THE UNIQUE INFLUENCE OF THE PRESSURE OF HYDROGEN AND ADSORBED WATER ON THE ACTIVITY OF AN ALUMINOPLATINUM CATALYST IN THE HYDROGENOLYSIS OF METHYLCYCLOPENTANE

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In [1] an unusual dependence of the activity of a 0.3% Pt-Al₂O₃ catalyst in the hydrogenolysis of methylcyclopentane on the pressure of hydrogen and water adsorbed by the catalyst was noted. The introduction of water into the catalyst (by long treatment of it with hydrogen with an oxygen impurity) led to an increase in the reaction rate in experiments at 10 atm, and, on the contrary, deactivated the catalyst in experiments at 50 atm. Hydrogen pressure also changes the reaction rate in opposite directions, depending on the presence of water in the reaction system: increasing p_{H_2} leads to an increase in the activity of a catalyst from which water was preliminarily removed; on the other hand, it deactivated the catalyst after its saturation with water. Thus, the sign of the effect of hydrogen pressure on the activity of a catalyst is determined by the presence of water in the system, while the sign of the influence of water on the activity of the catalyst, in turn, depends on the hydrogen pressure. A conclusion on these effects of p_{H_2} and water was drawn in [1] on the basis of a comparison of the results of the experiments described in [1-3] and conducted with various samples of the catalyst. To better substantiate this conclusion, in this work we conducted an analogous investigation of one catalyst sample.

EXPERIMENTAL METHOD

The hydrogenolysis of methylcyclopentane was conducted in a flow-type system. Methods of preparation of the catalyst [4] and analysis of the reaction products [5], as well as the method of purification of electrolytic hydrogen from oxygen and water [6], were described earlier. All the experiments were conducted with one sample of an aluminoplatinum catalyst (platinum content 0.3%, weight of the catalyst sample 9.0 g, bulk volume 14 ml, size of tablets 4×4 mm) at 350° and a total pressure of 10 and 50 atm. Two series of experiments were conducted: in the first hydrogen containing traces of oxygen (~0.1%) was used, while in the second oxygen and water were removed from the hydrogen. After the first series of experiments, the catalyst was treated for a long time (18 h) with purified hydrogen at 550° and a rate of flow of 90 liters/h to remove adsorbed water from the catalyst. Between experiments the catalyst was treated with hydrogen of the corresponding purity for 4 h at the indicated rate of flow, at 350° in the first series of experiments and at 550° in the second.

All the experiments at 10 atm and experiments 2, 6, and 8 at 50 atm were conducted at a rate of delivery of methylcyclopentane of 0.13 mole/h and a mole ratio $H_2: C_5H_9CH_3 = 9$ (Table 1). Under these conditions, when the pressure was increased from 10 to 50 atm, not only the partial pressure of hydrogen increased (from 9 to 45 atm), but also the partial pressure of methylcyclopentane (from 1 to 5 atm) and the conditional time of contact (from 8 to 40 sec).* A comparison of the results of experiments at constant

*The conditional time of contact was calculated according to the equation $\tau = V/\Sigma V$, where V is the volume of the catalyst; ΣV is the sum of the volumes of hydrogen and methylcyclopentane passed over the catalyst in 1 sec and reduced to the conditions of the experiments.

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nt	Pressure, atm	Conditional time of con- tact, sec	Mole ratio H₂ : C₀H₀CH₃	Content in catalysts, %				1 m
Experime No.				2- methyl- pentane	3- methyl- pentane	n- hexane	Sum of hy- drogenolysis products (ΣC ₆)	Ratio nh: (2-mp + mp)
Experiments with hydrogen containing an oxygen impurity								
1 3 5 2 4	10 10 10 50 50	8 8 40 8	9 9 9 50	22,318,218,72,21,18	6,5 5,9 6,9 1,05 0,70	14,1 8,5 10,2 1,24 0,65	42,9 32,6 35,8 4,5 2,5	$0,49 \\ 0,35 \\ 0,39 \\ 0,38 \\ 0,36$
Experiments with hydrogen freed of oxygen and water								
7 10 6 8 9	10 10 50 50 50		9 9 9 50 50	$0,63 \\ 0,46 \\ 0,72 \\ 0,70 \\ 0,28 \\ 0,32 $	$0,32 \\ 0,19 \\ 0,55 \\ 0,54 \\ 0,22 \\ 0,25$	$ \begin{array}{c c} 3,1 \\ 2,8 \\ 12,7 \\ 14,4 \\ 6,8 \\ 7,8 \\ \end{array} $	4,1 3,4 14,0 15,6 7,3	3,3 4,2 10,3 11,6 13,7 43,8

TABLE 1. Hydrogenolysis of Methylcyclopentane over a 0.3% Pt $-Al_2O_3$ Catalyst (Temperature 350°, amount of catalyst 9.0 g (14 ml), rate of delivery of $C_5H_9CH_3$ 0.13 mole/h)

pressure from the first and second series permitted us to judge the change in the activity of the catalysts when water was removed from it, but for unambiguous conclusions on the influence of the hydrogen pressure on the activity of the catalyst, the conditions described should be somewhat changed. Therefore, experiments 4, 9, and 11 were also conducted at 50 atm and at the same rate of delivery of methylcyclopentane (0.13 mole/h) but at a larger ratio of hydrogen to methylcyclopentane $-H_2: C_5H_9CH_3 = 50$. These experiments differed from the experiments at 10 atm only by a larger partial pressure of hydrogen (49 and 9 atm, respectively), while the conditional time of contact (8 sec) and partial pressure of methylcyclopentane (1 atm) remained constant.*

DISCUSSION OF RESULTS

The results obtained confirm the conclusions of [1]. From data of Table 1 it follows that the removal of water from the catalyst by high-temperature treatment led in the experiments at 10 atm to a decrease in the yields of products of hydrogenolysis of methylcyclopentane from 33-43 to 3-4% (see experiments 1, 3, 5, 7, and 10), and, on the contrary, to an increase in these quantities from 5 to 14-16% in the experiments at 50 atm (experiments 2, 6, and 8). The hydrogen pressure has the opposite influence on the reaction rate as a function of the presence of water in the catalyst. Increasing the hydrogen pressure from 9 to 49 atm in a series of experiments with a "fresh" catalyst caused a decrease in the yields of the products of hydrogenolysis from 33-36 to 3% (compare experiments 3 and 5 with experiment 4), while variation of p_{H_2} within the same limits after the removal of water from the catalysts led to an increase in the reaction rate – the sum of the products of hydrogenolysis rose from 3-4 to 7-8% (compare experiments 7 and 10 with experiments 9 and 11). The results obtained are illustrated by Fig. 1.†

In [1-3], on the basis of a study of the reaction kinetics, it was hypothesized that the hydrogenolysis of methylcyclopentane on an aluminoplatinum catalyst can proceed according to two mechanisms. The first mechanism predominates on a catalyst containing adsorbed water. This mechanism is characterized by predominant cleavage of bonds of the methylcyclopentane ring distant from the substituent and the formation of methylpentanes. When the reaction proceeds according to the first mechanism, the ratio of n-hexane (nh) formed to the sum of 2-methylpentane (2-mp) and 3-methylpentane (3-mp) is less than one [nh: (2-mp + 3-mp) < 1]. After the removal of water from a 0.3% Pt-Al₂O₃ catalyst, the reaction proceeds chiefly according to the second mechanism. The second mechanism is characterized by predominant formation of n-hexane as a result of hydrogenolysis of the bonds of the methylcyclopentane ring closest to the substituent [nh: (2-mp + 3-mp) > 1]. Then, on the basis of a comparison of the data of [1-3], it was assumed that the hydrogen pressure inhibits the reaction proceeding according to the first mechanism, and, on the contrary, accelerates it in the case of predominance of the second mechanism. The latter assumption is correlated with the results of this work: the activity of a catalyst containing adsorbed water decreases

^{*}Experiments 2, 6, and 8 at 50 atm and time of contact 40 sec were conducted to obtain a larger degree of reaction.

 $[\]dagger$ Figure 1 is only an illustration, and of course, cannot serve as a basis for conclusions of a linear dependence of the activity and selectivity of the catalyst on p_{H_2} .



Fig. 1. Influence of the hydrogen and water pressure on the activity (a) and selectivity (b) of a 0.3% Pt-Al₂O₃ catalyst: 1) experiments with a catalyst containing adsorbed water; 2) experiments after removal of water from the catalyst.

with the hydrogen pressure, and, on the contrary, increases with increasing p_{H_2} after the removal of water from the catalyst (see Fig. 1).

From the data of Table 1 it follows that in experiments with a catalyst containing adsorbed water, the ratio nh : (2-mp + 3-mp) was unchanged with the hydrogen pressure and was an average of 0.39. Evidently in these experiments the reaction proceeded according to the first mechanism. The removal of water from the catalysts led to a sharp increase in the ratio nh : (2-mp + 3-mp). However, this ratio increased in the experiments at 10 atm considerably less (from 0.35-0.49 to 3.3-4.2) than in experiments at 50 atm (from 0.36-0.38 to 10.3-13.8). In other words, the ratio nh : (2-mp + 3-mp) increased both when water was removed from the catalyst and when the hydrogen pressure was increased in experiments with a dehydrated catalyst (see Fig. 1). From the viewpoint outlined, the replacement of the first mechanism by the second occurred not only when water was removed from the catalyst, but also when p_{H_2} was increased. Possibly in experiments at 10 atm, conducted after the removal of water from the catalyst, the reaction still occurred to a substantial degree according to the first mechanism. Therefore, dehydrated catalyst, the second mechanism already dominated, and as a result of this, the removal of water from the catalyst led to an increase in its activity in experiments at the indicated pressure.

Thus, the unique influence of adsorption of water and the hydrogen pressure on the activity of an aluminoplatinum catalyst might be due to hydrogenolysis of methylcyclopentane according to two mechanisms. In this case the water adsorbed by the catalyst promotes the occurrence of the reaction according to the first mechanism, while hydrogen pressure promotes the second mechanism.

CONCLUSIONS

1. The influence of hydrogen pressure and adsorbed water on the activity of a 0.3% Pt-Al₂O₃ catalyst in the hydrogenolysis of methylcyclopentane was investigated.

2. The activity of the catalyst decreases both with increasing hydrogen pressure from 2 to 49 atm in experiments with a catalyst containing adsorbed water, and when water is removed from the catalyst in experiments at a total pressure of 10 atm.

3. The activity of the catalysts increases both when the hydrogen pressure is increased from 9 to 49 atm in experiments with a catalyst freed of adsorbed water and when water is removed from the catalysts in experiments at a total pressure of 50 atm.

4. On the basis of the assumption of two mechanisms of the reaction, an explanation was suggested for the opposite changes in the activity of the catalyst with increasing hydrogen pressure or with the removal of water from the system.

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