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Abstract

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CHEMISORPTION OF ISOPROPYL ALCOHOL ON MIXED CATALYSTS BASED ON γ-Al_2O_3

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Direct determination of the magnitude of chemisorption is almost always of interest not only from the standpoint of a detailed description of sorption phenomena and clarification of the role of chemical forces in them, but also in connection with questions of catalysis, since, when an activated complex is formed between molecules of the reacting substance and atoms or ions of the catalyst surface, more or less strong chemical bonds arise. Direct measurement of the magnitude of chemisorption makes it possible to assess the role of this stage in the catalytic process. The overwhelming majority of studies on chemisorption have been carried out with metals as adsorbents; among oxides, silica gel, alumina, and aluminosilicates have been studied in greater detail. In a number of works it has been shown ($^{1-3}$) that alcohols are chemisorbed by metal oxides at room temperature. The amount of chemisorbed alcohol depends on the chemical nature of the oxide (^{4,2}) and on the degree of dehydration of its surface (^{3}). With increasing degree of dehydration of the surface, the amount of chemisorbed alcohol increases. The following schemes of alcohol chemisorption have been proposed (^{3,5}).

On a hydrated surface

$$-\mathrm{Si}-\mathrm{OH}+\mathrm{RCH_2OH}\overset{|}{\underset{|}{\vphantom{X}}}\rightleftarrows -\mathrm{SiOR}+\mathrm{H_2O}. \qquad (1)$$

On a dehydrated surface

$$>\mathrm{Si}^{\mathrm{O}-\mathrm{Si}}_{\mathrm{O}-\mathrm{Si}}>\mathrm{O}+\mathrm{ROH}\rightarrow>\mathrm{Si}_{\mathrm{O}-\underset{}{\overset{\mathrm{OR}}{\mathrm{Si}}}-\mathrm{O}-\mathrm{Si}}^{\mathrm{OH}}. \qquad (2)$$

It has also been shown (^{6}) that, during adsorption of methanol on Al_2O_3 and aluminosilicates, surface alcoholates are formed. We arrived at analogous conclusions by measuring (^{7}) the chemisorption of isopropyl alcohol on catalysts—ferroalumogels.

Having at our disposal a series of mixed catalysts based on γ-Al_2O_3, in which the second component was NiO, Fe_2O_3, Cr_2O_3, or ZrO_2, i.e., metal oxides of different valence, we decided to measure the chemisorption of absolute isopropyl alcohol on them, since the activity of these catalysts had been tested ([8–11]) precisely in the decomposition reaction of this compound, and also because, in our laboratory, a study had been carried out of changes in the activity, selectivity, and phase composition of these same catalysts upon introduction into them of a third component—K_2O. The results of the last-mentioned works are the subject of a separate communication.

In the present work we set ourselves the aim: (a) to compare the adsorption properties, and in particular the chemisorption of iso-C_3H_7OH, on binary catalysts of different chemical composition containing γ-Al_2O_3, and (b) to determine the influence on the magnitude of chemisorption of introducing a third component—an alkali—into these catalysts.

Experimental Part

The binary catalysts were prepared* by the joint precipitation of hydroxides from mixed solutions of aluminum nitrate and the nitrate of the second metal with ammonia. The hydrogels were dried in air at 110°, and then calcined for 6 h in air at 600°. Catalysts with an alkali addition were obtained by impregnating the finished binary catalysts with a KNO_3 solution and calcining again at 600° in air. The composition of the investigated binary catalysts (in mol. %) is given in Table 1. The addition of K_2O was in all cases 3 wt. %, calculated on the weight of the binary catalyst.

Table 1

Catalyst composition	Specific surface, m^2/g (by C_6H_6)	Specific surface, m^2/g (by N_2)	Monolayer capacity, $\mu M/m^2$	Amount of chemisorbed alcohol, $\mu M/m^2$
25% NiO, 75% Al_2O_3		165	4.9	
25% NiO, 75% Al_2O_3 + 3% K_2O	162	155	5.0	
15% ZrO_2, 85% Al_2O_3		220	4.9	4.1

Catalyst composition	Specific surface, m^2/g (by C_6H_6)	Specific surface, m^2/g (by N_2)	Monolayer capacity, $\mu M/m^2$	Amount of chemisorbed alcohol, $\mu M/m^2$
15% ZrO_2, 85% Al_2O_3 + 3% K_2O	170	160	4.9	3.7
15% Cr_2O_3, 85% Al_2O_3	210		4.9	4.2
15% Cr_2O_3, 85% Al_2O_3 + 3% K_2O	255		5.2	4.4
18% Fe_2O_3, 82% Al_2O_3*	200		4.9	4.9

* Results taken from our work (7).

The adsorption of absolute isopropyl alcohol was studied in a gravimetric apparatus with quartz spring balances at 30°. The catalyst surface was determined from the adsorption of nitrogen vapor at the temperature of liquid nitrogen and from the adsorption of benzene vapor at 20°. In calculating the specific surface by the BET method, the molecular area was taken as 16.2 $\mathring{A}^2$ for nitrogen and 41 $\mathring{A}^2$ for benzene. The amount taken as chemisorbed alcohol was the amount that could not be removed from the catalyst by evacuation to constant weight at 30°. The data obtained are presented in Fig. 1 and in Table 1.

Discussion of Results

From Fig. 1a it is seen that the adsorption isotherms of absolute isopropyl alcohol on all binary catalysts coincide completely, since all points fall on one curve; it is also seen that filling of the surface occurs at low relative pressures (of the order of 0.01), after which adsorption in the studied range up to $p/p_s = 0.3$ depends only very weakly on pressure. Fig. 1b shows that introduction of a third component (K_2O) has almost no effect either on the form of the isotherms or on the amount of alcohol adsorbed in the monolayer. From the data of Table 1 it follows that the amount of alcohol chemisorbed at 30° is approximately the same for all catalysts, i.e., the introduction of various additives into γ-Al_2O_3,

Figure 1

Figure 1: Figure 1

including K_2O, within the concentration limits studied does not affect the magnitude of chemisorption of isopropyl alcohol. This would seem to agree poorly with the rather large differences in the chemical composition of the catalysts studied; however, for

for interpretation of the observed facts it is also necessary to take into account their phase composition. As was shown earlier, ZrO_2 in the mixed catalyst ([9]) was present in the form of an amorphous phase, whereas catalysts containing NiO, Fe_2O_3, and Cr_2O_3, at the concentrations of oxides studied in the present work, are single-phase and, being added to γ-Al_2O_3, form a solid solution in it that retains the cubic spinel lattice ([5,12,13]). It is precisely this circumstance that plays the decisive role in the present case.

Since, in the binary catalysts we studied, the structure of the crystal lattice is preserved at the given ratio of component concentrations, irrespective of the nature of the oxide added to γ-Al_2O_3, and since K_2O, as shown in our laboratory, does not change their phase composition, it is clear that the number of oxide ions per unit surface area for all catalysts must be the same. Consequently, the observed ability to form surface isopropylate must also be the same or very close to the same. Although the catalyst with ZrO_2 is not single-phase, it contains 85% Al_2O_3, to which the explanation just given is fully applicable. Let us note that it is more consistent with scheme 2 for the formation of the alcoholate given above than with scheme 1, since a difference in the degree of hydration of the surface (i.e., in the number of OH groups) in the catalysts of different chemical nature studied by us is not excluded.

Fig. 1. Adsorption isotherms of isopropyl alcohol at 30° on binary (a) and ternary (b) catalysts:
1 –Cr_2O_3—Al_2O_3 and Cr_2O_3—Al_2O_3—K_2O,
2 –NiO—Al_2O_3 and NiO—Al_2O_3—K_2O,
3 –ZrO_2—Al_2O_3 and ZrO_2—Al_2O_3—K_2O.

The fact that the introduction of K_2O does not exert a noticeable influence on the magnitude of isopropanol chemisorption also speaks in favor of scheme 2, for the following reasons. The amount of OH groups on an alumina-zirconia catalyst after evacuation at 300° in vacuum, determined from the weight loss on calcination to 1100°, is $5.4\,\mu\text{eq/m}^2$. K_2O, introduced into the catalyst in an amount of 3 wt.%, can react with OH groups, taken in an amount of $4\,\mu\text{eq/m}^2$, by the exchange reaction

$$> \text{AlOH} + \text{KOH} \rightleftarrows > \text{AlOK} + H_2O.$$

If chemisorption of isopropyl alcohol proceeded according to scheme 1, i.e., de-

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* The binary catalysts were prepared by N. A. Pribytkova, who determined their catalytic activity.

pended on the number of hydroxyl groups on the surface, then it is obvious that replacement of 70% of the OH groups by OK groups should have led to a sharp change in the amount of chemisorbed alcohol, which is not observed experimentally. Let us note that calcination of the catalysts at 600° leads to sufficiently strong dehydration of the surface for it to react according to scheme 2. From what has been said it does not follow that we assert scheme 1 to be unreal; we assert only that, in the cases studied by us, the sharply predominant mechanism of chemisorption was the mechanism depicted in scheme 2.

The degree of conversion in the decomposition reaction of iso-C_3H_7OH at 250–260° and a space velocity of 2.3 h^{-1} on the catalysts used in the present work as adsorbents, according to data from works ([8–11]), is, in the case of $NiO—Al_2O_3$, 85.8% (dehydration only), $Fe_2O_3—Al_2O_3$, 27% (26% dehydration, 1% dehydrogenation), $ZrO_2—Al_2O_3$, 84% (dehydration only), and $Cr_2O_3—Al_2O_3—K_2O$, 34% (6% dehydration, 28% dehydrogenation). Comparison of these results with the data on chemisorption of alcohol at low temperature shows that, in the cases we studied, its magnitude is not a factor determining the activity and selectivity of the cataly-

tors. Therefore, it is probable that under reaction conditions at temperatures of 250–350°, the mechanism of chemisorption may be different.

Thus it has been shown that the magnitude of chemisorption of *iso*-C_3H_7OH by binary catalysts based on Al_2O_3 and NiO, Fe_2O_3, and Cr_2O_3, in which these oxides are completely dissolved in γ-Al_2O_3, is the same and is determined by their phase composition (i.e., by the arrangement of O atoms or ions in their crystal lattice), and not by their chemical composition; the introduction of a third component (K_2O), which does not change the phase composition, also does not affect the magnitude of chemisorption of *iso*-C_3H_7OH.

The data obtained indicate the preferential formation of alcoholate during the chemisorption of *iso*-C_3H_7OH on the catalysts investigated in the present work through interaction of the alcohol with surface oxygen ions, and not with OH groups.

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