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## Abstract

## Full Text

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# ADSORPTION OF CYCLOHEXANE ON A CHROMIA-ALUMINA-POTASSIUM CATALYST

*(Presented by Academician B. A. Kazanskii, 13 IV 1963)*

In studying the adsorption of isopentane ([1,2]) and isopentene ([3]) on a chromia-alumina-potassium catalyst for paraffin dehydrogenation ([4]), we showed a very similar course of physical adsorption of both hydrocarbons under conditions in which chemisorption is not yet measurable (up to 150°), and very sharp differences in their chemisorption at higher temperatures. We found that desorption of the olefin cannot be the stage limiting paraffin dehydrogenation. A second reaction, practically and fundamentally important, carried out on chromia-alumina-potassium catalysts ([5,6]), is the dehydrocyclization of paraffins. In studying it, English researchers were unable to measure hydrocarbon chemisorption ([7]). Although the mechanism of this reaction on oxide catalysts as a whole is very complex, it is believed that cyclohexane in it proves to be either a primary or a secondary (formed from the olefin) intermediate product. Therefore, and also for the purpose of comparing the character of the sorption interaction of hydrocarbons of different classes with the catalyst over a wide temperature range, the study of the temperature course of cyclohexane adsorption is of undoubted interest. We carried it out on an apparatus ([8,9]) in which the vacuum microburet method is combined with the volumetric method. The pressure from a U-manometer and the position of the liquid meniscus in the microburet were measured with an accuracy of $±$0.01 mm. Adsorption of $C_6H_{12}$ was determined with an accuracy of 0.001 mM for the entire charge, or 0.0006 $\mu$M/m$^2$. The purity of the cyclohexane was proven chromatographically. The adsorbent—a K-544 catalyst of composition 13% $Cr_2O_3$, 84.6% $Al_2O_3$, and 2.4% $K_2O$—was reduced with isopentane ([2]) and contained no $Cr^{6+}$. The surface area of the entire catalyst charge, determined by the BET method from the Ar adsorption isotherm, was 1612 m$^2$, or 136 m$^2$/g; the effective pore diameter was 40 Å ([2]). Before the measurements the catalyst was pumped at 480-500° to a vacuum of $1 \cdot 10^{-3}$ mm Hg. Before the admission of $C_6H_{12}$, the pressure in the system at the experimental temperature was brought to $1 \cdot 10^{-5}$ mm Hg. The reproducibility of the isotherms was good. Up to 150°, adsorption of $C_6H_{12}$ vapor proceeds rapidly and reversibly (Fig. 1), and at a given $P$ decreases with increasing temperature. Adsorption at 20° and $P/P_s$ 0.07-0.2 obeys the BET

Fig. 1. Adsorption isotherms of cyclohexane vapor on the chromia-alumina-potassium catalyst at 20 (1), 50 (2), and 150° (3). Black symbols—desorption

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Figure 2

Figure 2: Figure 2

equation: the monolayer capacity is 3.12 $\mu$mol/m$^2$ $C_6H_{14}$, and the molecular area is $\omega = 53$ Å$^2$. With increasing temperature the form of the isotherms changes, and at 150° a linear dependence of the amount of adsorbed $C_6H_{12}$ on $P$ is observed. Mass-spectral analysis, for which we thank R. V. Dmitrieva, showed,

**Fig. 1.** Adsorption isotherms of cyclohexane vapor on the chromia-alumina-potassium catalyst at 20 (1), 50 (2), and 150° (3). Black symbols—desorption.

that in the gas above the catalyst at 150° only cyclohexane is present. The heats of its adsorption, calculated from the isotherms by the Clausius—Clapeyron equation, are as follows:

| $a$, $\mu$ mole/m$^2$ | 0.248 | 0.372 | 0.496 | 0.620 | 0.744 | 0.992 | 1.24 | 1.48 |
|---|---|---|---|---|---|---|---|---|
| $\theta$, % | 7.9 | 12 | 15.9 | 19.9 | 23.8 | 31.8 | 39.7 | 47.7 |
| $Q$, kcal/mole | 10.3 | 10.1 | 10.4 | 10.5 | 10.4 | 10.3 | 10.3 | 10.2 |

They are close to the heat of condensation at 20°, $Q_k = 7.92$ kcal/mole, and are almost independent of the degree of surface coverage. All the data we obtained indicate that up to 150° cyclohexane is adsorbed only physically and is not yet dehydrogenated.

**Fig. 2.** Adsorption isotherms on the chromia-alumina-potassium catalyst: 1 — cyclohexane at 150°; 2 —benzene at 250°; 3 —hydrogen at 250°; $a$ —cyclohexane at 250°

But at 250°, after admission of $C_6H_{12}$, the pressure above the catalyst first decreased and then began slowly to increase, which indicated its decomposition. After 150 h (for accumulation of products) the reaction was stopped; the hydrocarbons were frozen out from the gas phase and analyzed on a mass spectrometer. They contained only $C_6H_{12}$ (20%) and benzene (80%). Thus, at 250° and $P = 10$–$0.3$ mm Hg, cyclohexane is slowly dehydrogenated to benzene. The reaction was observed even at 200°. We calculated the amount of cyclohexane on the surface and in the gas phase at the moment the reaction was stopped and determined the magnitude of its chemisorption.

Denoting by $N_1$ the number of moles of $C_6H_{12}$ admitted into the volume above the catalyst; by $N_2 - N_6$, $N_1$ the number of moles of $C_6H_{12}$, $C_6H_6$, and $H_2$ in the adsorbed state; by $N_3$, $N_5$, $N_7$ the number of moles of the same substances in the gas phase; and by $N_8$ the total number of moles of substances in the gas phase at the moment the experiment was terminated, the reaction can be represented by the scheme:

$$\underset{N_1}{C_6H_{12}} \rightarrow \underset{N_2}{C_6H_{12,ads}} + \underset{N_3}{C_6H_{12,gas}} + \underset{N_4}{C_6H_{6,ads}} + \underset{N_5}{C_6H_{6,gas}} + \underset{N_6}{H_{2,ads}} + \underset{N_7}{H_{2,gas}},$$

in which the quantities of interest to us are $N_2$ and $N_3$. From stoichiometry we have that

$$N_2 + N_3 + N_4 + N_5 = N_1 \tag{1}$$

and

$$N_6 + N_7 = 3\,(N_4 + N_5). \tag{2}$$

The number of moles of gas in the system, determined from the final pressure,

$$N_8 = N_3 + N_5 + N_7. \tag{3}$$

According to the analysis data,

$$N_5/(N_3 + N_5) = \gamma = 0.8 \tag{4}$$

and from the adsorption isotherms of $C_6H_6$ and $H_2$, measured under the same conditions,

$$N_4 = f(N_5) \tag{5}$$

and

$$N_6 = f(N_7). \tag{6}$$

Figure 2 shows that the amount of adsorbed $C_6H_6$ and $H_2$ changes linearly with pressure at 250°. Therefore equations (5) and (6) can be written in the form $N_4 = \alpha N_5$ and $N_6 = \beta N_7$, where $\alpha$ and $\beta$ are constants. Solving the system of equations, we obtain that

$$N_2 = N_1 - N_8 \frac{1 + \alpha\gamma}{1 + \dfrac{3\gamma(1+\alpha)}{1+\beta}} \quad \text{and}$$

$$N_3 = \frac{N_8(1-\gamma)}{1 + \dfrac{3\gamma(1+\alpha)}{1+\beta}}.$$

schematic mechanisms of dissociative chemisorption: 1), 2), 3)

Figure 3: schematic mechanisms of dissociative chemisorption: 1), 2), 3)

Substituting the quantities known from the experiments and analysis,

$N_1 = 0.0458$ mmol, $N_8 = 0.0314$ mmol, $\gamma = 0.8$, $\alpha = 2.1$, and $\beta = 0.02$, we find that $N_2 = 0.0357$ mmol, $N_3 = 0.0007$ mmol, and the partial pressure of $C_6H_{12}$ in the gas phase is 0.29 mm Hg.

It is evident from Fig. 2 that the amount of adsorbed cyclohexane increased greatly with increasing temperature, i.e., at 250° its chemisorption takes place. After 150 hours of contact with the catalyst, 0.0357 mmol, or 78% of the amount introduced, had been chemisorbed; 2% was in the gas phase, and 20% had undergone dehydrogenation. Neither cyclohexene nor cyclohexadiene was detected in the gas phase.

The results obtained should formally lead to the conclusion that, under the conditions of our experiments, dehydrogenation is limited not by chemisorption but by the reaction itself, since there is a large amount of cyclohexane on the surface, which would be impossible if chemisorption were limiting: all the $C_6H_{12}$ would have had time to react. Neither desorption of $C_6H_6$ nor desorption of $H_2$ can limit the process at 250°, since under these conditions they are adsorbed only physically and in small amounts (Fig. 2). In addition, the surface of the catalyst is so large that all the introduced cyclohexane and all the reaction products could be adsorbed on it, even if they were adsorbed appreciably under these conditions. However, such a purely formal approach is not justified: it does not take into account the heterogeneity of the catalyst, arising from its complex chemical and phase composition. It is possible that a large fraction of the surface is active for chemisorption, while a small fraction is active for the reaction. In that case $C_6H_{12}$ would remain on the surface.

Turning to the question of the mechanisms of chemisorption and dehydrogenation and their relationship, let us consider two cases: a) associative chemisorption, if it occurs in our case, cannot be the first stage of dehydrogenation proper, since it proceeds without cleavage of the C–H bond in the hydrocarbon molecule*. For dehydrogenation, associatively chemisorbed molecules must pass into a state of dissociative chemisorption. Such a transition is associated with overcoming an activation barrier and, possibly, with the transfer of molecules from one adsorption center to another. If chemisorption had an associative character, then the transition from it to dissociative chemisorption could be the stage limiting the rate of dehydrogenation.

b) For dissociative chemisorption, the following mechanisms may be proposed:

each of which is essentially the first stage of dehydrogenation. In chemisorption according to any of these schemes, hydrogen must be formed in amounts

exceeding the total amount of gas present in the system in our experiment. Consequently, in assuming dissociative chemisorption, it is necessary at the same time to assume that the atomic hydrogen formed on the surface does not desorb from it. Since benzene at 250° is adsorbed physically and in small amounts, once formed it should rapidly desorb from the surface. In that case we would not have been able to detect chemisorbed cyclohexane on the surface. Contrary –

* By separate stages of the dehydrogenation reaction are meant the stages of successive abstraction of hydrogen atoms from the cyclohexane molecule.

contradiction with the experimental data makes it possible to exclude the sextet mechanism of dissociative chemisorption. Its probable variants may be taken to be chemisorption according to scheme 1 or 2. In these cases dehydrogenation is limited by the subsequent, slower detachment of the remaining hydrogen atoms. Such a representation is consistent with our experimental data, which show that, under the experimental conditions, desorption into the gas phase of intermediate products (cyclohexene and cyclohexadiene) does not occur. Another possible limiting stage of dehydrogenation in dissociative chemisorption may probably be recombination into molecules of hydrogen atoms bound to the catalyst surface. In this case, despite the reaction, chemisorbed cyclohexane would also remain on the surface.

We measured the chemisorption of cyclohexane in a static system at 250°, with a long contact time and a small amount of hydrocarbon on a large catalyst surface, i.e., under conditions far removed from the usual conditions for carrying out catalytic reactions in a flow system. Under other conditions, the relationships between the stages of the dehydrogenation mechanism may differ substantially from those described. This is already clear from the fact that, in work on the study of the temperature course of benzene adsorption, we established that it is chemisorbed at temperatures above 300°.

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## REFERENCES

1. A. M. Rubinshtein, K. I. Slovetskaya, T. R. Brueva, DAN, **134**, 836 (1960).

2. A. M. Rubinshtein, K. I. Slovetskaya, T. R. Brueva, *Kinetics and Catalysis*, **1**, 455 (1960).

3. A. M. Rubinshtein, K. I. Slovetskaya, T. R. Brueva, *Kinetics and Catalysis*, **2**, 584 (1961).

4. B. A. Kazanskii, M. N. Marushkin et al., DAN, **117**, 619 (1957).

5. A. F. Plate, *Catalytic Aromatization of Paraffinic Hydrocarbons*, Publishing House of the Academy of Sciences of the USSR, 1948.

6. M. O. Rosengart, B. A. Kazanskii, DAN, **119**, 716 (1958).

7. R. Chaplin, P. R. Chapman, R. H. Griffith, *Proc. Roy. Soc.*, **A-224**, 419 (1954).

8. A. M. Rubinshtein, Yu. A. Eltekov, T. R. Brueva, *Izv. AN SSSR, OKhN*, 1960, 2107.

9. Yu. A. Eltekov, *Advanced Scientific-Technical Production Experience*, Publishing House of the Academy of Sciences of the USSR, 1961.

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