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Abstract

Full Text

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ON THE QUESTION OF THE ROLE OF HYDROXYL GROUPS ON THE SURFACE OF OXIDE CATALYSTS IN ADSORPTION AND CATALYSIS PROCESSES

(Presented by Academician A. N. Terenin, January 4, 1965)

Until recently there has existed the view that the hydroxyl groups of the catalyst surface (OH groups) are active centers responsible for adsorption and catalytic transformations ($^{1-5}$). On the other hand, there are a number of experimental facts indicating that OH groups play a more secondary role than had previously seemed ($^{6-9}$). Thus, at present there is no clarity concerning the role of OH groups in adsorption and catalysis phenomena, and therefore it seems important to carry out research in this direction. The most effective method for this purpose is the study of the infrared spectra of the hydroxyl covering. It was shown in the work of Terenin and his co-workers ($^{10-12}$) that, upon adsorption of molecules of basic character, OH groups enter into a hydrogen bond with them, which indicates their acidic properties.

Fig. 1. Dependence of the shift of the O–H vibration bands, $\Delta\nu$, on pK_B of bases for various catalysts

We undertook an attempt to characterize the acid strength of the OH groups of a catalyst by the strength of the acid-base interaction between them and base molecules, using the method of infrared spectroscopy (^{13,14}). Ultimately this was done in order to compare the acidity of the OH groups of a catalyst and its catalytic activity. It was shown that there is a linear dependence between the shift of the OH-vibration band and the negative value of the logarithm of the basicity constant of the reacting molecules. Such dependences were obtained for an aluminosilicate and a silica-zirconia catalyst, aluminum oxide, silicon oxide, and aluminum borate (Fig. 1). The degree of withdrawal of the H atom from O in the system O—H···X will depend, on the one hand, on the basicity strength of the molecule X, and, on the other hand, on the degree of protonation of the H atom, which also characterizes its acid strength. If one considers the influence of one and the same base molecule on the shift of the O—H vibration band, it is easy to see that it will be different for different catalysts. This is precisely a characteristic of the acid strength of the OH groups of the catalyst. To the same extent, the acidity of the OH groups of the catalyst may be characterized by the tangent of the angle of inclination of the straight line. From Fig. 1 it is seen that different catalysts possess different acid strengths of OH groups.

Attention is drawn to the fact that the acidities of the OH groups of aluminosilicate and silica-zirconia catalysts and of silicon oxide

are the same. A silica-zirconia catalyst is an active catalyst for alcohol dehydration, and an aluminosilicate catalyst is a basic catalyst in the petroleum-refining industry, whereas silicon oxide is completely inactive in these processes. The fact that the acid strength of their OH groups is the same, while their catalytic activity ranges from very high to zero, indicates that it is not the hydroxyl groups that are responsible for the catalytic activity.

To test this assumption, we carried out more direct experiments. It is known that treatment of a catalyst with alkalis or salts of alkali metals leads to suppression of its catalytic activity ([2,15–17]), up to complete poisoning. If the OH groups are the active centers of the catalyst that are put out of action upon poisoning, this can be detected by comparing the spectra in the region of O—H vibrations before and after poisoning.

Aluminosilicate (5% Al_2O_3) and silica-zirconia (7.5% ZrO_2) catalysts were studied. Poisoning was carried out with a 0.01 *M* solution of LiOH or NaOH in water. After poisoning, the catalysts almost completely lost their catalytic activity. The initial and poisoned samples were carefully ground and subjected simultaneously to thermal treatment in a muffle furnace with two compartments at 500°, or in vacuum at 300° for ~ 30 h. The spectra were recorded on a double-beam IKS-2 spectrometer (IKS-14 type). Immediately after pretreatment, the catalyst powder, while hot, was poured in air or in a dry chamber into a liquid cell and wetted with dried CCl_4. In this process the sample adsorbed a small amount of water from the surrounding space. The figures show paired spectra of poisoned and unpoisoned catalysts under identical pretreatment conditions and identical residence times in air or in the chamber. In all experiments, surface coverage was less than a monolayer, as evidenced by the presence in the spectra of bands of free hydroxyls.

Fig. 2. Spectra of poisoned and unpoisoned catalysts in the region of O—H stretching vibrations. Silica-zirconia (*I*) (7.5% ZrO_2), treated in a furnace at $T = 500°$, $t = 30$ h; poisoned with LiOH. Aluminosilicate (*II*) (5% Al_2O_3), treated in vacuum at $T = 300°$, $t = 28$ h; poisoned with NaOH.

Figure 3

Figure 2: Figure 3

As can be seen from Fig. 2, poisoning of the catalyst with alkali does not lead to destruction of its hydroxyl cover. Moreover, the appearance of the spectrum in the region of O—H stretching vibrations is, in general outline, the same for poisoned and unpoisoned samples, and is characterized by a narrow intense band at 3740 cm^{-1}, corresponding to the vibration of free hydroxyls, and by a broad low-frequency band corresponding to the vibration of interacting hydroxyls. To determine whether the functions of the hydroxyl cover had changed, the interaction of the OH groups of poisoned and unpoisoned samples with a basic substance—pyridine—was studied (Fig. 3). It is easy to see that the spectral picture is the same in both cases. The band of free hydroxyls disappears, and a broad band shifted into the lower-frequency region is observed, characteristic of the formation of a hydrogen bond between surface OH groups and mole-

bases, identical for poisoned and unpoisoned samples in shape and position in the spectrum. Thus, on the basis of the experimental data, we come to the conclusion that the hydrogen ions of the hydroxyl groups are not replaced by alkali-metal ions and that the functions of the hydroxyl covering, in general terms, apparently are not disturbed upon poisoning.

Although, in general terms, the spectra of the hydroxyl covering of poisoned and unpoisoned samples are identical, there is a significant difference in the structure of the low-frequency absorption band (Fig. 2). In the spectrum of the unpoisoned catalyst there is a broad band with a clearly expressed maximum at ~ 3450 cm^{-1}, characteristic of the adsorption of water on surface hydroxyls (^{7}). In the spectra of the poisoned catalyst, the band characteristic of interacting hydroxyls has the form of a triangle adjoining the band of free hydroxyls. Such a difference in the form of the low-frequency bands is not accidental and was always observed on sufficiently well-annealed samples. This apparently indicates that adsorption of water on poisoned samples is somewhat hindered. With a longer exposure of the samples to air, the difference in the spectral patterns of the hydroxyl covering of poisoned and unpoisoned catalysts disappears.

Fig. 3. Spectra of poisoned ( ) and unpoisoned ( ) silica–zirconia catalyst after interaction with pyridine

On the basis of the fact that: 1) the acid strength of the surface OH groups of the catalyst does not correlate with catalytic activity and 2) poisoning of the catalyst, leading to complete loss of catalytic activity, is not accompanied by significant changes in the spectrum of the hydroxyl covering, we come to the conclusion that OH groups are not the active centers responsible for catalytic activity. And although this has been shown only on a few examples, it seems to us that this conclusion may prove to be quite general. The loss of catalytic activity is probably associated with the poisoning of some other active centers.

Their poisoning, in turn, may exert a screening effect on OH groups, which can explain why adsorption of water on them is initially somewhat hindered.

Our conclusions are in agreement with a number of works, which also indicate the existence of centers more active than OH groups.

It is known that adsorption of the first portions of water on the dehydrated surface of porous glass occurs not on OH groups, but on centers of a second kind ([6,7]). In work ([8]) it was found that adsorption of water on silica gel initially proceeds with an energy of 17-20 kcal/mol, i.e., significantly exceeding the energy of a hydrogen bond. The authors of work ([9]) come to the conclusion that, in the process of ethylene oxide polymerization, OH groups do not participate in the catalytic act itself. In works ([18–21]), the formation of new chemical bonds between the catalyst surface and the reacting molecule or radical was observed. In the example of the reaction of methyl, ethyl, and isopropyl alcohols and cresols ([18,20–21]) on Al_2O_3 or on catalysts containing Al_2O_3, bonds of the type Al—O—R and Al—R (where R is a hydrocarbon radical) were detected. In this case, the aluminum atom acts as the active center. The question arises, what then is the role of OH groups after all? Apparently, after occupation of more

of the active centers of the catalyst, the adsorption of water and other substances proceeds through the formation of hydrogen bonds on OH groups. In addition, according to Weil' s concepts, it is precisely the OH groups that create the coordinative unsaturation of atoms located on the catalyst surface (22).

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