Reports of the Academy of Sciences of the USSR

CHEMISTRY

1963

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1963. Volume 151, No. 3

CHEMISTRY

A. M. RUBINSHTEIN, K. I. SLOVETSKAYA, T. R. BRUEVA

STUDY OF THE ADSORPTION OF BENZENE IN THE TEMPERATURE RANGE FROM 20 TO 450° ON A CHROMIUM-ALUMINUM-POTASSIUM CATALYST

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

This work is one of a series of our studies devoted to investigating the nature and temperature course of the adsorption of hydrocarbon vapors on chromium catalysts for the dehydrogenation and dehydrocyclization of paraffinic hydrocarbons ([1,2]). We have shown that at low pressures under static conditions at 250° cyclohexane is chemisorbed on such a catalyst and is slowly dehydrogenated. Although these conditions differ very greatly from the usual conditions of dehydrocyclization (760 mm, 550–550°), in order to determine the limiting stage of the slow dehydrogenation observed by us at such a low temperature it was also necessary to study the adsorption properties of the reaction products—benzene and H_2—under the same conditions. Naturally, it was of interest to extend these measurements to higher temperatures, possibly closer to those customary for dehydrocyclization, which we have done in the present study, measuring adsorption isotherms on a vacuum apparatus and by the procedure described previously ([1,3,4]). The catalyst of composition 13% Cr_2O_3 –84.6% Al_2O_3 –2.4% K_2O, used by us also in studies ([1,2,5]), during all work with it did not come into contact with air and contained no Cr^{6+}. The catalyst sample weighed 11.85 g. The specific surface of the catalyst, calculated by the BET equation from data on the adsorption of Ar vapors, was 136 m^2/g, and the total surface of its sample was 1612 m^2. Before measuring each isotherm the catalyst was trained by evacuating it at 480–500° to a vacuum of $1 \cdot 10^{-3}$ mm Hg, and then the experimental temperature was set and, by further evacuation, a vacuum exceeding $1 \cdot 10^{-5}$ mm Hg was attained. The reproducibility of the isotherms was checked.

Table 1

Heats of adsorption of benzene vapors on the catalyst

Amount of adsorbed substance, μmol/m^2	θ, %	Q, kcal/mol
0.018	0.56	13.0
0.024	0.76	13.7
0.031	0.95	12.4
0.037	1.14	11.9
0.043	1.33	11.8
0.049	1.52	11.9
0.056	1.71	11.9
1.488	45	11.5
1.736	53	11.0
1.985	61	11.4
2.233	68	11.0

The adsorption isotherms of C_6H_6 vapors by the catalyst were measured at 20–250° up to a pressure of 20 mm Hg (Fig. 1), and at 300–450° up to a pressure of 2 mm Hg. At 20–250° the adsorption of C_6H_6 occurs rapidly and reversibly. The desorption points fall on the adsorption isotherm within the limits of experimental accuracy. All this, as well as the values of the heats of adsorption calculated from isosteres constructed from isotherms measured at 20–250° (Table 1), indicates physical adsorption of C_6H_6 on our catalyst in this temperature range. The figure shows that with increasing temperature the shape of the isotherms changes from convex at 20° to rectilinear at 250°. The adsorption isotherm at 20° is well linearized in the coordinates of the BET equation in the range p/p_s from 0.06 to 0.2. The amount of C_6H_6 adsorbed upon completion of a monolayer over the entire catalyst surface (1612 m^2) is 5.26 mmol. The area occupied by 1 molecule of C_6H_6 on the catalyst surface is 50 Å^2.

The heat of adsorption of C_6H_6, calculated from the constant of the BET equation $c = 29.3$, and the heat of condensation of C_6H_6 vapor, equal to 8.14 kcal/mole, is 12 kcal/mole. The data of Table 1 show that in the region of small surface coverages (up to $\theta = 1.5\%$) a decrease in the heat of adsorption is observed with increasing degree of filling. This indicates the heterogeneity of the surface for adsorption (possibly due to the presence of several phases

[Figure 1 and Figure 2]

Fig. 1. Isotherms of adsorption of benzene vapors on an aluminochromium-potassium catalyst (A) at 20° (1), at 50° (2). B –the same at 151° (1), at 200° (2), at 250° (3). Black symbols –desorption; symbols with strokes –independent repeated measurements

Fig. 2. Isotherms of adsorption of benzene vapors on an aluminochromium-potassium catalyst: 1 –at 250°, 2 –300°, 3 –354°, 4 –400°, 5 –450°

in the catalyst) and the filling, first of all, of its most active sites. In the region

of larger degrees of surface filling by benzene ($\theta > 1.5\%$), the heat of adsorption changes hardly at all with filling and is 11.5 ± 0.5 kcal/mole. Thus, the data of the calculation of Q from the constant of the BET equation and the heat of condensation agree well with the results given in Table 1 for the determination of Q from isosteres.

[Figure 3]

Fig. 3. Isotherms of hydrogen adsorption on an aluminochromium-potassium catalyst at 250° (1), 450° (2)

On going to higher temperatures, namely in the range 300–450°, the form of the adsorption isotherms of C_6H_6 vapors changes sharply. Fig. 2 shows that the rectilinear dependence on pressure, which exists at 250°, is disturbed; the isotherms again become convex, and with increasing temperature the amount of adsorbed C_6H_6 increases, in contrast to what is observed at 20–250°. These facts indicate that the character of the interaction of C_6H_6 with the surface has changed, i.e., that at 300–450° it is chemisorbed by the catalyst. This is also confirmed by the kinetics of adsorption: in the region of physical adsorption, equilibrium was reached in 0.5 hour. At 300° this required 17 days, since chemisorption requires activation energy. With an increase in temperature, the establishment of equilibrium accelerated: at 450° it was established in 1 day, with the amount of adsorbed C_6H_6 being 0.033 mmole as compared with 0.026 mmole at 300°, and the equilibrium pressure being 0.07 and 0.82 mm Hg, respectively. Since, in following the adsorption kinetics, we monitored only the pressure drop in the system and attributed it to the chemisorption of C_6H_6, it was very important to determine whether any other processes were taking place.

side processes leading to a decrease in pressure. In our view, the only reaction that could give a decrease in pressure in the system (and then only under the condition of strong adsorption by the catalyst of one or both reaction products) is the formation of diphenyl

$$2C_6H_6 \rightarrow C_6H_5 - C_6H_5 + H_2 \qquad (1)$$

which is much less volatile than C_6H_6. It is shown below (Fig. 3) that H_2 is adsorbed under these conditions in negligible amounts. Diphenyl, however, is probably removed from the surface with more difficulty than benzene. In any case, proof was required that reaction (1) did not have a substantial influence in our experiments. Only under this condition could it be asserted that benzene is chemisorbed as such. The results of a detailed study of the process at 450° show with complete clarity that, if reaction (1) did occur under our conditions, it did not exert a substantial influence on the pressure drop in the system, i.e., that the measurement results were due only to chemisorption of benzene. The relevant data are as follows. Into the volume above the catalyst, 0.096 mmole of C_6H_6 was admitted ($p = 43$ mm Hg). By the time equilibrium was established, p had fallen to 0.75 mm Hg. Calculation shows that in this case there are

Fig. 4. Adsorption isobars of cyclohexane vapor (1) and benzene (2) on an alumochromopotassium catalyst, $p = 1$ mm Hg.

Figure 1: Fig. 4. Adsorption isobars of cyclohexane vapor (1) and benzene (2) on an alumochromopotassium catalyst, $p = 1$ mm Hg.

0.094 mmole of substance on the catalyst surface and 0.0017 mmole in the gas phase. From the adsorption isotherm of H_2 (Fig. 3) it can be found that at 450° and 0.75 mm Hg the adsorption of H_2 is negligible—less than 0.00001 mmole. Consequently, all the hydrogen that could be formed according to reaction (1), if it occurred, would have to be in the gas phase. Thus, if it is assumed that the entire residual pressure in the system at equilibrium is due only to H_2, and that all the diphenyl and all the unreacted benzene are completely adsorbed on the surface, it follows that only 0.0017 mmole of H_2 could have formed. This means that only 0.0034 mmole of C_6H_6 from the 0.096 mmole admitted could have participated in reaction 1. Consequently, reaction 1 could have proceeded to a maximum extent of 4%, while the remaining 96% would have been benzene chemisorbed on the surface.

Fig. 4. Adsorption isobars of cyclohexane vapor (1) and benzene (2) on an alumochromopotassium catalyst, $p = 1$ mm Hg.

In addition to the previously measured ([1]) H_2 adsorption isotherm at 250°, in the present work we measured the isotherm at 450° (Fig. 3): threefold repeated measurements fall well on one straight-line isotherm. This indicates the reversibility of H_2 adsorption. Comparison of the H_2 adsorption isotherms at 450 and 250° shows that the amount of adsorbed H_2 decreases as the temperature of the experiment is raised. Apparently, on this catalyst under the conditions investigated, H_2 is adsorbed only physically. Such a conclusion is in full agreement with the fact that at 450° preliminary treatment of the catalyst with hydrogen has no influence on the subsequent adsorption of benzene at the same temperature.

Figure 4 gives the adsorption isobars of benzene and cyclohexane on the catalyst we studied, showing that in the temperature region in which physical adsorption of these hydrocarbons takes place, benzene is adsorbed in larger amount than cyclohexane. This result, as well as the larger heat of its adsorption (11.5 kcal/mole) compared with the heat of adsorption of cyclohexane (10 kcal/mole), may, by analogy with data on the adsorption of these same hydrocarbons on silica gel ([6]), be attributed to the additional interaction of the π-electron cloud of benzene with the catalyst surface. Under chemisorption conditions, however, ob-

opposite relations: cyclohexane begins to chemisorb at a temperature 100° lower than benzene. This means that its chemisorption proceeds with a lower activation energy and in a larger amount than the chemisorption of benzene.

Institute of Organic Chemistry

named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
8 IV 1963

REFERENCES

[1] A. M. Rubinshtein, K. I. Slovetskaya et al., DAN, **151**, No. 2 (1963). [2] A. M. Rubinshtein, K. I. Slovetskaya, T. R. Brueva, *Kinetika i kataliz*, **2**, 585 (1961). [3] A. M. Rubinshtein, Yu. A. El' tekov, T. R. Brueva, *Izv. AN SSSR, OKhN*, 1960, 2107. [4] Yu. A. El' tekov, *Peredovoi nauchno-tekhnich. proizvodstvennyi opyt*, *Izdatel' stvo AN SSSR*, 1961. [5] A. M. Rubinshtein, K. I. Slovetskaya, T. R. Brueva, *Kinetika i kataliz*, **1**, 455 (1960). [6] A. V. Kiselev, B. A. Frolov, *Kinetika i kataliz*, **3**, 774 (1962).

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