DUAL ACTION OF HYDROGEN ON THE CATALYTIC ACTIVITY OF NaY, Na-MORDENITE, AND NAA ZEOLITES IN HYDROGENATION REACTIONS OF ACETONE AND BENZENE

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The capacity of zeolites not containing transition elements to hydrogenate unsaturated hydrocarbons was observed for the first time by us in 1968 [1]. Later, this property of zeolites was confirmed both by us [2-11] and by others [12-15]. During this not only the various classes of hydrocarbons undergo hydrogenation but also compounds containing oxygen [16-19]. Significant influence of the treatment of zeolite catalysts with H_2 or air was noted already in these investigations. So, with the investigation of the dependence of the activity of NaA, NaY, and Na-mordenite (NaM) zeolites during the hydrogenation of 2-methyl-2-butene at 200°C and 30 atm on the preliminary treatment of the catalysts with H_2 it was established that with an increase in the treatment temperature from 200 to 500°C the activity of the catalysts increases at first and, going through a maximum at 275-300°C, decreases [11]. Analogous data were obtained with the study of the hydrogenation of propylene at 200°C in a quartz microreactor over NaA, NaX, and NaY zeolites: upon a temperature increase of the preliminary treatment of these zeolites with hydrogen from 200 to 400-500°C their hydrogenating activity passed through a maximum at 250-300°C [15]. According to the data in [20], the adsorption of H_2 on NaY increases with an increase in temperature to 350°C; however, in the opinion of the authors, the hydrogen activity is not connected with the adsorption of H_2 but with the removal of the hydroxyl coating or chemisorbed O_2 .

Thus, H_2 exhibits a dual action on zeolites in hydrogenation reactions of olefins, activating the catalysts at a relatively low temperature and, on the other hand, quenching their activity at a higher temperature. The present work was conducted with the goal of explaining the influence of H_2 on zeolites during the hydrogenation of acetone and benzene. Besides this, experiments were made to explain the reasons of the dual action of H_2 on the hydrogenating activity of zeolites.

EXPERIMENTAL

The amount of catalyst was 7-15 g. The experiments were conducted in a flow-through apparatus under H₂ pressure, purified from O_2 and H₂O by passage through granular copper at 300°C and then through a drying agent with zeolite or KOH. Experiments were conducted at molar ratios of H₂:acetone = 3 and H₂:benzene = 5.

TABLE 1. The Influence of the Preliminary Treatment of Na-Mordenite on Its Activity in the Hydrogenation Reaction of Benzene (250°C, 50 atm, C_6H_6 flow rate of 0.01 mole/h on 1 g NaM)

Expt.	Conditions of treatment of catalyst before expt.	Conversion of C_6H_6 to C_6H_{12} , %
4'	Air, atmospheric pressure, 520 °C, 5 h;H ₂ 50 atm, 400 °C 2h	1 ,0
2 3	Air, atmospheric pressure, 520 °C, 5 h Air, atmospheric pressure, 520 °C, 5 h; H ₂ 50 atm, 400 °C 2 h	86,9 1,0
4	Air, atmospheric pressure, 520 °C, 5 h	88,2

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Fig. 1. The dependence of the extent of the hydrogenation of benzene (a) and acetone (b) on the temperature of the treatment of the zeolites (Ct) with air (5 h). Experimental conditions with benzene are 190°C, 30 atm, benzene flow rate of 0.016 mole/ h on 1 g of Ct; with acetone they are 220°C, 40 atm, acetone flow rate of 0.019 mole/h on 1 g Ct: 1) NaM; 2) NaY; 3) NaA.

DISCUSSION OF RESULTS

For a clarification of the role of H_2 we investigated the activity changes of zeolites during a gradual temperature elevation of their treatment with air. It follows from Fig. 1 that the yields of reaction products increase linearly with an increase in temperature of the preliminary treatment of the catalysts with air from 250 to 500°C during the hydrogenation of acetone on NaM, NaY, and NaA and of benzene on NaM. An analogous linear dependence of the activity of zeolites on the temperature of their treatment with air was observed in [11] during the hydrogenation of 2-methyl-2-butene. Such zeolite activity can be explained by both a removal of water from the catalysts, and by an increase in the chemisorption of O_2 and its entrance into active centers. In conformance with [21, 22], O_2 is adsorbed on zeolites in the Na form in a wide temperature interval (from ~ 20 to 400-550°C).

Elucidation of the role of H_2 began with the study of its influence on the activity of NaM, NaY, and NaA in the hydrogenation of acetone. All experiments were conducted at 220°C, while the preliminary hydrogen treatment of the zeolites was conducted in an interval from 250 to 450-500°C. The obtained results (Fig. 2) completely correlate with the data in [11, 15]: the activity of the zeolites passes through a maximum with an increase in the temperature of the H_2 treatment.

Data concerning the changes of the extent of the hydrogenation of benzene on NaM with temperature are presented in Fig. 3. All experiments are conducted on one sample of catalyst; each experiment was conducted immediately after the treatment of the catalyst with air, then the experiments at relatively low and relatively high temperatures were alternated. Upon an increase in temperature from 200 to 250°C the extent of the reaction was increased from 70 to 90% and then was sharply decreased to 1% at 400°C. One can assume that such a sharp drop in the hydrogenating activity of NaM is caused by deposition of the condensation products which are removed as a result of the subsequent treatment with air. For verification of this assumption we conducted another series of experiments at 250°C and a pressure of 50 atm (Table 1), with the alternation of the two types of preliminary treatment of NaM; either with air and then with H_2 or only with air. With this we conducted the treatment of the catalyst with H_2 at 400°C, a pressure of 50 atm for 2 h, i.e., under conditions during which the extent of the hydrogenation of benzene was 1%. The data of Table 1 shows that additional treatment of NaM with hydrogen led to practically its complete deactivation (conversion 1%), while treatment of the catalyst with only air reduced its activity by a conversion of 87-88%. Consequently, the observed deactivation of NaM with an increase in temperature is not determined by "clogging with coke" of the zeolite, but is caused by some other reasons. One could assume, for example, that 0_2 of the air not only removes the carbonaceous deposit but also enters into the active centers of the zeolites. With this, H2 is capable of removing 0_2 at a high temperature (400-500°C) and of destroying the active centers. It is impossible to exclude another role of H_2 : that of its chemisorption on zeolite at 400-500°C and its



Fig. 2. The dependence of the extent of the hydrogenation of acetone on the temperature of the treatment of the zeolites with hydrogen (4 h). Experimental conditions are designated in Fig. 1.

Fig. 3. The dependence of the extent of the hydrogenation of benzene on zeolite NaM on temperature. Experimental conditions are 50 atm, benzene flow rate of 0.01 mole/h on 1 g NaM.

deactivation of the catalyst. We will look at the example of the hydrogenation of benzene over NaY for the validity of these two alternative assumptions about the reasons for the deactivation of zeolites by H_2 .

The following series of experiments was conducted with NaY (Fig. 4). In this series the experiments were conducted both immediately after air treatment (curve 1) and also after additional H₂ treatment which was carried out at the temperature of the experiment and pressures of 1, 5, and 30 atm (corresponding to curves 2, 3, and 4). Data presented in Fig. 4 permit the following conclusion: treatment of a zeolite with H₂ at 225-275°C increased its hydrogenating activity, while the effectiveness of the treatment is decreased according to the degree of increase in pressure of the H₂ from 1 to 5 atm and further to 30 atm; on the other hand, H₂ treatment at 350-400°C deactivated the catalyst.

We note here the effect established earlier [23] of the activation of the zeolite NaM by hydrogen, which also appeared in those cases where experiments of the hydrogenation of benzene at 190°C were supplemented with treatment of the catalyst with H_2 for 5 h at that same temperature. An increase in the number of treatments up to 10 led to a gradual increase in the yield of cyclohexane from 10 to 86%.

Further, a series of experiments was conducted (analogous to those described earlier, see Table 1) with the goal of explaining whether or not the deactivation of NaY at 400°C (as this indicates from Fig. 4) is connected with the formation of a carbonaceous deposit.

TABLE 2. The Influence of the Preliminary Treatment of Zeolite NaY on Its Catalytic Activity in the Hydrogenation Reaction of Benzene (250° C, 30 atm, C₆H₆ flow rate of 0.01 mole/h on 1 g NaY)

Expt.	Conditions of treatment of catalyst before expt.	Conversion of C_6H_6 to $C_6H_{12_6}$ %
f	Air 520 °C atmospheric pressure, 5 h	58,0
23	Air 520 °C atmospheric pressure 5 h Air 520 °C atmospheric pressure 5 h; H ₂ 400 °C, 30 atm	53,9 0,5
4 5	Air, 520 °C, atmospheric pressure, 5 h Air, 520 °C, atmospheric pressure, 5 h; H ₂ ,400 °C, 30	68,5 0,3
6 7 8	atm, 2 ft Helium, 520°C, atmospheric pressure, 5 h Hydrogen, 400°C, 30 atm, 2 ft Helium, 520°C, atmospheric pressure, 5 h	50,4 4,4 60,7



Fig. 4. The dependence of the extent of the hydrogenation of benzene on NaY zeolite on the temperature and pressure of the preliminary treatment of the catalyst with H₂. Experimental conditions are 30 atm, C₆H₆ flow rate of 0.01 mole/h on 1 g NaY. All H₂ treatments are conducted for 2 h at the temperature of the experiments. Before each experiment and prior to the H₂ treatment the catalyst was treated with air (520°C, 5 h): 1) without H₂ treatment; 2) H₂ treatment at 1 atm; 3) H₂ treatment at 5 atm; 4) H₂ treatment at 30 atm.

Fig. 5. The influence of the length of the preliminary H_2 treatment of zeolites at 400°C and various pressures on the extent of the hydrogenation of benzene. Experimental conditions are 400°C, 50 atm, C₆H₆ flow rate of 0.01 mole/h on 1 g Ct. Before each experiment and prior to the H₂ treatment the Ct was treated with air (520°C, 5 h): 1) NaY, H₂ treatment at 1 atm; 2) NaY, H₂ treatment at 5 atm; 3) NaY, H₂ treatment at 50 atm; 4) NaM, H₂ treatment at 5 atm.

One can conclude from the data in Table 2 that after the treatment of NaY with only air at 520°C the extent of the reaction reached 50-70% (expts. 1, 2, and 4), while additional H_2 treatment of the catalyst at 400°C and 30 atm led to practically its complete deactivation (expts. 3 and 5). Consequently, the deactivation of the catalyst at 400°C is not connected with the deposit of "coke" in experiments with NaM and NaY. In order to explain the necessity of atmospheric 0_2 for the reduction of the hydrogenating activity which is suppressed by H_2 treatment at 400°C, the air treatment of the zeolite in expts. 6 and 8 of the series was replaced by treatment with pure helium (which was passed over reduced copper at 300°C for additional purification from O_2). The presented data indicates that the helium reduces the hydrogenating activity of the zeolite as successfully as air. We note that a similar result was obtained in [11] during the study of the hydrogenation of 2-methyl-2-butene on zeolite NaY: after the treatment of two samples of the catalyst with H_2 at 500°C the extent of the reaction did not exceed 1%, and subsequent treatments at the same temperature by both air and helium led to a sharp and practically identical increase in activity, the yields of isopentane from both samples being $\sim 50\%$. Thus, the data obtained by us in conjunction with the results in [11] allow one to assume that the suppression of the hydrogenating activity of zeolites by H_2 at 400-500°C is explained by its chemisorption at this temperature, and the reduction of the activity of the catalysts after their treatment with air or helium is connected with the removal of chemisorbed H2.

Comparison of our results with data in [11, 15] leads to the conclusion that hydrogen, depending on temperature and pressure, exerts opposite influences on the hydrogenating activity of zeolites in the Na form; i.e., either increases it or suppresses it. In connection with this one must consider the existence of at least two forms of chemisorbed hydrogen. One of them is mainly formed at a relatively low temperature (200-300°C) and pressure (1-5 atm) and increases the hydrogenating activity of zeolites in the Na form, whereas the second deactivates the catalysts, the optimum conditions for its onset being a relatively high temperature (400-500°C) and pressure. Evidently both forms of chemisorbed hydrogen emerge simultaneously. One must suppose that the decrease in the effectiveness of H₂-treated NaY at 250°C with a change in pressure from 1 to 30 atm (see Fig. 4) is connected with an increase in the portion of the second proposed form of chemisorbed hydrogen. Therefore, one should also investigate the question as to whether H_2 can activate zeolites at 400°C, i.e., under conditions which are optimum for the formation of its second form. With this goal in mind, experiments on NaY and NaM were conducted and the influence of the length of the H_2 treatment at 400°C on the hydrogenating activity was cleared up (Fig. 5). An increase in the length of the H_2 treatment from 1 to 4 h led to a substantial increase in the extent of the reaction. Consequently, H_2 is capable of both activating and suppressing the hydrogenating activity of NaY and NaM in almost the entire temperature interval which was studied.

CONCLUSIONS

1. The influence of hydrogen on the catalytic activity of Na-mordenite, NaY, and NaA zeolites in hydrogenation reactions of acetone and benzene was studied. Hydrogen at 400-500°C practically completely deactivates the catalysts. Air or helium reduces the hydrogenating activity of the catalysts.

2. Treatment of NaY with hydrogen at 190-250°C and atmospheric pressure leads to a sharp increase in the hydrogenating activity of the catalyst.

3. The obtained results in conjunction with literature data permits the assumption of the existence of two forms of hydrogen, chemisorbed on zeolites in the Na form. The first of these is formed mainly at relatively low temperature and pressure and activates the catalyst, whereas the second form, which is formed at relatively high temperature and pressure, suppresses the hydrogenating activity of the zeolites.

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GAS PERMEABILITY OF COMPOSITE MEMBRANE CATALYSTS

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Membrane catalysts which are selectively permeable to hydrogen are active and selective with respect to reactions involving the splitting off or addition of hydrogen. The usual membrane catalysts represent thin-walled tubes or foils made of alloys based on Pd [1, 2]. In order to reduce the consumption of noble metals, composite membrane catalysts have been developed which have all the advantages of the membrane catalysts in the form of foils or tubes but contain less noble metals per unit surface area by a factor of 100. These catalysts consist of a strengthening metal-ceramic support, a layer of polymer which allows the passage of H_2 , and of a thin catalytically active layer of Pd or its alloy [3]. We have studied the gas permeability of composite membrane catalysts.

EXPERIMENTAL

Sheets of porous copper with the dimensions $118 \times 23 \times 0.5$ mm were thoroughly washed with CCl₄, then with acetone, and ethanol. A polymer film was then applied, 0.15 mm thick and based on polydimethylsiloxane rubber. The film was cured in air for 48 h at $\sim 20^{\circ}$ C and evacuated at 10^{-3} torr for 3-4 h at $\sim 20^{\circ}$. A Pd alloy with 9.8% Ru was then sublimated onto the film in an IEE-3B vacuum apparatus at 10^{-4} torr to give a layer 20-80 nm thick. The deviations from a uniform layer thickness of the metal were ± 5 -10%. The membrane was fastened hermetically between two steel plates with depressions so that two identical chambers were formed. H₂ or He, or their mixtures with Ar, were supplied to one of the chambers, while Ar alone was passed through the other chamber at a flow rate of 10 ml/min. The amount of H₂ or He diffused through the membrane was measured by means of an LKhM-8MD gas chromatograph with a katharometer detector (column 1 m × 3 mm, packed with CaA zeolite after preliminary evacuation; temperature 22°, carrier gas flow rate 50 ml/min); the chromatograms were processed on a PEP-1 computer.

DISCUSSION OF RESULTS

The permeability of the polymer film and of the composite membrane catalysts were studied at pressure drops between the inlet and outlet sides varying from 1-2 atm at 20-200°. The linear increase of the permeability with increasing pressure drop (Fig. 1) indicates the participation of individual atoms, not molecules of H_2 , in the limiting stage of hydrogen transfer through the composite catalyst. This conclusion is confirmed by the fact that the hydrogen permeability of the composite membrane catalysts is independent whether the H_2 is entering the polydimethylsiloxane film (black dots on the straight line 3 in Fig. 1) or the layer of Pd-Ru alloy that covers it (white circles on the same straight line). In the latter case one would expect an increase in permeability when H atoms are passing through the polydimethylsiloxane film. In all specimens studied the permeability towards He is lower than towards H_2 (compare the straight lines 3 and 3', and 5 and 5'). The

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