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Abstract

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CHEMISTRY

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CHANGE IN THE RATE AND DIRECTION OF HYDROGENOLYSIS OF METHYLCYCLOPENTANE DURING HIGH-TEMPERATURE TREATMENT OF AN ALUMINA-PLATINUM CATALYST WITH HYDROGEN

(Presented by Academician B. A. Kazanskii, 8 V 1964)

In our papers (^{1,2}) it was shown that purification of $Pt-Al_2O_3$ catalysts from oxygen and water by treatment with hydrogen at 500–550° leads to practically complete deactivation of these catalysts in the reactions of benzene hydrogenation and cyclohexane dehydrogenation. Hydrogenation and dehydrogenation of hydrocarbons, as well as hydrocracking of hydrocarbons (a special case of which is the hydrogenolysis of methylcyclopentane), are usually assigned to one class of reactions–oxidation-reduction reactions (see, for example, (^{3})). It could therefore be expected that high-temperature treatment of an alumina-platinum catalyst with hydrogen would also cause a decrease in the rate of hydrogenolysis of methylcyclopentane.

Cleavage of the five-membered ring of methylcyclopentane during its hydrogenolysis may proceed in different directions, with formation of *n*-hexane, 2-methylpentane, and 3-methylpentane. From the data of the work of Sinfelt and Rohrer (^{4}) it follows that, in the hydrogenolysis of methylcyclopentane over a 0.3% $Pt-Al_2O_3$ catalyst at 471° and a pressure of 7–21 atm, the ratio of the *n*-hexane formed to the sum of 2- and 3-methylpentanes ($n\text{-}C_6H_{14}/\Sigma\text{-iso-}C_6H_{14} = \gamma$) was 1. In the work of Barron and coauthors (^{5}) it was found that, in the presence of a 0.2% $Pt-Al_2O_3$ catalyst at 270–330° and atmospheric pressure, $\gamma = 0.5$. Data on the influence of oxygen and water on the rate and direction of the catalytic hydrogenolysis of methylcyclopentane are absent from the literature. In the present work we have investigated the change in the rate and direction of hydrogenolysis of methylcyclopentane during purification of a 0.3% $Pt-Al_2O_3$ catalyst from oxygen and water by prolonged treatments with hydrogen at 550°.

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Experimental part

The apparatus, the method of preparing the catalyst, and the method of purifying electrolytic hydrogen from oxygen and water have been described previously ([1]). All operations were carried out with purified hydrogen. The catalyst was treated with hydrogen at 350 and 550°, a pressure of 60–120 atm, and a hydrogen flow rate of 2.7 mol/hr. Hydrogenolysis of methylcyclopentane was studied at 350° and 50 atm. The chromatographic method used for analysis of the catalyzates is described in work ([6]). Table 1 gives the results of a study of the hydrogenolysis of methylcyclopentane over two portions of catalyst (12.0 g each, pellet size 4 × 4 mm). The first experiments over each portion were carried out after treatment of the catalyst with hydrogen at 350°. Then each portion was treated with hydrogen at 550°, after which two more experiments were performed. From the data of Table 1 it is seen that treatment of the catalyst with hydrogen at 550° caused not a decrease (as might have been expected –see above), but, on the contrary, a sharp increase in the rate of hydrogenolysis of methylcyclopentane. At the same time, the composition of the reaction products also changed. Before

high-temperature (550°) treatment of the catalyst with hydrogen, the values of γ were 0.65 and 0.48, i.e., the direction of hydrogenolysis of methylcyclopentane practically did not differ from that observed by other authors ([4,5]). After purification of the catalyst from oxygen and water, the values of γ increased and reached 11–13 and 4, i.e., the main reaction product became *n*-hexane.

Table 1

Effect of high-temperature treatment with hydrogen of a 0.3% Pt–Al_2O_3 catalyst on the rate and direction of hydrogenolysis of methylcyclopentane; 350°, 50 atm, $H_2 : C_5H_9CH_3 = 7$ (mol.)

Treatment of catalyst with hydrogen before experiment	Feed rate of $C_5H_9CH_3$, mol/hour per 1 g of catalyst	2,2-dimethylbutane	2-methylpentane	3-methylpentane	*n*-hexane	methylcyclopentane	cyclohexane	*n*-C_6 / Σ iso-C_6
350°, 4 hours	0.022	–	1.1	0.6	1.1	95.5	1.7	0.65

Treatment of catalyst with hydrogen before experiment	Feed rate of $C_5H_9CH_3$, mol/hour per 1 g of catalyst	2,2-dimethylbutane	2-methylpentane	3-methylpentane	*n*-hexane	methylcyclopentane	cyclohexane	*n*-C_6 / Σ iso-C_6
550°, 19 hours	0.022	–	1.4	–	18.0	75.8	4.8	12.9
Without treatment *	0.022	–	1.1	–	12.5	83.0	3.4	11.4
350°, 4 hours **	0.005	–	4.2	2.4	3.2	88.2	2.0	0.48
550°, 55 hours	0.006	0.6	10.2	7.6	65.3	13.8	2.5	3.5
Without treatment *	0.006	traces	9.0	7.0	65.4	16.4	2.2	4.1

* The experiment was carried out after the preceding one without additional treatment of the catalyst with hydrogen.
** New portion of catalyst.

Table 2

Change in the activity of a 0.3% $Pt{-}Al_2O_3$ catalyst as a result of its high-temperature treatment with hydrogen

Reaction	Temp., °C	P, atm	Hydrocarbon feed rate, mol/hour per 1 g of catalyst	Hydrogen : hydrocarbon	Conversion, wt. %, before high-temperature treatment with hydrogen	Conversion, wt. %, after treatment with hydrogen at 500—550°
Hydrogenolysis of methylcyclopentane	350	50	0.006	7	12	84—86
Isomerization of n-hexane	350	50	0.006	7	1	23—26
Isomerization of cyclohexane	350	50	0.006	7	1	40—50
Hydrogenation of benzene	300	80	0.7	20	31	4
Dehydrogenation of cyclohexane	420	20	0.25	25	18	4—5

It might have been supposed that the primary product of the hydrogenolysis of methylcyclopentane over alumoplatinum catalysts is n-hexane, which then undergoes a secondary isomerization reaction to isohexanes*. In this case, the observed increase in the value of γ after treatment of the catalyst with hydrogen at 550° could have been due only to a decrease in the rate of isomerization of n-hexane as a result of this treatment. In fact, however, it turned out that as a result of high-temperature treatments of the catalyst with hydrogen, its activity in the reactions of isomerization of n-hexane and cyclohexane does not decrease but, on the contrary, sharply increases. The experiments on the isomerization of these hydrocarbons were carried out over the same portion of catalyst and alternated with experiments on the hydrogenolysis of methylcyclopentane. The main results for the isomerization of n-hexane and cyclohexane are given in Table 2, from consideration of the data

* The assumption of isomerization of n-hexane is thermodynamically quite jus-

tified: the equilibrium value of γ calculated by us from the data of (7) at 350° is 0.42, i.e., close to the values of γ obtained in experiments with a catalyst not subjected to treatment with hydrogen at 550°.

which shows that before high-temperature treatment of the catalyst with hydrogen, isomerization reactions practically do not occur; however, after such treatment the isomerizing activity of the catalyst becomes very considerable. Consequently, the increase in the ratio *n*-hexane/Σ-isohexanes as a result of high-temperature treatment of the catalyst is not the result of secondary isomerization reactions. Finally, one might have supposed that the formation of *n*-hexane is due to a significant extent to the isomerization of methylcyclopentane into cyclohexane and the subsequent hydrogenolysis of the latter. In this case the formation of *n*-hexane from cyclohexane should proceed considerably faster than from methylcyclopentane. However, the data obtained by us indicate the opposite: the content of *n*-hexane in methylcyclopentane catalyzates considerably exceeds the content of *n*-hexane in cyclohexane catalyzates. Thus, at a feed rate of 0.006 mole/hour/g catalyst, methylcyclopentane catalyzates contained 65% *n*-hexane, whereas cyclohexane catalyzates contained only from 18 to 28%. Thus, it may be considered proven that the substantial increase in the value of γ as a result of high-temperature treatment of the catalyst with hydrogen is due to a change in the site of preferential cleavage of the five-membered ring during hydrogenolysis of methylcyclopentane.

In Table 2, for comparison, previously obtained (2) data on the hydrogenation of benzene and the dehydrogenation of cyclohexane over the same catalyst are presented. These data show that high-temperature treatment of the catalyst with hydrogen led to a very sharp increase in the activity of the catalyst in isomerization and hydrogenolysis reactions and, conversely, to deactivation of the catalyst in hydrogenation and dehydrogenation reactions.

Discussion of Results

As a result of the work carried out, it has been established that purification of the catalyst from oxygen and water by means of high-temperature treatments with hydrogen caused a change in the direction of methylcyclopentane hydrogenolysis: whereas on a catalyst treated with hydrogen at 350° the five-membered ring of methylcyclopentane was cleaved predominantly at bonds distant from the substituent, with formation of isohexanes, after treatment of the catalyst with hydrogen at 550° the preferential cleavage of the five-membered ring occurred at the bonds nearest to the substituent, with formation of *n*-hexane. It seems obvious that the change in the direction of methylcyclopentane hydrogenolysis is due to a change in the state of the catalyst surface upon its purification from oxygen and water. It may further be assumed that the different directions of hydrogenolysis are associated with different orientations of the methylcyclopentane molecule on the purified and unpurified surfaces of the catalyst. If it is accepted that, on the catalyst studied before its high-temperature treatment with hydrogen, methylcyclopentane is adsorbed predominantly through the carbon atoms of the ring most distant from the substituent, then it is natural to assume that after purification of the catalyst surface from oxygen and water the molecule is adsorbed from the side of the substituent.

In recent years, data have been published on small permanent dipole moments of isobutane ([8]) and propane ([9]) molecules. Ferreira ([10]) analyzed the possible causes of the appearance of these dipole moments and came to the conclusion that molecules of other saturated hydrocarbons as well (with the exception of such as methane, ethane, and neopentane) may also have small permanent dipole moments. It may therefore be assumed that the methylcyclopentane molecule also has a small dipole moment. It is further known that, during adsorption on semiconductors, a charge arises in the surface layer of the adsorbent —positive upon adsorption of molecules with acceptor properties and negative upon adsorption of donors.

electrons ([11,12]). It is also known that oxygen is an acceptor, whereas hydrogen and water usually exhibit donor properties ([12,13]). It is possible that the removal (complete or partial) of oxygen and water from the catalyst we studied* during its high-temperature treatments with hydrogen led to a change in the sign of the charge of the surface layer and, as a consequence, to a change in the orientation of the methylcyclopentane molecule upon adsorption on the catalyst surface. Verification of the correctness of this assumption will be the subject of our further studies.

Senior laboratory assistant E. A. Udaltsova took part in the work.

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* Nicolescu and Popescu (^{14}), on the basis of studies of the dependence of the change in the electrical conductivity of a 1% Pt—Al_2O_3 catalyst on temperature, concluded that this catalyst behaves as a weak *p*-type semiconductor.

Note: Figure translations are in progress. See original paper for figures.

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