INFRARED SPECTROSCOPIC STUDIES OF DIHYDROGEN ADSORBED ON OXIDE SURFACES

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The complex structure of the IR spectra of dihydrogen adsorbed at 60–77 K on several oxide adsorbents, in the 4300–4000 cm⁻¹ region, is supposed to be due to the combination of νH-H with a low-frequency vibration of the H₂ molecule with respect to the surface.

В области 4300–4000 см⁻¹ получены ИК-спектры молекулярного H₂, адсорбированного при 60–77 K на ряде окисных адсорбентов. Предполагается, что сложная структура наблюдаемых спектров обусловлена комбинацией νH-H с низкочастотным колебанием молекулы относительно поверхности.

When homonuclear diatomic molecules are adsorbed on dispersed adsorbents, in the region of vibrational frequencies, an absorption forbidden in the absorption spectra, is observed. This absorption, induced by surface electrostatic fields, has been revealed previously after H₂ adsorption on porous glass /1/, aerosil /2/, zeolites /3/, alkali halides /4/ and ZnO /5/. High intensity and a noticeable frequency shift of the absorption bands indicate a rather strong perturbation of the molecules by the surface.

We have studied H₂ adsorption on various oxide adsorbents at temperatures of liquid and solid nitrogen using a low-temperature cell like in Ref. /2/. The temperature of solid nitrogen was attained via evacuation of the coolant (N₂) from the cell cooling reservoir. IR spectra were recorded on an UR-20 double-beam spectrophotometer.

Pellets were tabletced from commercial SiO₂, BeO, Al₂O₃, Sc₂O₃, Ca₂O₃, ZnO, TiO₂, silica-alumina catalyst and NaX zeolite. In the course of thermal vacuum treatment, CaO, NiO and ZrO₂ prepared from hydroxides and MgO from carbonate were transformed into oxides with sufficiently high surface areas. To clean surfaces, the samples were heated in vacuum to 700–1300 K, treated in oxygen and evacuated
at the same temperature for a period of 30 min. Thickness of the samples was 30–300 mg cm\(^{-2}\).

The admission of H\(_2\) at P = 30–100 Torr into the cell with a sample cooled to 77 K for all adsorbents, except CaO, MgO and NiO, leads to the appearance of absorption bands at the frequencies listed in Table 1. Temperature decrease to 60 K exerts almost no effect on the positions of these bands, but noticeably increases their intensity. Evacuation of gaseous H\(_2\) at 77 K immediately restores the initial spectrum.

The spectra of H\(_2\) adsorbed on SiO\(_2\), BeO, ZrO\(_2\), Sc\(_2\)O\(_3\) and Ga\(_2\)O\(_3\) exhibit only one band with the intensity of 10%. For SiO\(_2\) the appearance of the band at 3750 cm\(^{-1}\) is accompanied by a shift of the OH group band from 3750 to 3735 cm\(^{-1}\), implying that the silanol groups are the sites of H\(_2\) adsorption. Upon H\(_2\) adsorption on silica-alumina, besides the band at 4135 cm\(^{-1}\), similar to that of SiO\(_2\) at 4140 cm\(^{-1}\), a weak band at 4040 cm\(^{-1}\) is observed. This band is absent in the spectrum of the sample treated with water vapor and evacuated at 300 K when surface Al atoms are saturated by water molecules. Therefore, we attribute the band at 4040 cm\(^{-1}\) to H\(_2\) molecules bonded to coordinatively unsaturated Al atoms.

When H\(_2\) is adsorbed on \(\gamma\)-Al\(_2\)O\(_3\), a wide band with poorly resolved peaks at 4110 and 4060 cm\(^{-1}\) is observed. The first peak increases more rapidly with decreasing temperature. The presence of several absorption bands with relative intensities depending on the temperature or treatment conditions, was also observed for ZnO.

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**Fig. 1.** IR spectrum of TiO\(_2\) (anatase) after evacuation at 800 K (1), admission of H\(_2\) (135 Torr) (2), and D\(_2\) (100 Torr) (3) at 77 K.