INFRARED SPECTRA OF CATALYSTS AND ADSORBED MOLECULES
COMMUNICATION 5. METHANOL ON THE SURFACE OF ALUMINUM OXIDE

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In our previous communication [1] it was shown that dimethyl ether—the dehydration product of methanol—is adsorbed on hydrated and dehydrated surfaces of aluminum oxide, forming several types of surface structures. The information obtained in an investigation of the adsorption of dimethyl ether created the prerequisite for a study of the nature of the adsorption and mechanism of dehydration of methanol.

EXPERIMENTAL†

Adsorption was conducted on a sample of γ-Al₂O₃, the production of which was described in [2]. A preparation of heavy methanol, labeled in the methyl radical, CD₃OH, contained 98.6% by weight of the basic substance; the total content of the isotope comprised 70.5 atomic %. Normal methanol, CH₃OH, was produced by rendering absolute and purification according to the well-known procedure [3]. Conditioning of the samples of Al₂O₃ and a spectral investigation of adsorption were conducted in a glass vacuum cuvette, soldered onto an adsorption apparatus [4]. The spectra in the region of 4000-1000 cm⁻¹ (LiF and NaCl prisms) were recorded on the IKS-14 two-beam instrument; in addition, in certain cases a CaF₂ prism was used. The method of spectral investigation of the adsorption and treatment of the spectra were described earlier [1]. The adsorbates were admitted to surfaces of γ-Al₂O₃, treated with oxygen at 450° and dehydrated under vacuum (10⁻⁵-10⁻⁶ mm Hg).

DISCUSSION OF RESULTS

Participation of the Surface of Aluminum Oxide and the OH-Groups of Methanol in the Adsorption of Hydroxyl Groups. The IR spectrum of Al₂O₃, after conditioning at 450° (10⁻⁵-10⁻⁶ mm Hg), exhibits bands at 3600 cm⁻¹ with a shoulder at 3680 cm⁻¹ and at 3560 cm⁻¹ in the region of vibrations of the valence hydroxyl. The adsorption and desorption of CH₃OH at all temperatures changed neither the intensity nor the contour of the high-frequency band at 3680 cm⁻¹. This is an unambiguous indication that the so-called free hydroxyl groups [5, 6], perturbed to the least degree by the force field of the surface and not participating in the formation of a hydrogen bond with the neighboring hydroxyls, also do not take part in the process of adsorption of methanol. The adsorption of CH₃OH (Table 1) at 20° leads to an intensification of the intensity of the bands in the low-frequency adsorption region ν(OH) (~3560 cm⁻¹), while desorption at 100° reduces the absorption intensity, additionally permitting the detection of a band at 3520 cm⁻¹. Adsorption at increased temperature (before decomposition) forms bands on the surface with a simultaneous shift into the high-frequency region. Experiments on the adsorption of CD₃OH (Fig. 1 and Table 2) gave an analogous picture. Thus, alcohol molecules at low temperatures (before decomposition) form a system of hydrogen bonds on the surface of Al₂O₃, both on account of interaction with perturbed OH groups of the surface, and bonded together by hydrogen bonds, and also as a result of interaction of the alcohol molecules among themselves.

Forms of Adsorption of Methanol on Al₂O₃. Weak Adsorption of Methanol as was shown above, is accomplished as a result of interaction with the "bound" hydroxyls of the surface. At 20°, the band

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‡Henceforth the valence vibrations will be denoted as ν.

with the greatest contribution of planar deformational vibrations* of the OH groups at 1346 cm\(^{-1}\) disappears from the spectrum of adsorbed CH\(_3\)OH [7-10], and a new band appears at 1400 cm\(^{-1}\), belonging to the planar \(\delta\) (OH) in alcohol, perturbed by a hydrogen bond [7, 9, 10]. The latter, well-known fact, served as the basis for the incorrect assignment of this band in the spectrum of CH\(_3\)OH adsorbed on Al\(_2\)O\(_3\) to "liquid" alcohol [11], which can be correct only for large degrees of coverage of the surface and low temperatures of adsorption. In the IR spectrum of CD\(_2\)OH (gas), the band of the planar \(\delta\) (OH) is situated at 1289 cm\(^{-1}\), i.e., lower than in the spectrum of CH\(_3\)OH (gas), being shifted to 1391 cm\(^{-1}\) in the case of transition to a liquid as a result of the formation of hydrogen bridges [7]. The closeness of the positions of the frequencies \(\delta\) (OH) in the spectra of CH\(_3\)OH (liq) and CD\(_3\)OH (liq) indicates an increase in the characteristic nature of the vibration in the case of the formation of hydrogen bonds. Actually, in the case of adsorption, a band at 1400 cm\(^{-1}\), corresponding to the frequency of the planar \(\delta\) (OH), shifted as a result of the formation of hydrogen bonds, appears in the IR spectrum of CD\(_2\)OH, as well as CH\(_3\)OH. The virtual absence of a shift of the frequency \(\nu\) (C-O) (1025 cm\(^{-1}\) in CH\(_3\)OH and 990 cm\(^{-1}\) in CD\(_2\)OH in the case of the formation of a hydrogen bond is in full agreement with the results obtained for solutions of CH\(_3\)OH, CD\(_3\)OD, and CH\(_3\)OD [12]. According to the thermodesorption data, the form of adsorption with temperature maximum 135° corresponds to weakly adsorbed molecules of methanol [13]; above this temperature the alcohol molecules are retained on the surface by stronger bonds than hydrogen bonds.

**Strong Adsorption of Methanol.** The adsorption of CH\(_3\)OH at 20° leads immediately to the appearance of \(\nu\) (C-H) at 2940 and 2830 cm\(^{-1}\), shifted into the low-frequency region in comparison with the spectrum of the gas 2977 and 2844 cm\(^{-1}\), the position of the bands in which coincides with the literature data [7]. The coincidence of the positions of the bands in the spectrum of CH\(_3\)OH in the case of adsorption with the positions of the bands in the spectrum of CH\(_3\)OH (liq.) (2934 and 2822 cm\(^{-1}\)) [7] should be recognized as formal, since all the way up to 350°, when it is impossible to speak of any liquid state of alcohol on the surface, the positions of the frequencies are unchanged. In this case it is a matter of the influence of the force field of the surface upon the spectral characteristics of the methyl group. Desorption at increased temperature reduces the intensity of the bands \(\nu\) (C-H), as well as the band \(\delta\) (C-H) at 1470 cm\(^{-1}\). The increase in the intensity of the absorption bands in the case of adsorption is the substantial decrease in the case of desorption is in characteristic of this group of bands in the entire range of temperatures (20 to 400°), just as in the case of isopropanol [14]. In the IR spectrum of adsorbed CD\(_2\)OH, in the region of \(\nu\) (C-D), four bands can be resolved at 2190-2220, 2120, 2050-2060, and 2030 cm\(^{-1}\), the behavior of which is analogous to the behavior of the bands in the spectrum of adsorbed CH\(_3\)OH. The multiplicity of the absorption bands in comparison with the data on the IR spectra of CH\(_3\)OH [7] and CH\(_3\)ODCD\(_3\) [15], and considering the possibility of the formation of surface alcoholates [11, 16], permits the assignment of these bands to adsorbed CD\(_2\)OH (up to 300°, \(\nu\)\(\text{as}\) 2190 cm\(^{-1}\)), in the gas 2235 cm\(^{-1}\); \(\nu\)\(\text{s}\) 2120 cm\(^{-1}\), in the gas 2094 cm\(^{-1}\), CD\(_3\)ODCD\(_3\), and the structure CD\(_3\)-O-Al [2190 cm\(^{-1}\), ether (gas), 2134 and 2248; 2050 and 2030 cm\(^{-1}\)].

*Henceforth the deformational vibrations will be denoted as \(\delta\).*