | 0·8 |
| Poisoning with diheptyl sulfide | | | | |
| 0 | 197·0 | 54·9 | 99·4 | 79·9 |
| 0·55 | 89·6 | 33·4 | 84·5 | 64·4 |
| 0·93 | 63·7 | 29·8 | 73·0 | 48·5 |
| 5·89 | 47·8 | 19·5 | 42·4 | 45·0 |
| 6·88 | 31·8 | 14·4 | 28·1 | 15·5 |
| 9·63 | 29·1 | 9·4 | 13·8 | 8·2 |

(Table 1), that the sorption is of the areal type[2], and that the molecule of thiophene occupies the area of 33 Å[2]. The thus-calculated area is about 112 m[2] per one gram of nickel; this value is in good accordance with that determined earlier for this catalyst by chemisorption of hydrogen[7].

Sulfidation of the surface of the catalyst up to the sulfur content of 0·2% S leads to a considerable decrease of the activity in hydrogenations of the triple bond. Additional sulfidation from 0·2% S to the limit value of S results in a moderate gradual decrease of the activity up to 10−20% of the original activity (this value does not change on further sulfidation). It may be seen from Table I that the rate of hydrogenation of isomeric octines over a poisoned nickel catalyst depends on the position of the triple bond. Thus the hydrogenation rate of 1-octine and 3-octine is higher than that of 2-octine and 4-octine, and the hydrogenation of 1-octine is quicker than that of 3-octine. These findings are similar to those obtained with the use of an unpoisoned catalyst[3].

Composition of the reaction mixture in hydrogenations of isomeric octines over a poisoned catalyst is similar to that in hydrogenations over an unpoisoned catalyst. Also the selectivity (for the definition see the earlier paper[3]) does not depend on the degree of sulfidation. The average selectivity values in hydrogenations of isomeric
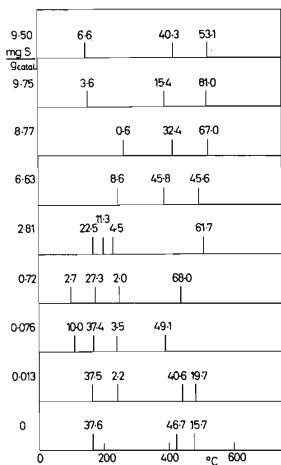


Fig. 1

Dependence of Desorption Characteristics of Hydrogen from a Nickel Catalyst Sulfidated with Thiophene on the Amount of Bound Sulfur

octines over a poisoned catalyst are as follows: 0·64 (1-octine), 0·74 (2-octine and 4-octine) and 0·75 (3-octine). The two reaction steps thus occur at the same active center and the selectivity depends on the ratio of reaction rates of the two steps. The amount of hydrogen (in % of the total amount of hydrogen) desorbed at particular temperature maxima is shown on Fig. 1. The total amount of hydrogen did not practically depend on the degree of sulfidation; some change in desorption was observed especially at temperatures up to 300°C.

In spite of the fact that there does not exist any direct dependence between the activity and the amount of the bound hydrogen, it may be assumed from the shift of temperature maxima to higher temperatures that sulfidation of the catalyst leads to an increased energy of the bonding between hydrogen and the surface of the catalyst. The decreased reaction rate in hydrogenations of octines might be consequently due to a lower ability of the poisoned surface to activate the molecular hydrogen.

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