Russian Chemical Bulletin, International Edition, Vol. 49, No. 8, August, 2000

Physical adsorption and chemisorption of hydrocarbons on a reduced alumina-chromia catalyst

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Adsorption of ethane, butane, hexane, and benzene on a reduced alumina-chromia catalyst was investigated at 20—460 °C. The temperature ranges of physical adsorption and chemisorption were determined. The rate of hydrogen evolution is directly proportional to the rate of chemisorption of hydrocarbons. It was suggested that chemisorption of hydrocarbons results in the formation of intermediates in which Cr^{2+} ions and carbon atoms are linked by σ-bonds.

Key words: ethane, butane, hexane, benzene, physical adsorption, chemisorption, alumina-chromia catalyst.

Chromium oxide compounds are components of the active phase of catalysts for the dehydrogenation and aromatization of paraffins. The nature of active sites in these reactions has not been adequately studied. Some researchers[1] believe that the active sites of heptane aromatization in zinc-chromium catalysts contain Cr^{3+} ions. However, the previous study[2] on the adsorption of paraffins on alumino-chromium catalysts indicated that the crucial role in the active sites for the conversion of paraffins to olefins is played by Cr^{2+} ions. Investigation of adsorption of paraffins can throw light on the composition and structure of active sites. The purpose of this work is to study physical adsorption and chemisorption on an alumino-chromium catalyst.

Experimental

Adsorption of ethane, butane, hexane, and benzene was studied on an alumino-chromium catalyst (surface area 168 $m^2 g^{-1}$) containing Cr_2O_3 (9.3%) and Al_2O_3 (90.8%). The catalyst was prepared by impregnating aluminum hydroxide of bayerite structure with chromic acid. The impregnated material was dried at 20 °C and then at 100 °C and calcined in an air stream at 500 °C for 6 h. The catalyst reduced in a stream of H_2 at 550 °C contained 94 μg-ion g^{-1} of Cr^{2+}, which accounted for 6% of the total chromium content; 94% of the chromium occurred as Cr^{3+} ions. According to GC, the alkanes and benzene used in experiments were more than 99.5% pure. The amounts adsorbed were determined using a combined setup, which allowed operation with gaseous and liquid adsorbates. The design of the setup and the methods of operation were described in detail previously.[3] With use of a large sample of the catalyst (6.50 g) small (down to 10^{-2} μmol) adsorbed amounts can be measured with an accuracy of 0.002 μmol. Adsorption isotherms of hexane at 20—60 °C were obtained by the method of a capillary microburette for a liquid adsorbate. The volumetric method was also used to study adsorption of ethane, butane, hexane, and benzene in the temperature range from 20 to 500 °C. To construct the temperature dependences of the adsorbed amounts at a constant volume and a constant amount of the adsorbate in the system (adsorption isochores), a precisely measured hydrocarbon sample (~5—10 μmol) was introduced into an ampule with a catalyst maintained at a desired temperature. After the hydrocarbon had contacted with the catalyst for 1 h, the temperature was raised to the subsequent value. The contact time (1 h) was sufficient for an equilibrium in the physical adsorption processes to be established and for chemisorption (nonequilibrium process) to reach measurable values. The temperature was raised stepwise from 20 to 500 °C with a step of about 50 °C. The volumes of adsorbed ethane, butane, and benzene were found as the difference between the amount of adsorbate introduced in the tube and its amount in the gas phase. The volumes (cm^3) and pressures (Torr) were measured by a McLeod gage.

During adsorption of hexane, noncondensing gas appears in the gas phase over the catalyst starting from a temperature of 130 °C. Qualitative mass-spectral analysis of the gas phase showed that it contained only hexane and hydrogen. The amount of hydrogen evolved was measured and calculated in the following way. A gas in the sealed capillary of the McLeod gage was compressed to the limit, *i.e.* the cock used to lift mercury in the manometer was opened to air. As this was done, a ring of condensed liquid hexane and a column of noncondensed gas appeared in the sealed end of the capillary over the mercury column. Then the height of the column of noncondensed gas was measured and, taking into account the capillary cross-section, the volume of the gas was calculated. The partial gas pressure (P_1) in this space was calculated using the relation

$$P_1 = P_2 - h - P_3,$$

where P_2 is atmospheric pressure (Torr), h is the height of the mercury column in the gage measured from the level contacting with air to the level in the sealed end of the capillary, and P_3 is the pressure of saturated hexane vapor at 25 °C. When calculating the adsorbed amount of hexane, corrections were applied by subtracting the partial pressure of hydrogen from the total pressure measured.

Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1375—1378, August, 2000.

1066-5285/00/4908-1369 $25.00 © 2000 Kluwer Academic/Plenum Publishers

In the case of ethane and butane, it was impossible to determine separately the partial pressures of these gases and hydrogen by the methods used here because ethane and butane did not condense upon compression in the McLeod gage. Therefore, the calculated adsorbed amounts could be somewhat underestimated. However, it should be noted that the enhancement of adsorption at higher temperatures is a reliable experimental criterion pointing to chemisorption of the adsorbate.

In experiments on the kinetics of hexane adsorption, a required amount of a hydrocarbon was let into an ampule with a catalyst at the corresponding temperature. The variation of the amounts of adsorbed hexane and evolved hydrogen was monitored based on the change in their partial pressures. To ensure that the hexane pressure does not change by more than 10%, small amounts of hexane were added at intervals to the operation section of the setup, thus maintaining an approximately constant pressure. During the injection, the ampule with the catalyst was sealed. The change in the adsorption rate at a virtually constant pressure permitted differentiation of physically adsorbed and chemisorbed hexane. Physical adsorption is completed over a short initial period of about 2—3 min and then the amount adsorbed remains constant, whereas the chemisorbed amount continuously increases. The rates of hexane chemisorption and hydrogen evolution were calculated from the slope ratio of the straight lines reflecting the variation of the amount of adsorbed or evolved substance *vs.* time.

Results and Discussion

The ethane, butane, hexane, and benzene adsorption isochores measured at 20—500 °C on the alumino-chromium catalyst are shown in Fig. 1. It can be seen that, as the temperature increases in the 20—200 °C range, the amount of alkanes adsorbed decreases, while adsorption of benzene decreases in the 20—300 °C temperature range. The isotherms of hexane adsorption at 20—60 °C shown in Fig. 2 indicate that adsorption is a fast equilibrium process. The isosteric heats of hexane adsorption for a surface coverage of less than 5% amount to 44 kJ mol^{-1} (Table 1). The heats of adsorption of hexane on the alumino-chromium catalyst and on the chromium oxide systems studied previously[2] are higher than those on Al_2O_3 or SiO_2. The enhancement of hexane adsorption on chromium oxide systems is related neither to the pore size nor to the surface area of the catalyst. The adsorption heats decrease with decrease in the content of Cr^{2+} and approach the heats of nonspecific physical adsorption. These processes should be classified as physical adsorption or specific physical adsorption.

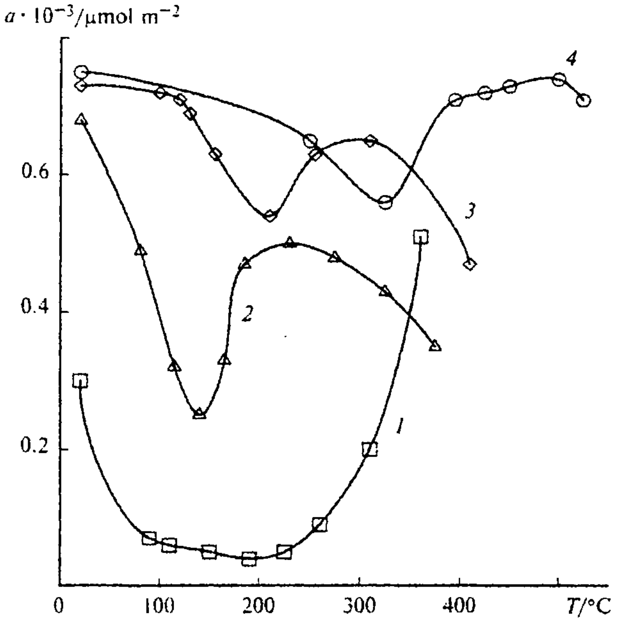

Fig. 1. Adsorption isochores (*a*) of ethane (*1*), butane (*2*), *n*-hexane (*3*), and benzene (*4*) on alumina-chromia catalyst.

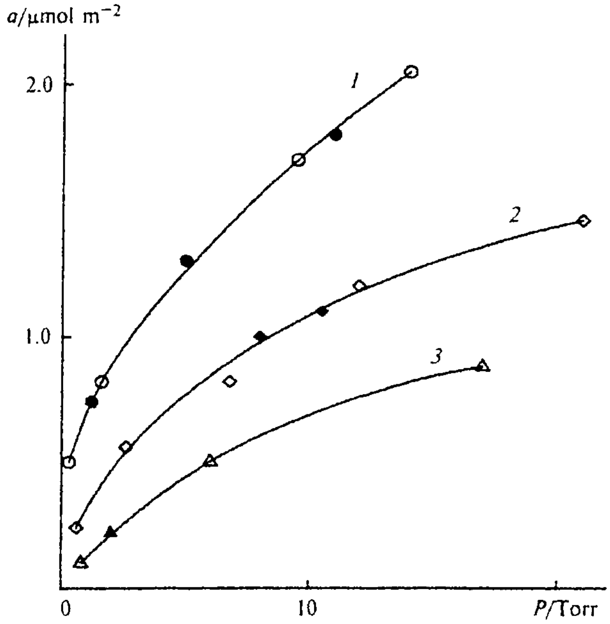

Fig. 2. Adsorption isotherms (*a*) of *n*-hexane on alumina-chromia catalyst at 20 (*1*), 40 (*2*), and 60 °C (*3*). Black dots correspond to desorption.

Table 1. Heats of adsorption of hexane (Q) on reduced chromium oxide catalysts

Catalyst	S* /m^2 g^{-1}	Pore diameter/Å	[Cr^{2+}] /μg m^{-2}	Q /kJ mol^{-1}
Cr_2O_3	17	140	3	67
Cr_2O_3 (9.3%)—Al_2O_3 (90.7%)	168	60	0.56	44
Cr_2O_3 (13%)—K_2O (2.5%)—Al_2O_3 (84%)	135	40	0.17	39
Al_2O_3[4]				35
SiO_2[5]	26			33

* The surface area of the catalyst.

In addition to the physical adsorption of ethane, butane, hexane, and benzene, chemisorption processes also take place on the alumina-chromia catalyst, as indicated by the increase in the amount of adsorbed hydrocarbon following an increase in temperature (see Fig. 1). The temperatures of the onset of chemisorption, corresponding to the minimum on the adsorption isochore, are 100, 150, 200, and 300 °C for ethane, butane, hexane, and benzene, respectively. Similar minima on the isochores of adsorption of ethane, butane, hexane, and benzene are displayed in the case of alumina-chromia-potassia catalyst.[2] Comparison of the temperatures of the onset of chemisorption of hydrocarbons, which characterize qualitatively the activation energy of chemisorption, shows that the activation energy of the chemisorption of the hydrocarbons increases with an increase in the molecular weight and with weakening of the electron-withdrawing properties of the hydrocarbons. The electron affinities[6] for the C_3—C_6 alkanes vary from 0.65 to 1.38 eV and those for benzene are −0.057 to −1.63 eV. The activation energies on the alumina-chromia-potassia catalyst increase almost twofold on passing from paraffins (17—47 kJ mol^{-1}) to benzene (80 kJ mol^{-1}). Correspondingly, the temperatures of the onset of chemisorption on both the alumina-chromia and alumina-chromia-potassia catalysts increase from 100—200 °C to 300 °C on passing from paraffins to benzene. Unlike sorption on the alumina-chromia-potassia system, chemisorption of hexane on the alumina-chromia catalyst is accompanied by hydrogen evolution to the gas phase. The evolution of hydrogen on the alumina-chromia-potassia catalyst is due to dehydration rather than to chemisorption. Thus, chemisorption of paraffins on alumina-chromia catalyst is a dissociative process, while that on alumina-chromia-potassia catalyst is an associative process. Benzene is chemisorbed on both catalysts without hydrogen evolution to the gas phase. In the case of chemisorption of hexane, the amount of compound sorbed increases with temperature and H_2 is evolved to the gas phase as a noncondensing gas. The time dependences of the evolved hydrogen and chemisorbed hexane at various pressures and temperatures are shown in Fig. 3. The rates of hydrogen evolution and hexane chemisorption calculated from the data obtained are proportional to each other (Fig. 4). The relationship between the amounts of chemisorbed hexane and evolved hydrogen (1 : 0.53) indicates that a hydrogen atom rather than an H_2 molecule is eliminated from the hydrocarbon molecule at 130 °C. Adsorption of H_2 under conditions of chemisorption of paraffins is negligible (C_6H_{14} : H_2 = 10 : 1). When the adsorption

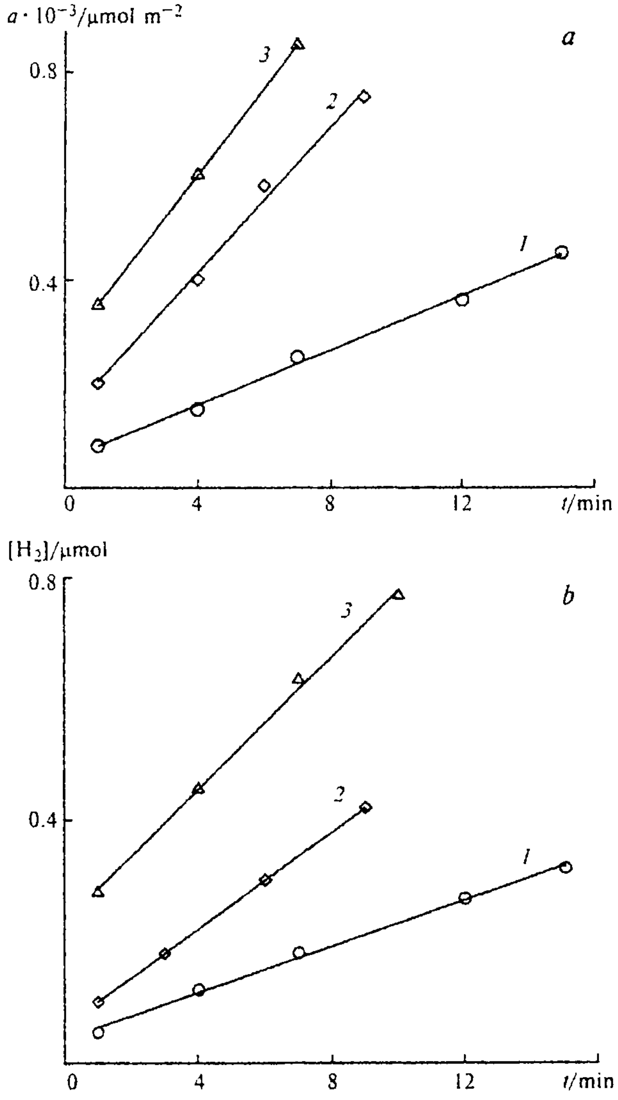

Fig. 3. Amounts of C_6H_{14} chemisorbed (*a*) and H_2 evolved (*b*) on alumina-chromia catalyst at 130 °C and a pressure of 0.08 (*1*), 0.16 (*2*), and 0.37 Torr (*3*).

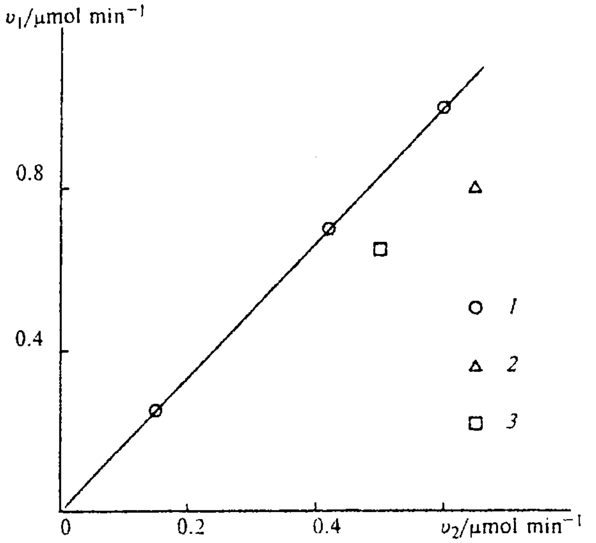

Fig. 4. Ratio of the rates of chemisorption of *n*-hexane (v_1) and evolution of hydrogen (v_2) on alumina-chromia catalyst at temperatures of 130 (*1*), 138 (*2*), and 152 °C (*3*).

temperature is raised from 130 to 150 °C, the ratio of the number of hydrogen molecules evolved to the gas phase to the number of hexane molecules adsorbed on the catalyst approaches 1. Thus, the abstraction of hydrogen from an alkane molecule on alumina-chromia catalyst occurs in two steps: first, when the chemisorption complex is formed and, second, when it is destroyed. When paraffins are chemisorbed on alumina-chromia-potassia catalyst, the abstraction of hydrogen occurs in one step upon decomposition of the chemisorption complex; this accounts for the much higher activity of alumina-chromia-potassia catalyst compared to alumina-chromia catalyst.

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Received June 25, 1999;
in revised form February 15, 2000