

## MECHANISM OF THE DEACTIVATION OF NICKEL CATALYSTS BY STEAM UNDER PRESSURE

L. Kh. Freidlin, A. A. Balandin, N. V. Borunova, and A. E. Agronomov

Water is one of the most frequently encountered impurities in catalytic reduction and hydrogenation processes; it is formed by the reduction of metal oxides and oxygen-containing organic compounds. Water is a reaction component in transformations of hydrocarbons and carbon monoxide; it is used as a solvent and diluent. However, the effect of water vapor on nickel hydrogenation catalysts has been inadequately investigated.

Tsutsumi and coworkers [1] noted that small amounts of water greatly reduce the activity of a nickel catalyst in fat-hydrogenation reactions. Slovokhotova and Ivanov [2] found that the rate of dehydrogenation of cyclohexane at 250-300° over a nickel-alumina catalyst was reduced by a factor of five in presence of water vapor. Arnold and Atwood [3] state that nickel deposited on a complex mixture of oxides is of low stability as a catalyst for the transformation of hydrocarbons by means of steam.

In an investigation of the properties of nickel catalysts prepared by reduction with hydrogen at a pressure of 500 atm, we concluded that the cause of their low activity was the presence of water vapor in the sphere of the reduction reaction. In this connection we studied the effect of water vapor purposely introduced into the reduction zone in the treatment of nickelous oxide with hydrogen under pressure. It was found that steam under pressure brings about a far-reaching irreversible change in the catalyst components, namely their recrystallization. Our results make it possible to approach the question of the mechanism of the deactivation of metal catalysts with water vapor from a new viewpoint.

### EXPERIMENTAL

#### Experimental Procedure

The catalysts were prepared by coprecipitation from a mixture of molar nitrate solutions with 30% sodium hydroxide. The product was decomposed to give a mixture of oxides corresponding to 35% NiO and 65% Al<sub>2</sub>O<sub>3</sub> (or 65% MgO).

The reduced catalyst or carrier-supported nickelous oxide was placed in a stainless-steel beaker and treated for five hours at 350° with a mixture of steam (100 atm) and hydrogen (700 atm) in a special high-pressure reactor. The treated mass was removed from the cooled reactor and reduced with electrolytic hydrogen at 350° and normal pressure. The activity of the catalyst was characterized by the degree of hydrogenation of benzene (at 120° and at a space velocity of 0.3 hour<sup>-1</sup>) or the degree of dehydrogenation of cyclohexane (at 300° and at a space velocity of 0.3 hour<sup>-1</sup>), determined in continuous-flow apparatus. The degree of hydrogenation of benzene and the degree of dehydrogenation of cyclohexane were determined refractometrically [4].

#### Effect of a Mixture of Steam and Hydrogen under Pressure on the Activity of a Nickel-Alumina Catalyst

Experiments 1 and 2 were carried out with commercial nickel-alumina catalyst containing 50% of nickel. Over this catalyst benzene was hydrogenated to the extent of 97% at 120°. It will be seen from Table 1 that, after the steam-hydrogen treatment, the degree of hydrogenation of benzene was only 14.4%. The catalyst was then reduced with hydrogen for five hours at 350° and normal pressure. Its activity then increased

considerably: the degree of hydrogenation of benzene was 56.2%. After a further reduction with hydrogen for six hours under the same conditions, the activity of the catalyst was almost completely recovered. It is thus possible to regenerate a reduced catalyst that has been deactivated by treatment with steam. However, the deactivated catalyst must be treated with hydrogen for a fairly long time.

TABLE 1

Effect of Treatment with a Steam-Hydrogen Mixture Under Pressure on the Activity of a Nickel-Alumina Catalyst. Conditions of treatment: hydrogen pressure 700 atm; steam pressure 100 atm; duration five hours; temperature 350°

Expt. No.	Sample of Ni-Al <sub>2</sub> O <sub>3</sub>	Duration of reduction with hydrogen* (hours)	Degree of hydrogenation of benzene (%)
1	Untreated	6	97.4
2	Treated	<div style="display: flex; align-items: center;"> <div style="font-size: 3em; margin-right: 5px;">{</div> <div style="display: flex; flex-direction: column; gap: 5px;"> <div>—</div> <div>5</div> <div>6</div> </div> </div>	<div style="display: flex; flex-direction: column; gap: 5px;"> <div>14.4</div> <div>56.2</div> <div>94.0</div> </div>

\* At 350° under normal pressure.

#### Effect of Treatment of Carrier-supported Nickelous Oxide with a Mixture of steam and Hydrogen under Pressure

Nickelous oxide on a carrier was treated for five hours at 350° with a mixture of steam and hydrogen. It will be seen from Table 2 that sample No. 7 of nickelous oxide on alumina, treated in this way and then reduced with hydrogen for five hours at 350° and normal pressure, was almost completely inactive as a catalyst: the degree of hydrogenation of benzene at 120° was only 6.4%. After further reduction with hydrogen for eight hours, the activity of the catalyst did not increase. After a third reduction with hydrogen for eight hours, the activity of the catalyst was still low: the degree of hydrogenation of benzene at 180° was 9.5% (Experiment 4). For a catalyst prepared from the same sample without treatment with steam, the degree of hydrogenation of benzene was 91.6% and the degree of dehydrogenation of cyclohexane was 63% (Experiment 3).

Similar results were obtained with sample No. 8. The catalyst prepared from this sample and not subjected to the action of steam was very active; the degree of hydrogenation of benzene was 98.8%, and the degree of dehydrogenation of cyclohexane was 78.8%. The sample was treated with a mixture of steam and hydrogen under pressure at 350°, and subsequent reduction with hydrogen at atmospheric pressure at 350° gave an inactive catalyst: the degree of hydrogenation of benzene at 120° was 1.2%. After further reduction with hydrogen at ordinary pressure and 350° for eight hours and then at 425° for five hours, it remained almost inactive (Experiments 5 and 6).

Similar results were obtained when the catalyst was prepared from nickelous oxide and magnesia, subsequently treated with a mixture of steam and hydrogen under pressure. Reduction with hydrogen for five hours at 350° and ordinary pressure gave an inactive catalyst: the degree of hydrogenation of benzene was 0.2% at 120° and 8.8% at 180°. After further reduction with hydrogen for eight hours under similar conditions, the degree of hydrogenation of benzene attained 19%. The catalyst prepared from the same sample of nickelous oxide on magnesia, but not subjected to the action of steam, hydrogenated benzene to the extent of 91.6% and dehydrogenated cyclohexane to the extent of 46.4% (Experiments 7 and 8).

The results obtained with three samples of nickelous oxide on alumina or magnesia show that, when reduced with hydrogen in presence of steam, carrier-supported nickelous oxide suffers an irreversible change. An active catalyst was not obtained from the nickelous oxide even after reduction with hydrogen for 13-21 hours at 350° and ordinary pressure.

Similar results were obtained when nickelous oxides on carriers were treated with a mixture of steam and nitrogen under pressure. However, they were somewhat more active than samples treated with a mixture of steam and hydrogen (Experiments 9 and 10) (Table 3).

#### Effect of Treatment of Alumina-supported Nickelous Oxide with Steam

In order to determine the effect of treating nickelous oxide with steam in absence of hydrogen or nitrogen, a series of experiments was carried out in which the following procedure was adopted. Nickelous oxide on alumina was heated in an autoclave with a definite volume of distilled water. The temperature was measured with a thermocouple placed in the pocket of the autoclave. At the end of the experiment, the contents were unloaded, dried at 100°, formed into shape, and reduced with hydrogen at 350°. The activity of the catalyst was then tested for the hydrogenation of benzene or the dehydrogenation of cyclohexane by the usual method.

TABLE 2

Effect of Treatment of Carrier-supported Nickelous Oxide with a Mixture of Steam and Hydrogen under Pressure\*. Conditions of treatment: hydrogen pressure 700 atm; steam pressure 100 atm; duration five hours; temperature 350°

Experiment No.	Sample		Duration of reduction with hydrogen (hours)**	Temperature (°C)	Degree of hydrogenation of benzene (%)
	composition	treatment			
3	NiO—Al <sub>2</sub> O <sub>3</sub>	Untreated	3	120	91.6
4	№ 7	Treated	$\begin{cases} 5 \\ 13 \\ 21 \end{cases}$	$\begin{matrix} 120 \\ 120 \\ 180 \end{matrix}$	$\begin{matrix} 6.4 \\ 6.0 \\ 9.5 \end{matrix}$
5	NiO—Al <sub>2</sub> O <sub>3</sub>	Untreated	1,5	120	98.8
6	№ 8	Treated	$\begin{cases} 5 \\ 13 \\ 18*** \end{cases}$	$\begin{matrix} 120 \\ 180 \\ 180 \end{matrix}$	$\begin{matrix} 1.2 \\ 0.8 \\ 1.2 \end{matrix}$
7***	NiO—MgO	Untreated	10	120	91.6
8	№ 2	Treated	$\begin{cases} 5 \\ 13 \end{cases}$	$\begin{matrix} 120 \\ 180 \\ 180 \end{matrix}$	$\begin{matrix} 0.2 \\ 8.8 \\ 19.0 \end{matrix}$

\* The catalysts prepared from the untreated samples dehydrogenated cyclohexane at 300° to the following extents: No. 7, 63%; No. 8, 78.8%; No. 2, 46.4%.

\*\* At 350° under normal pressure.

\*\*\* The last five hours of the reduction were at 425°.

TABLE 3

Effect of Treatment of Carrier-supported Nickelous Oxide with a Mixture of Steam and Nitrogen under Pressure. Conditions of treatment: nitrogen pressure 700 atm; steam pressure 100 atm; duration five hours; temperature 350°.

Experiment No.	Sample		Duration of reaction with hydrogen (hours)*	Temperature (°C)	Degree of hydrogenation of benzene (%)
	composition	treatment			
3	NiO—Al <sub>2</sub> O <sub>3</sub>	Untreated	3	120	91.6
9	№ 7	Treated	5	120	20.8
7	NiO—MgO	Untreated	10	120	91.6
10	№ 2	Treated	$\begin{cases} 5 \\ 13 \\ 21 \end{cases}$	$\begin{matrix} 120 \\ 180 \\ 180 \end{matrix}$	$\begin{matrix} 1.2 \\ 50.0 \\ 59.0 \end{matrix}$

\* At 350° under normal pressure.

It will be seen from Table 4 (Experiment 11) that nickelous oxide on alumina, treated for five hours at 350° with steam under a pressure of 100 atm and then reduced with hydrogen, becomes quite inert as a catalyst. A

similar result was obtained with the same sample of nickelous oxide on alumina treated with steam for two hours (Experiment 12). The two catalysts from Experiments 11 and 12 were then mixed and further reduced with hydrogen for 20 hours at 350° at normal pressure, the total duration of the hydrogen treatment then being 25-33 hours. Even then, however, the catalyst was found to be quite inactive (Experiment 13). It follows from Experiment 14 that, when the temperature of the steam treatment of nickelous oxide on alumina in the autoclave was lowered to 300°, a catalyst was obtained which was again of low activity: the degree of hydrogenation of benzene in its presence was 3.4%. In Experiment 15 no water was added. It was found that even the very small amount of water vapor that is liberated during dehydration at 350° is sufficient to reduce the activity of the catalyst appreciably (Table 4).

TABLE 4  
Effect of the Treatment of Alumina-supported Nickelous Oxide (Sample No. 8) with Steam under Pressure. Conditions of treatment: steam pressure 100 atm; duration five hours; temperature 350°.

Experiment No.	Duration of reduction with hydrogen (hours)*	Degree of hydrogenation of benzene(%)	Degree of dehydrogenation of cyclohexane (%)
5	1.5	98.8	78.8
11	5	0.3	—
12**	5	0.3	—
	13	0.2	0.0
13	25—33	0.2	—
14***	5	3.4	10.6
	13	0.2	—
15****	5	71.2	40.8

\* At 350° and normal pressure.

\*\* Duration of steam treatment two hours.

\*\*\* Treated with steam at 300°

\*\*\*\* No water was added.

prepared from the steam-treated nickelous oxide was considerably lower: degree of hydrogenation of benzene 52-60% and degree of dehydrogenation of cyclohexane 20-21%. As will be seen, the effect of steam under given conditions on nickelous oxide without carrier is much less than on nickelous oxide supported by a carrier. This shows the very close association between the nickelous oxide and the carrier in the coprecipitated mixture.

#### Effect of Steam on the Activity of Nickel Catalysts

Investigations were made also on the effect of steam treatment on the activities of Raney nickel and of a catalyst prepared by the reduction of nickelous oxide.

a) Effect on the Activity of Nickel Prepared by the Reduction of Nickelous Oxide. A catalyst prepared by the reduction of 4.2 g (10 ml) of nickelous oxide with hydrogen (ten hours at 350°) was treated for five hours at 350° with steam at atmospheric pressure. The space velocity of passage of water was 0.5-0.6 hour<sup>-1</sup>, and the total amount of water passed was 30 ml. After steam treatment, the catalyst was reduced with hydrogen for five hours at 350°. There was little change in activity: before steam treatment the degree of hydrogenation of benzene was 93.8%; after steam treatment it was 87.6%. It will be seen that treatment of reduced nickel with steam at ordinary pressure has only a slight effect on catalytic activity.

b) Effect on the Activity of Raney Nickel Catalyst. Samples of catalyst were prepared by leaching 50% nickel-aluminum alloy with 20% caustic alkali at 100°. The activity of the catalyst before and after steam treatment was characterized by the rate of hydrogenation of 0.25 g of phenyl vinyl ether in alcohol at 20°. A paste of the catalyst (10 g) was placed in a glass tube filled with nitrogen. The tube was heated in an electric furnace

The results given in Table 2 and 4 show that a catalyst prepared from carrier-supported nickelous oxide treated with steam is just as inactive as a nickelous oxide preparation treated with a mixture of steam and hydrogen.

#### Effect of Treatment of Nickelous Oxide Alone with Steam

The above-described results refer to nickelous oxide supported on a carrier. It was essential to determine the effect of steam treatment of nickelous oxide alone, in absence of carrier. With this object, nickelous oxide prepared by precipitation of a molar solution of the nitrate with sodium hydroxide was taken in an amount of 4.2 g (10 ml) and reduced with hydrogen for ten hours at 350°. Another portion of the same sample of nickelous oxide was pretreated for five hours at 350° with steam at 180 atm, and some of the product (4.2 g, i.e., 2.5 ml) was reduced for ten hours at 350°. Activity tests showed that, with the catalyst prepared from nickelous oxide not treated with steam, benzene was hydrogenated to the extent of 93.4%, and cyclohexane was dehydrogenated to the extent of 37.8%. The activity of the catalyst pre-

TABLE 5

Deactivation of Raney Nickel Catalyst (10 g) with Steam at Atmospheric Pressure

Experiment No.	Conditions of steam treatment*		Amounts of hydrogen adsorbed in the first four minutes in the hydrogenation of 0.25 g of phenyl vinyl ether at 20° (ml/min)**
	Temperature (°C)	Duration (hours)	
16	Untreated		28.4—14.8—1.9—0.5
17	150	2	27.1—14.2—2.2—0.4
18	200	2	25.6—17.3—1.2—0.4
19	250	2	19.3—17.7—6.8—0.4
20	300	2	16.5—15.8—9.7—2.5

\* 12 ml of water passed.

\*\* 1 g of catalyst.

temperature of the experiment. At the end of the experiment the autoclave was cooled to room temperature. It was then opened rapidly, and water was poured over the catalyst. It will be seen from Table 6 that, when 10 g of catalyst was heated under pressure with 6-12 ml of water at only 150°, its activity was reduced by a factor of 3-4. Even the small amount of water contained in the moist Raney nickel paste was sufficient to deactivate the catalyst at 150° (Experiments 25 and 26). It is interesting to note that heating of the catalyst at 150° under pressure in presence of a large amount of water (100 ml) scarcely reduced the activity (Experiment 23). In this case the catalyst was covered with a layer of water, which probably protected it from the deactivating effect of steam. Steam, therefore, is more aggressive in its action than water in the liquid state.

TABLE 6

Deactivation of Raney Nickel Catalyst with Steam under Pressure

Experiment No.	Conditions of steam treatment*			Amounts of hydrogen adsorbed in the first four minutes in the hydrogenation of 0.25 g of phenyl vinyl ether at 20° (ml/min)**
	Pressure (atm)	Temperature (°C)	Duration (hours)	
16	Untreated			28.4—14.8—1.9—0.5
21	37	150	5	10.3—9.2—8.6—7.1
22	75	150	2	7.5—7.2—7.2—7.0
23**	4.8	150	2	25.2—17.5—2.7—0.9
24	Untreated ***			19.7—16.1—6.3—2.5
25		100	3	18.9—15.4—6.8—1.4
26		150	3	3.6—2.3—2.2—2.3

\* Amount of catalyst 1 g.

\*\* Catalyst under a layer of water.

\*\*\* Another sample of nickel. The moist paste was heated.

provided with a thermoregulator. During the warming-up period and throughout the experiment, a slow stream of oxygen-free nitrogen was passed through the tube. Water was admitted to the tube at a uniform space velocity of 0.6 hour<sup>-1</sup>. The steam-treated catalyst was cooled in a stream of nitrogen and emptied out into water. It will be seen from Table 5 that treatment of the catalyst with steam for two hours at 150-200° did not lower the activity. Only steam treatment at 250-300° lowered the activity of the catalyst to an appreciable extent. Our results are in conflict with Aubry's assumption [5] concerning the interaction of Raney nickel and water at room temperature.

c) Effect of Treatment of Raney Nickel Catalyst with Steam at High Pressure. The catalyst was placed together with a definite volume of water in a 200-ml autoclave. The autoclave was hermetically sealed, blown out three times with nitrogen, and heated to the

#### Effect of Steam on the Specific Surface of a Mixture of Nickelous Oxide and Alumina

The effect of water vapor on the reduction of nickelous oxide by hydrogen at normal pressure has been studied by several investigators. It was established that water vapor retards the reduction of nickelous oxide, lengthens the induction period, raises the temperature at which reduction begins, and increases the time necessary for complete reduction [6-8]. The inhibiting effect of water vapor on the reduction of metal oxides has been explained by investigators by the formation of a firmly adsorbed film on the metal surface, the oxide surface, or the interface

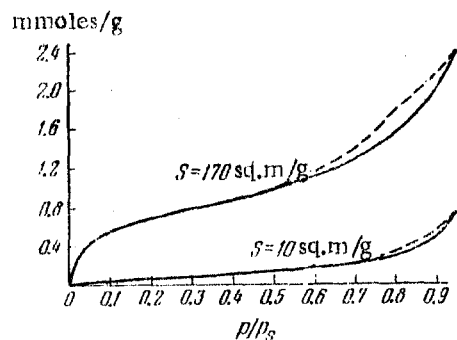


Fig. 1.

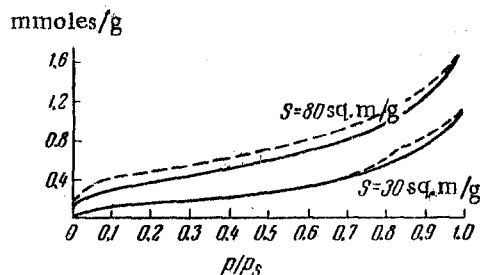


Fig. 2

between the metal and oxide phases. As the degree of reduction of metal oxides (under given conditions of temperature and pressure) depends on the relative concentrations of hydrogen and water vapor in the system, the effect of the latter tends to be equivalent to a change in the thermodynamic conditions of the process, thus resulting in a displacement of equilibrium.

However, this cannot explain the almost complete inertness of nickel prepared by the reduction of steam-treated carrier-supported nickelous oxide. The processes of forming films of adsorbed water vapor, and also oxide films or phases, are reversible. Water vapor may be desorbed, and a metal oxide may be reduced. However, as the results of our experiments show, treatment of nickelous oxide on a carrier with steam under pressure has an irreversible effect on the activity of the catalyst prepared from it.

Our results led us to the view that, in the course of steam treatment, nickelous oxide undergoes extensive recrystallization. In order to verify this we investigated the effect of steam treatment on the specific surfaces of samples No. 7 and 8 of alumina-supported nickelous oxide. A 30-40 mg sample was placed in a high-vacuum apparatus containing a quartz spring balance, and it was freed from adsorbed gases and vapors by treating it for many hours at 250° at a residual pressure of the order of  $10^{-5}$ – $10^{-6}$  mm. Adsorption isotherms were then determined for benzene vapor at 0°. The benzene was first freed from traces of thiophene and moisture and had b.p. 79.7–80° (755 mm) and  $n_D^{20}$  1.5035. The benzene was freed from dissolved air and was thoroughly dried over magnesium perchlorate in the apparatus itself. The pressure of benzene vapor in the system was measured with a mercury manometer accurately within 0.01 mm. The extension of the spirals was measured with a microcathetometer accurately within 0.01 mm, which made it possible to determine changes in weight accurately within  $1 \cdot 10^{-5}$  g. The surface area was calculated by the Brunauer, Emmett, and Teller method [9] on the assumption that the area of the benzene molecule is 46.5 Å<sup>2</sup> [10]. The isotherms for the adsorption of benzene on samples No. 7 and 8 are shown in Figures 1 and 2.

Sample No. 8 of nickelous oxide on alumina was found to be nonporous, and its specific surface was 170 sq.m/g. The specific surface of the same sample after treatment for five hours at 350° with a mixture of steam and hydrogen at pressure of 700 atm was only about 10 sq.m/g; the volume of benzene adsorbed by the sample at saturation was reduced to about one-third by the treatment. The specific surface of sample No. 7 of nickelous oxide on alumina was reduced from 80 to 30 sq.m/g by treatment for five hours at 350° with a mixture of steam and nitrogen. The specific surface of alumina, treated with steam under similar conditions, was reduced by a factor of almost three (from 355 to 125 sq.m/g) [11].

These results confirmed that steam treatment brings about extensive recrystallization both of carrier-supported nickelous oxide and of the carrier itself. They are in accord with the results of van Eyk van Voorthuisen and Franzen, which show that steam treatment facilitates the perfection of the crystal structure of nickel hydrosilicate [12].

#### Discussion of Experimental Results

Our results show that catalysts prepared by the reduction of steam-treated nickelous oxide supported on a carrier (Al<sub>2</sub>O<sub>3</sub>, MgO) are almost completely inactive for the hydrogenation of benzene at normal-pressure; they catalyze the hydrogenation of an ethylene bond (3-octene, styrene) at ordinary pressure, and they will hydrogenate

also an aromatic bond at high pressure [13]. Even after long treatment with hydrogen, the extent to which the nickelous oxide in these catalysts is reduced does not exceed 20-30%. This, however, does not explain the low activity of catalysts prepared in this way. In our experiments, catalysts (prepared from carrier-supported nickelous oxide which had not been subjected to the action of steam) in which the nickelous oxide was reduced to the extent of, for example, 40-50%, were very active for the hydrogenation of benzene. It is known also that benzene can be readily and completely hydrogenated over a catalyst containing only 1-4% of nickel supported on charcoal [14].

Our adsorption measurements showed that, when treated with steam at high temperature and pressure, a mixture of nickelous oxide and carrier, as also the carrier itself, undergoes far-reaching recrystallization. It appears that the main cause of the inactivity of our catalysts is the low dispersity of the nickel obtained by the reduction of recrystallized nickelous oxide. Lachinov [15] suggested that, owing to the presence of water vapor during reduction with hydrogen under pressure, the iron catalyst for the ammonia synthesis undergoes alternate oxidation and reduction with recrystallization of metal particles and reduction of the activity of the catalyst.

The results that we have obtained on the effect of steam treatment of carrier-supported nickelous oxide on the activity of the catalyst prepared from it enable us to examine the mechanism of the deactivation of metal catalysts by steam in a new light. It was found that steam treatment had the greatest effect on carrier-supported nickelous oxide, and not on reduced nickel. Steam treatment of a prepared nickel catalyst under similar conditions lowered the activity of the catalyst to a much lower extent. When the steam treatment was at ordinary pressure, the difference was difficult to detect, but at high pressure the difference was great. Treatment of carrier-supported nickelous oxide with steam alone had an even greater effect, than treatment with a mixture of steam and hydrogen.

It is clear that the deactivation of the catalyst is due to the recrystallization not of the metal, but of its lower oxide (film or phase), which is formed by the action of steam at high temperature, particularly when the pressure is also high. The subsequent reduction of the coarsely dispersed particles of recrystallized oxide proceeds with great difficulty, being slower and requiring a higher temperature. The metal particles obtained after the reduction of the recrystallized oxide are also of low dispersion and of low activity. We consider that the mechanism that we have proposed is applicable also to the deactivation of iron catalysts by steam.

Kamzolkin and Lívshits [16] stated that a few hundredths of a percent of water vapor in the gas mixture lower the productivity of an ammonia-synthesis column by hundreds of kilograms per hour. It is known that it is exceptionally important to have a small admixture of alumina for lasting activity in the iron catalyst of the ammonia synthesis [17]. It may be assumed that, under the action of steam at high temperature, alumina will recrystallize and its promoting effect will be lost. In this lies one of the causes of the deactivation of an iron catalyst by steam.

Shurmovskaya and Bruns [18] consider that in this process at low concentrations of water vapor it is impossible to expect that an iron oxide phase will appear. Reaction of iron is here of a purely surface character. The results of our work show that the deactivating effect of small amounts of water vapor on an iron catalyst can be explained by the formation of a recrystallized, and therefore difficultly reducible, surface film of oxide. The work of Bashkirov and coworkers [19] shows that one of the causes of the irreversible deactivation of an iron catalyst in the synthesis of hydrocarbons from carbon monoxide and hydrogen under pressure is reaction between the water vapor liberated and the catalyst with formation of an iron oxide phase. This conclusion requires supplementation by a demonstration of the occurrence of recrystallization in the metal oxide phase formed by the action of water vapor in a high-pressure system.

#### SUMMARY

1. An investigation was made into the deactivating effect of steam on nickel catalysts in the course of their preparation by reduction with hydrogen under pressure.

2. It was shown that pretreatment of a mixture of nickelous oxide and carrier ( $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ) with steam under pressure results in the formation of catalysts of low activity. Similar treatment of a reduced carrier-supported nickel catalyst has a very much smaller effect on activity.

3. It was shown that steam treatment of a coprecipitated mixture of nickelous oxide and alumina ( or magnesia) under pressure results in a far-reaching irreversible change, namely recrystallization with great reduction in specific surface.

4. It is evident that the deactivation of reduced nickel catalysts by steam in the course of their use is due to the formation of nickelous oxide films or phases that rapidly recrystallize and are reduced with difficulty with formation of coarsely dispersed nickel. It is probable that the mechanism here proposed is applicable also to the deactivation of iron catalysts by water vapor.

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N. D. Zelinsky Institute of Organic  
Chemistry of the Academy of Sciences  
of the USSR

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