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Proceedings**

**Vol. 3**

# 8th International Congress on Catalysis

Volume III: New methods in catalysis research  
Dynamics of catalytic reactions  
Contribution of catalysis to ensuring  
the energy requirements  
Catalysis and environmental protection



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## **New methods in catalysis research**



## IR Diffuse Reflectance Study of Oxide Catalysts. Use of Molecular Hydrogen Adsorption as a Test for Surface Active Sites

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### Summary

Diffuse Reflectance spectroscopy in the near IR region was proved to be much more sensitive than the standard transmittance spectroscopy of the pellets. It was applied to the study of an interaction between molecular hydrogen and active sites on the surface of oxide catalysts ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ , zeolites and silica-aluminas). The shift of the fundamental stretching vibration of the H-H bond caused by low-temperature adsorption was found to be dependent on the nature of a surface site involved in the interaction. Using hydrogen molecule as a probe the nature of different Lewis acidic sites in dehydroxylated H-forms of zeolites was studied. The advantages of low-temperature adsorption of hydrogen as a test for surface sites of oxides as compared to other widely used molecular probes were discussed.

IR spectroscopy is widely used for the investigation of adsorption and heterogeneous catalysts. Traditionally, these studies are carried out by means of transmittance technique with the use of very thin semitransparent pellets pressed of powders. To accomplish their thermovacuum pretreatment and adsorption of different substances one has to use rather complicated IR cells, especially if the measurements are performed at low temperatures /1/.

Significant disadvantage of the transmittance method is its moderate sensitivity since it allows the detection of  $10^{18}$ - $10^{20}$  molecules adsorbed per gramm of a catalyst, depending on the extinction coefficient of the surface species. In addition, transmittance IR spectra of solids are usually measured in a rather narrow spectral range ( $1000$ - $4000\text{cm}^{-1}$ ). The upper limit of this region is determined both by contraction of commercial IR spectrophotometers and by intensive scattering of the high-frequency radiation by the samples. Therefore, the conclusions about the nature of surface species are usually made on the basis of IR spectra measured in the region of the fundamental stretching and bending vibrations of adsorbed molecules. The combina-

tion bands and overtones providing additional valuable information on interaction between adsorbate and adsorbent usually are not detected in transmittance IR spectra as their bands have very low intensity and often are located in the near IR region which is out of working spectral range of regular IR spectrophotometers.

The use of the modern IR-FT spectrometers gives some new possibilities both for increase of the sensitivity and for the expansion of the spectral range. Another way to achieve these purposes is the application instead of transmittance technique the diffuse reflectance spectroscopy. In addition, this method allows the direct investigation of powdered materials placed in IR cells of small volume. Therefore, it significantly simplifies the preparation of the samples as well as the procedure of their pretreatment and the measurements of IR spectra, especially at low temperatures. It should be pointed out that the attempts to use the diffuse reflectance IR spectroscopy for the investigation of solids have been made before in /2-4/. However, this method has not been widely used up till now and its advantages were not enough clarified.

#### Experimental

In the present work the diffuse reflectance IR spectra in the near and middle IR regions were measured using double-beam "Beckman Acta M-VII" and "Perkin-Elmer 580B" spectrophotometers, respectively. They were supplied with the diffuse reflectance units developed in our institute. For the measurements in the near IR region the thin-walled quartz ampoules were used as IR cells. For the work in the middle IR range they were supplied with  $\text{CaF}_2$  windows. An ampoule with a pretreated sample was placed in front of the spectrophotometer's entrance slit and illuminated by the focussed beam of light from the external irradiation source (150W quartz iodine lamp). The intensity of the light reflected by the samples was about 15% of that of the reference beam. For the measurements at 77K the ampoule with a powdered sample was placed in a quartz Dewar vessel filled with liquid nitrogen.

Our experimental experience /5-7/ shows that in the near IR region, where for many adsorbents the reflectance coefficient is close to unity, diffuse reflectance spectroscopy has a considerably higher sensitivity than has the standard transmittance technique. This conclusion is also confirmed by a theoretical consideration. The results of this analysis based on the Kubelka-Munk theory /8/ are presented in Fig.1. Here the intensity of the band in a transmittance spectrum measured

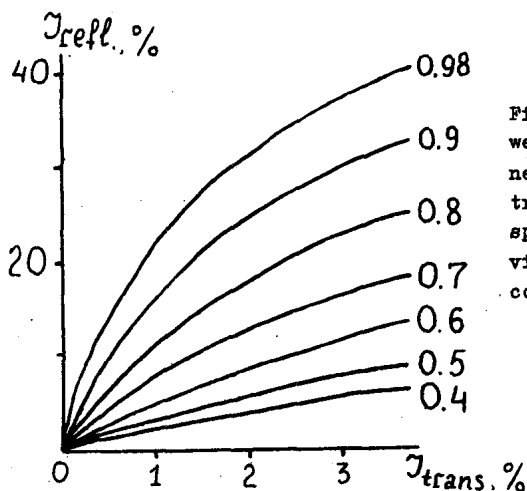


Fig.1. The relationship between an intensity of the line in a reflectance IR-spectrum and in a transmittance spectrum for the samples having different reflectance coefficients ( $R_{\infty}$ ).

in the optimal conditions ( $\sim 35\%$  of the pellet transmittance) is plotted against the intensity of the corresponding line in a diffuse reflectance spectrum assuming the complete collection of the scattered light. It is evident that for the samples having large reflectance coefficients ( $R_{\infty} > 0.8$ ), the intensity of the bands in a reflectance spectrum considerably exceeds that one in a transmittance spectrum. The maximum gain in sensitivity for diffuse reflectance spectroscopy is the following:  $\mathcal{Q}_{\text{max}} = e R_{\infty} (1 + R_{\infty}) / (1 - R_{\infty})$ , where  $e$  is the basis of the natural logarithm. For example, at  $R_{\infty} = 0.95$   $\mathcal{Q}_{\text{max}} > 100$ . However, even with the external irradiation source, the intensity of the reflected light didn't exceed in our measurements of 15% of that of the reference beam. Therefore, the real sensitivity increase was approximately by 5-6 times lower.

In /5,6/ we have used this method for the investigation of OH-groups in oxides and zeolites. In the present work it was applied to the study of low-temperature adsorption of molecular hydrogen.

#### Results and discussion

According to the selection rules the transition corresponding to the stretching vibration of nonpolar H-H bond in molecular hydrogen is forbidden. Therefore, this band could be obtained in IR spectra only if  $H_2$  molecule is perturbed by adsorption centers. This results also in a decrease of the frequency of H-H vibrations being dependent upon the extent of polarization of  $H_2$  molecules by surface sites of diffe-

rent nature. The standard transmittance IR spectroscopy has a low efficiency for the study of adsorption of hydrogen. It is connected both with some technical difficulties of the work at low temperatures and with low sensitivity of this method in the near IR region. In addition, the vibration of H-H bond is located in the  $4000-4200\text{cm}^{-1}$  region, i.e. out of the working spectral range of the commercial available IR spectrophotometers. The most suitable for this purpose is the diffuse reflectance IR spectroscopy. Let's consider some results obtained by this technique on the study of molecular hydrogen adsorption at 77K on the surface of different catalysts.

Oxides. Hydrogen adsorption at 77K on the surface of the silicagel which contains only SiOH groups results in appearance of a single band at  $4130\text{cm}^{-1}$  (Fig.2a). It is shifted by  $30\text{cm}^{-1}$  to lower frequencies as compared to the frequency of H-H vibrations in the gaseous hydrogen. An increase of the pretreatment temperature of the silicagel from 870K to 1270K reduces the intensity of this band. Since in this temperature range a strong dehydroxylation of the surface takes place the band at  $4130\text{cm}^{-1}$  should be ascribed to  $\text{H}_2$  molecules interacting with the SiOH groups [6,7].

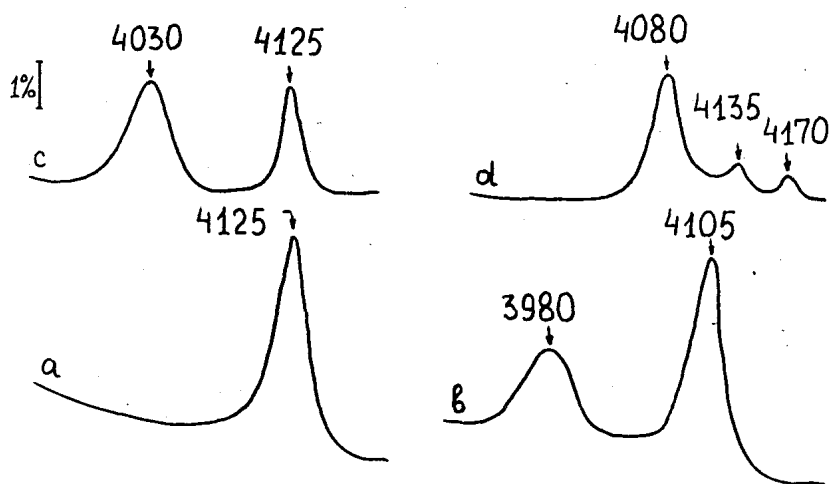


Fig.2. IR-spectra of molecular hydrogen adsorbed at 77K and the pressure of 40kPa on the surface of  $\text{SiO}_2$  (a),  $\gamma\text{-Al}_2\text{O}_3$  (b), amorphous silica-alumina (c) and MgO (d), pretreated at 870K in a vacuum.

Similar decrease of the intensity of the bands near  $4110-4130\text{cm}^{-1}$ , belonging to hydrogen perturbed by OH groups is also observed in the spectra of  $\text{H}_2$  adsorbed at 77K on the surface of  $\text{Al}_2\text{O}_3$  and amorphous silica-aluminas (Fig.2b,c). However, unlike to silicagel dehydroxylation of these adsorbents results in an appearance of additional low-frequency bands of adsorbed hydrogen at  $3980\text{cm}^{-1}$  for  $\text{Al}_2\text{O}_3$  and at  $4030\text{cm}^{-1}$  for silica-aluminas. On the contrary, the intensities of these bands increase in the course of dehydroxylation of the surface. These sites hold hydrogen more strongly than OH groups, since the evacuation of the samples at 77K (1-2min) leads to a complete disappearance of the high-frequency bands and doesn't change the intensity of the low-frequency lines.

It is known that in such catalysts at high temperatures of the pre-treatment oxygen vacancies are formed, having the properties of Lewis acidic sites. Hence, the bands at  $3980-4030\text{cm}^{-1}$  should be assigned to hydrogen interacting with such sites. Adsorption measurements show that their concentration is not high and for both samples is about of  $10^{17}$  sites/ $\text{m}^2$ .

The electron-accepting properties of magnesium oxide are known to be not so strong as for  $\text{Al}_2\text{O}_3$  or silica-aluminas. In accordance with this concept one has to expect the less strong interaction of hydrogen with surface sites of this adsorbent. Our results are in agreement with such assumption as in IR spectrum of hydrogen adsorbed at 77K on MgO pretreated at 870K there is only one line with the frequency of  $4080\text{cm}^{-1}$  which is higher than that for hydrogen adsorbed on electron-acceptor sites of alumina and silica-alumina. This band due to rather low frequency doesn't correspond to hydrogen interacting with surface OH groups. It is more likely connected with  $\text{H}_2$  molecules adsorbed on some cationic centers, perhaps, on  $\text{Mg}^{+2}$  cations.

Cationic forms of zeolites. Cationic forms of zeolites are appropriate objects for the study of an interaction between metal cations and adsorbed molecules. In Fig.3 IR spectra of hydrogen adsorbed at 77K and the pressure of 40kPa on Na-forms of zeolites A (1), X (2), Y (3), mordenite (4) and LaY-zeolite (5) are presented.

For all these samples the absorption bands are observed in the  $4075-4160\text{cm}^{-1}$  range. Since Na-forms of zeolites don't contain any structural OH groups, all of the bands in the spectra of adsorbed hydrogen should be assigned to  $\text{H}_2$  molecules interacting with  $\text{Na}^+$  cations. At higher hydrogen pressures additional lines at  $\nu > 4160\text{cm}^{-1}$  could be ob-

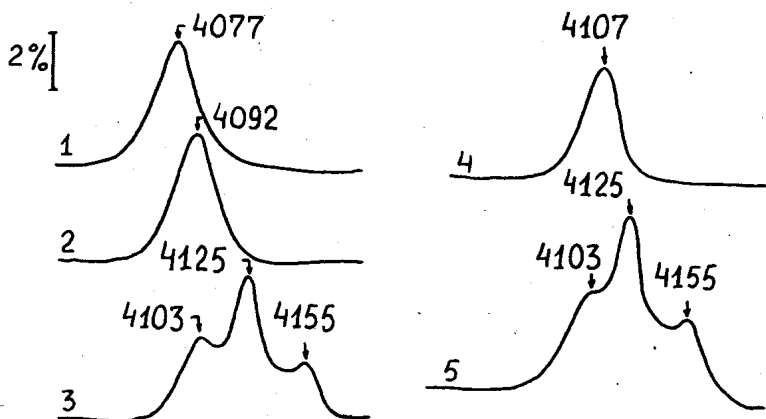


Fig.3. IR-spectra of  $H_2$  adsorbed at 77K and the pressure of 40kPa on Na-forms of zeolites A (1), X (2), Y (3), mordenite and LaY (5), pretreated at 770K in a vacuum.

served which accordingly to Förster<sup>9/</sup> are attributed to combination modes of the stretching vibration of H-H bond with low-frequency vibrations of the whole molecule on the surface.

The spectrum of hydrogen adsorbed on NaY zeolite unlike to other Na-forms consists of three lines with the maxima at 4105, 4125 and 4155  $cm^{-1}$ . They are likely to be attributed to  $H_2$  molecules interacting with  $Na^+$  cations located in different positions of the framework. Indeed, in accordance with the data on X-ray diffraction analysis /10/ in dehydrated NaY zeolite the  $Na^+$  cations do prefer three types of localization sites ( $S_I$ ,  $S_I'$  and  $S_{II}$ ) which obviously are accessible to  $H_2$  molecules having small kinetic diameter.

Analysis of the spectra of Na-forms shows also that an increase of the aluminium content in the framework leads to a stronger polarization of  $H_2$  molecules adsorbed on  $Na^+$  cations. This is clearly demonstrated by additional low-frequency shift of the bands for hydrogen adsorbed on the samples with lower Si/Al ratio (from 4107 $cm^{-1}$  for NaM to 4077 $cm^{-1}$  for NaA). This shift may occur due to an additional polarization of the molecules by internal electrostatic field of the zeolite whose strength should increase with an increase of the aluminium content in the lattice.



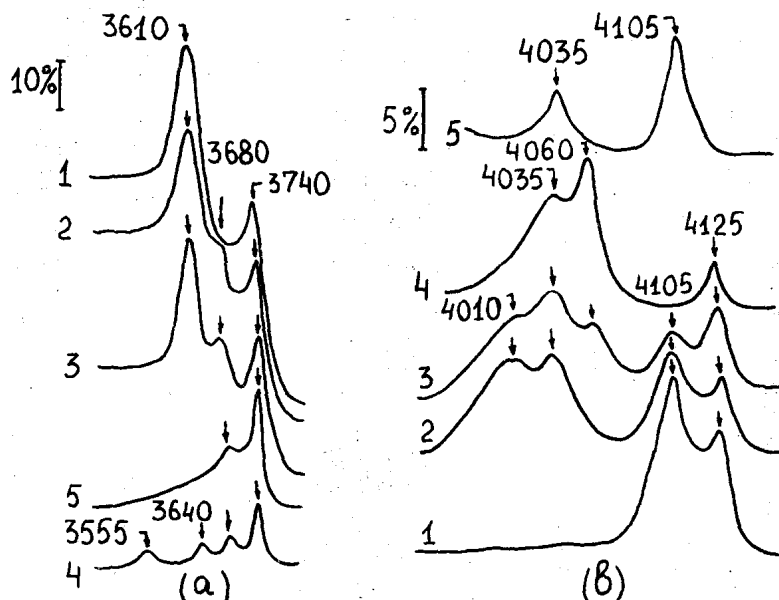


Fig.4. IR-spectra of OH groups (a) and of adsorbed hydrogen (b) for zeolites HZSM-5 (1-3) and HY (4,5). Pretreatments are the following: 1 - 77OK, 0,1Pa; 2 - 97OK, 0,1Pa; 3 - 127OK, 0,1Pa; 4 - 97OK in air, "deep bed" conditions; 5 - 97OK, 0,1Pa, "deep bed".

**Hydrogen forms of zeolites.** In Fig.4 IR-spectra of OH groups and of molecular hydrogen adsorbed at 77K on the decationated zeolites HZSM-5 (1-3) and HY (4,5) pretreated under different conditions are shown. For HZSM zeolite evacuated at temperatures lower than 87OK there are only two high-frequency bands at 4105 and 4125cm<sup>-1</sup> in the spectra of adsorbed hydrogen. They belong to the molecules interacting with acidic hydroxyls of the bridged type ( $\nu_{OH}=3610\text{cm}^{-1}$ ) and with SiOH groups ( $\nu_{OH}=3730\text{cm}^{-1}$ ), respectively. At higher temperatures of the samples pretreatment the structural OH groups of the first type are removed. This leads to a decrease of the intensity of the band at 4105cm<sup>-1</sup> in the spectra of adsorbed hydrogen and to appearance of low-frequency bands with the maxima at 4010, 4035 and 4060cm<sup>-1</sup>.

According to [11] dehydroxylation of the H-forms of zeolites may result in formation of two types of electron-accepting Lewis sites which are coordinatively unsaturated aluminium atoms and silicon ions of the lattice: