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Abstract

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Chemisorption of Isopropyl Alcohol on Catalysts –Ferroalumogels

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To characterize the activity and selectivity of oxide catalysts, the decomposition reaction of isopropyl alcohol is often used as a standard. This reaction can proceed in two directions: dehydration (for example, on Al_2O_3) and dehydrogenation (for example, on metals or oxides, including Fe_2O_3). A similar study, which is the subject of a separate communication, was carried out in our laboratory with ferroalumogels. It was therefore of interest to study the adsorption of isopropyl alcohol on $Fe_2O_3 \cdot Al_2O_3$ catalysts, on which both of these reactions take place; this was done in the present work. The study was carried out by the vacuum method on a McBain balance at 30°. The initial samples were prepared by coprecipitation of $Al(OH)_3$ and $Fe(OH)_3$ with a 10% aqueous solution of NH_4OH. The precipitates obtained were washed, dried, and molded into tablets (diameter 1.2–1.3 mm). Separate portions of these catalysts were heated for 7 hours at 400 and 600°. Before the experiments, the samples were evacuated to a pressure of 10^{-5} mm Hg and a temperature of 300°. Under analogous conditions, weighed portions of the same samples were evacuated and then calcined in air at 1250° in a crucible furnace in order to determine the loss in weight. This loss in weight was attributed to removal of structural water, the content of which in the experimental samples is given in Table 1.

Table 1

Fe_2O_3 content, mol. %	8	18	32	40	46	57
H_2O content, wt. %, at 400°	5.1	3.5	2.6	2.2	2.13	1.93

Fe_2O_3 content, mol. %	8	18	32	40	46	57
H_2O content, wt. %, at 600°	1.3	1.2	–	0.9	–	0.7

Since the molecular areas and the behavior of i-C_3H_7OH on the catalysts studied were not known, the values of the specific surface area

Table 2

	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %
	8	8	18	18	32	32	40	40	46	46	57	57
Treatment temperature, °C	400	600	400	600	400	600	400	600	400	600	400	600
Specific surface area s, m^2/g	360	215	350	200	320	160	280	150	270	160	260	120
Concentration of OH groups, $\mu eq/m^2$	15.6	6.7	11.1	6.6	9.0	–	8.8	6.8	8.8	–	8.2	4.9

	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %	Fe_2O_3 content, mol. %
Chemisorption fraction a_x, μmol/m^2	3.5	4.5	3.5	4.9	3.8	4.4	4.3	4.3	4.0	4.1	4.2	4.0
Area ω_0, Å^2	48	39	49	37	45	40	41	41	45	42	43	42

The samples were calculated by the BET method from adsorption isotherms of benzene vapor at 20°, taking the area per molecule in a close-packed monolayer to be 41 Å^2. From these isotherms the pore diameters and the total pore volume were calculated for each sample. The measurements showed that all the samples studied have comparatively wide pores, on the order of 60–100 Å; the exceptions were samples calcined at 400° and containing 8 and 46 mol.% Fe_2O_3, for which the pore diameter was somewhat smaller—about 50 Å. The values of the specific surface area are given in Table 2.

In experiments with absolute u-C_3H_7OH, the influence of the composition and the conditions of thermal treatment of the catalysts on its adsorption was studied. Figure 1 presents experimental isotherms of adsorption and desorption of u-C_3H_7OH on catalysts with different ratios of Fe_2O_3 and Al_2O_3, calcined at 400 and 600°. Desorption is indicated by black points. It is evident from Fig. 1 that isopropyl alcohol at 30° is chemisorbed on the surface of all the samples studied. The composition of the catalysts has little effect on the magnitude of chemisorption, which depends much more strongly on the magnitude of their specific surface area. This indicates that in the surface layer of the catalyst there is either only one component, or both components, chemisorbing isopropyl alcohol to the same extent. However, the first assumption proves untenable, since the catalysts were prepared by coprecipitation. The second assumption is confirmed by phase-analysis data, which showed that the catalyst components are dissolved in one another, forming two solid-solution phases: 1) up to 8 mol.% Fe_2O_3 in Al_2O_3 and 2) up to 25 mol.% Al_2O_3 in Fe_2O_3. Figure 1 also shows that increasing the calcination temperature of each catalyst leads to a decrease both in the total adsorption of u-C_3H_7OH and in its chemisorbed amount. This latter circumstance should be taken into account in elucidating the nature of chemisorption, since with more severe heat treatment: a) the water content decreases, and b) the specific surface area of each catalyst decreases. It is necessary to discuss the question of which surface groups undergo chemisorption.

Fig. 1. Sorption isotherms of isopropyl alcohol on $Fe_2O_3 \cdot Al_2O_3$ catalysts. Fe_2O_3 content in the catalyst (mol.%): 1–8, 2–18, 3–32, 4–40, 5–46, 6–57. Calcination temperature: a–400°, b–600°.

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In 1950, Kiselev and co-workers [1] discovered irreversible sorption of CH_3OH by silica gel as a result of the formation of a surface ether. In the work of Topchieva and Ballyod [2], it was established that, on interaction with aluminum oxide and an aluminosilicate catalyst, methyl alcohol forms analogous surface compounds through a surface reaction with hydroxyl groups according to the scheme:

$$CH_3OH + H{-}O{-}Al <-> H_2O + CH_3{-}O{-}Al <$$

Terenin and co-workers [3,4], and later Babushkin and co-workers [5,6], studying the infrared spectra of substances adsorbed on glasses, silica gel, and aluminum oxide, showed that, during adsorption of alcohols, there is a disappearance of the frequency characterizing unperturbed hydroxyl groups and the appearance of a frequency characterizing the C–O–M bond in bulk alco-

alcoholates. By optical methods, the formation of a surface complex due to the hydrogen bond

$$\begin{array}{c} M{-}O{-}H \\ \vdots\ \vdots \\ H{-}O{-}R \end{array}$$

was also detected. In the case investigated by us, the strong adsorption of *i*-C_3H_7OH indicates the formation of a surface alcoholate of the type: R–O–Me, which under catalysis conditions (with increasing temperature) can decompose, giving propylene.

Thus, it may be concluded that at room temperature chemical adsorption of isopropyl alcohol occurs on the surface of the catalysts, with the formation of surface alcoholates.

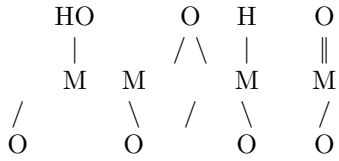
In considering the mechanism of chemisorption of isopropyl alcohol we proceeded from the assumption that hydroxyl groups are present on the catalyst surface. It is obvious that the concentration of OH groups on the surface depends on the composition of the bulk phase and on thermal treatment. From Table 1 it is seen that the water content in the catalyst decreases with increasing treatment

temperature and with increasing Fe_2O_3 content; moreover, the amount of water decreases faster than the value of the specific surface area (cf. Tables 1 and 2). This indicates that the concentration of OH groups per unit surface area of the catalyst decreases under these changes. In this case, it would seem, a decrease in the fraction of chemical adsorption should also occur. From the desorption kinetics, we estimated the fraction of chemisorption from that part of the sorbed amount of alcohol which is not removed by evacuating the samples at room temperature and a pressure of $5 \cdot 10^{-5}$ mm Hg for 2 h. This amount was calculated per unit surface area in order to exclude the factor of the magnitude of the surface itself, which changes both upon thermal treatment and as a function of the Fe_2O_3 content in the catalyst.

Table 2 gives the values of the fraction of chemisorption (a_x) and the concentration of OH groups, calculated on the assumption that all water is present on the surface in the form of OH groups. This table also includes the values ω_0 of the areas occupied by an isopropanol molecule in a monolayer on the surface of the catalyst. These values were calculated from the formula $\omega_0 = \dfrac{s}{a_m N}$, where s is the value of the specific surface area of the catalyst, calculated by the BET equation from the adsorption isotherms of benzene vapor; N is Avogadro' s number; and a_m is the capacity of the monolayer of chemisorbed isopropanol, calculated by the same equation for the desorption branch of the sorption isotherm of i-C_3H_7OH.

From Table 2 it is seen that the amount of chemisorbed isopropanol remains practically unchanged at about 4 μmol/m^2 and, to a first approximation, does not depend on the composition or the treatment temperature. Similarly, the concentration of OH groups on samples calcined at 600° also does not depend on the composition and is 6.7 μeq/m^2. At the same time, this concentration in samples heated at 400° decreases with increasing Fe_2O_3 content and proves to be greater than in analogous samples calcined at 600°. This probably indicates that there is a sufficient amount of hydroxyl groups on the catalyst surface for chemisorption to proceed. If one compares the effective cross-sectional areas of the isopropanol molecule (40 Å^2) and of the OH group (12 Å^2), it may be concluded that even upon removal of 60% of the surface OH groups covering the catalyst particles with a dense monolayer, the chemisorbed isopropyl alcohol can cover the entire surface, since the cross section of the alcohol molecule is three times greater than the cross section of the OH group. The literature also gives a value for the capacity of 1 m^2 for saturation with OH groups of $\alpha = 13$ μeq/m^2 for the surface of crystalline quartz and silica gel ([7]). Only for one sample is this value exceeded. In the remaining cases the calculated capacity values are less than 13 μeq/m^2, and therefore for the majority

it is characteristic of the samples that there are present on the surface not only hydroxyl groups, but also oxygen atoms attached to the metal according to the scheme:



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