Journal of International Scientific Publications:
Materials, Methods & Technologies, Volume 6, Part 1

THE STUDY OF CATALYTIC ACID SITES ON THE SURFACE OF ZEOLITE H-ZSM BY MEANS OF IR-SPECTROSCOPY AND QUANTUM CHEMISTRY METHODS

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Abstract

By means of ATR FTIR and high temperature diffusive reflectance FTIR investigated the structure of zeolite H-ZSM-5 at 25 and 350 °C temperature treatment in inert atmosphere (in situ). Spectral changes were observed when H-ZSM-5 mixing with Al_2O_3 and modifying with Mg and Rh salts. Absorption bands of free and associate OH groups on the zeolite surface were identified after water removal and zeolite modification. Using quantum chemical calculations theoretical spectra of the zeolite models isolated or bonded OH surface groups found.

1. INTRODUCTION

Zeolites of ZSM-5 type with regular nanoporous structure and pore diameters of about 5.6–5.8 Å used in different chemical processes: separation and purification of hydrocarbons, dehydration of refrigerants, producing substrates for catalysts of plastics and rubber vulcanization processes, extraction of radioactive isotopes from liquid wastes of nuclear industry, separation of CO_2 and sulfur compounds from natural gas, etc. Catalytic activity of zeolites in different hydrocarbon reactions is one of the most important areas of their application, The structure of catalyst and origin and number of active sites are crucial factors in the study of efficiency and selectivity of any catalytic hydrocarbon conversion on zeolite surface. Crystalline structure of natural and synthetic zeolites are made via tetrahedral $SiO_{2/4}$ and $AlO_{2/4}$ groups connected by joint vertices in 3D 2-15 Å nanoporous structure. Open skeleton-cavity zeolite structure $[AlSi]O_4^-$ has a negative charge that is compensated by cations (metal, ammonium, alkylammonium and others injected by ion exchange) and water molecules able for dehydration[i]. Catalytic reactions are processed on Bronsted and Lewis acid sites of zeolites. In industry zeolites are modified with transition metals and (γ-Al_2O_3) is added to improve the mechanical properties of the catalyst.

This work describes changes in the structure of the zeolite when it is modified studied by FTIR-spectroscopy.

2. EXPERIMENTAL PART

FTIR-Methods are listed below:

- registration of transmission spectra of the catalyst suspension in Vaseline oil using vacuum FTIR spectrometer IFS-66 v/s («Bruker»);
- registration of ATR spectra of catalyst powder in the air at room temperature using FTIR microscope HYPERION 2000 («Bruker») connected with FTIR spectrometer IFS-66 v/s;

- spectra registration under temperature treatment in inert (Ar) atmosphere was carried out using in situ diffuse IR method. Spectra were registered in the in the range 25 – 350 °C in high temperature IR cell (PIKE Diffuse) connected with FTIR spectrometer VERTEX-70 («Bruker»). Results processing were completed using OPUS software.

Quantum chemical calculation were carried out with the Gaussian03[ii] and PRIRODA software depending on the task. In Gaussian03 Hartree-Fock (HF) method and 6-31G basis for models optimization and theoretical vibration spectra calculations were used.

In PRIRODA software functional PBE (Perdew-Burke-Ernzerhof) and three exponential basis set 3z were used.

3. RESULTS AND DISCUSSIONS

3.1 Structure studies of Al2O3 by means of high temperature Diffuse Reflectance FTIR spectroscopy in situ

Zeolites as well as Al_2O_3, used as a binder in zeolite catalysts production, tend to absorb water under room temperature, therefore studying of active sites of these materials should be carried out only after complete water desorption. Alumina structure contains OH groups that could contribute to wrong interpretation of catalyst spectra. That is why it was necessary to begin the work from research aimed to study of alumina functional groups spectral behavior under different conditions.

To valid and complete interpretation of the spectral behavior of absorbed water molecules on Al_2O_3 surface the following experiment was performed. Initial γ-Al_2O_3 was put in a cuvette of high temperature cell, than it was annealed at 450°C and cooled down to 250°C under Ar flow. Next under the same temperature water vapor was passed through the system for 2 hours and again for 1 hour system was flowed with Ar. FTIR spectra registered during the whole experiment are presented below:

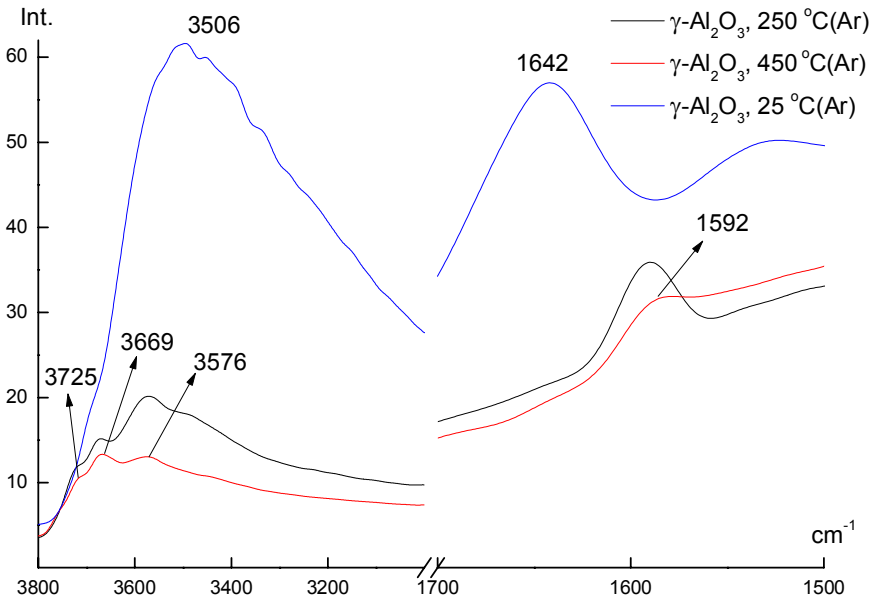


Fig. 1. γ-Al_2O_3 Diffusive Reflectance IR spectra γ-Al_2O_3 at room and high temperature

At 25 °C in FTIR-DR spectrum absorption bands of H_2O adsorbed on the surface of aluminium oxide are observed: a peaks at 3506 cm^{-1} (stretching vibrations of associated -OH groups (ν_{OH})) and 1642 cm^{-1} (deformation vibrations δ_{HOH}). At 250 °C intensity of both bands decreases, and at 450°C they finally non being registered in the spectrum. In this conditions we see only low intensive bands at 3669 cm^{-1} which we refer to low associated OH-groups, band of unassociated OH-groups (at 3725 cm^{-1}), also we have detected band of low intensity at 3576 cm^{-1}, which could be referred to more associated OH groups at one atom of aluminum. All this –OH groups may take place in catalysis of conversion of oxygenates (methanol, dimethyl ether) on the surface of aluminum oxide.

Attention should be paid on spectral display in region of deformation vibrations, which characterize geometry of angle H–O–H (δ_{HOH}). In FTIR-DR spectrum of the initial sample deformation vibrations (δ_{HOH}) of adsorbed water registered at 1642 cm^{-1}. This band disappeared in spectrum at 250 °C, and we register band at 1592 cm^{-1}, which certainly characterizes deformation vibrations of H···O – H and strongly asymmetric bonds –O–H. That is easily could be in Brensted acid site (BAS). If at 250°C we let water vapor above surface of aluminum oxide, we detect that band at 1592 cm^{-1} would slightly shift towards shorter wavelengths and increase in intensity, and at 1642 cm^{-1} there is only a slight increase in the background of absorption. In region of absorption of valence vibrations –OH-groups in this conditions we detect strong growth in intensity of the band at 3576 cm^{-1}, intensity of the bands from isolated –OH groups (3725 cm^{-1}) and low associated –OH (3669 cm^{-1}) also grows, but insignificantly. This behavior of the absorption bands of stretching and deformation vibrations of –OH groups leads to the conclusion, that bands 3576 and 1592 cm^{-1}, respectively, can be attributed to stretching and deformation vibrations of bands –OH in BAS. From this experiment we can conclude that passage of water vapor above aluminum oxide at 250°C does not lead to its sorption on the oxide surface, but on the contrary, accompanied by an increase in the number of BAS, as well as isolated and weakly associated –OH groups.

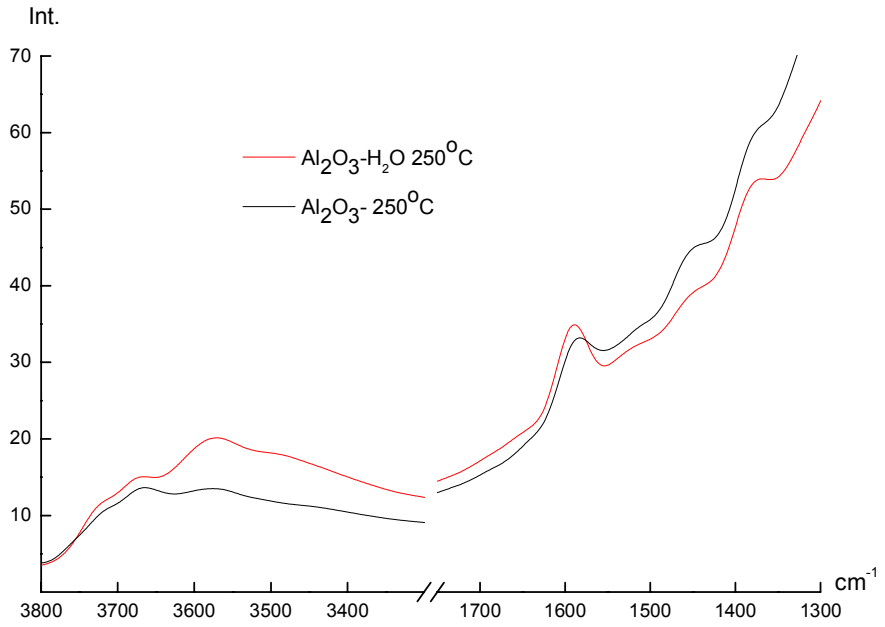
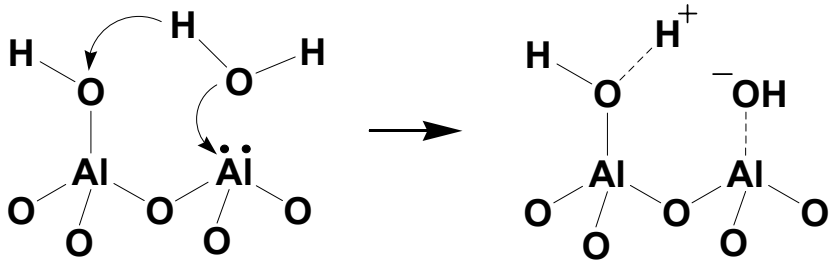


Fig. 2. Comparison of spectra of Al_2O_3, evacuated after heating at 450°C and cooled in dry argon at 250°C (black curve), and also Al_2O_3 after passage of water vapor for 2 hours at 250 °C(red curve), in region of absorption of deformation and stretching vibrations of bonds OH.

It can be assumed that the passage of water vapor above surface aluminum oxide after thermo treatment, water molecules coordinating to the nearer Al-OH and LAS centers on the surface of γ-Al_2O_3, would dissociate on H^+ and OH^-, while creating new BAS and increasing content of isolated and weakly associated OH groups:



According to the detailed analysis of the spectral behavior of aluminum oxide, which is used as the binder in the preparation of catalysts, it is possible to correctly identify the acid sites of zeolite catalyst, shown in its heat treatment. Fig. 3 shows the IR-spectra of Diffusive Reflectance of the binder (aluminum oxide studied above) – blue curve, zeolite HZSM-5 without the addition of a binder (red curve) and a sample obtained by mixing the zeolite and the binder (black curve).

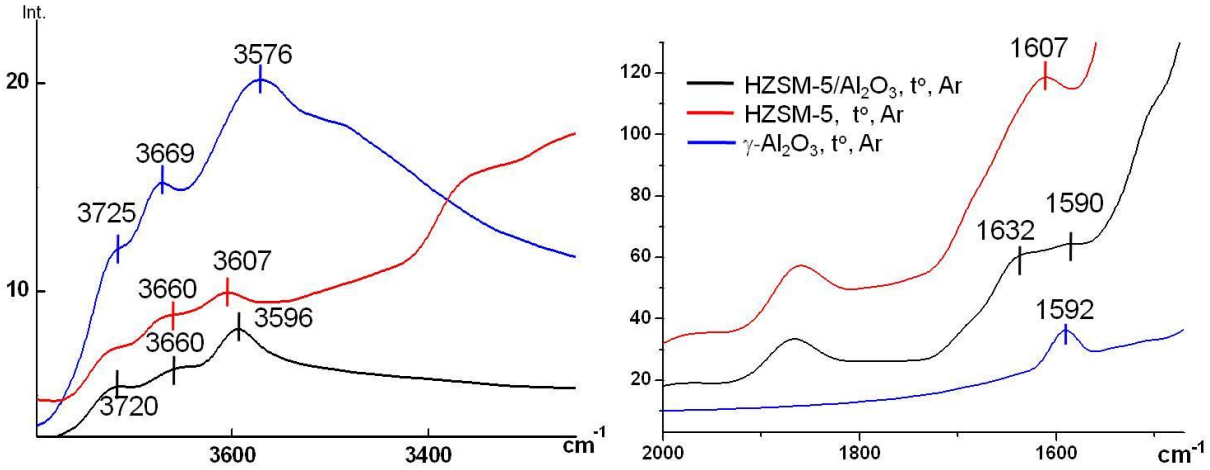
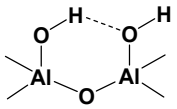
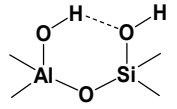
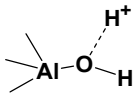


Fig. 3. IR-spectra of samples ZSM-5, ZSM-5/Al_2O_3 and γ-Al_2O_3 after heating at 350 °C in region of BAS and stretching vibration of OH bonds.

Analysis of Fig.3 showed that the absorption bands in region ~ 3700–3400 cm^{-1} can be attributed to active sites on zeolite surface. Table 1 shows the assignment of the absorption bands of hydroxyl groups and BAS in spectrum of zeolite ZSM-5 and γ-Al_2O_3.

Table 1. Adsorbtion bands of hydroxyl groups and BAS in spectra of zeolite ZSM-5 and γ-Al_2O_3

	Group	γ-Al_2O_3, cm^{-1}	HZSM-5/Al_2O_3, cm^{-1}	HZSM-5, cm^{-1}	Calculational data
IS	Si-OH is	-	-	3732 (w)	3780
	Al-OH is	3760	3720		3820
AS		3715 3674	-	-	Calculation in progress
		-	3660	3660 (w)	3625 3770
BAS		3571 1591	3596 1590 1632	3607 (w) 3611 (w)	Calculation in progress

Bands in the IR-spectrum of calcined γ-Al_2O_3, which characterize BAS (3572 and 1592 cm^{-1}), can also be found in the spectra of HZSM-5 and HZSM-5 – Al_2O_3 registered under the same conditions; while their small shift into the range of short wavelength is associated with the influence of the neighbouring Si-O bonds. Quantum-chemical calculations of models of fragments of the zeolite structure with isolated and associated hydroxyl groups can serve as an additional justification for the correctness of such assignment of frequencies. Calculations were performed using the method of density functional theory (DFT) in quantum-chemical program PRIRODA. During these calculations geometry optimization of selected models with further calculation of the vibrational spectrum was carried out, afterwards the correlation of vibration bands of hydroxyl groups in the theoretical and experimental spectra was held. Despite the significant overestimation of the calculated values of vibrational frequencies, the overall trend of shifting their position while being associated remains, which lets us say that the held analysis confirmed the correctness of the assignment of the vibration frequencies of hydroxyl groups, described above.

3.2 Investigation of the structure of the catalyst modified by magnesium nitrate by the method of DR high-temperature spectroscopy in the in situ mode.

Having studied the spectral demonstration while heat treatment of aluminum oxide, unmodified zeolite and their mixtures, one can correctly analyze changes in the structure of the catalyst surface, prepared by mixing the zeolite, modified with magnesium, and aluminum oxide as a binder. Heat treatment of the catalyst was carried out by heating the sample up to 300°C in the argon atmosphere, complete desorption of water was controlled by diffuse reflectance spectra.

Diffuse reflectance spectra of zeolite, modified by magnesium nitrate at room temperature (black curve) and with heat treatment to 150 (red curve) and 300°C (blue curve), are shown in Fig. 4. At room temperature, the water which is adsorbed on the surface of the zeolite, is demonstrated in the spectrum by a wide split band in the range of 3100 – 3650 cm-1 with the most intense peak at 3400 cm^{-1}. After heat treatment the intensity of this absorption band decreases, and at 300°C only in the region above 3600 cm^{-1} low-intensity bands appear, which are interpreted in the spectral literature as isolated OH-groups and, as it was shown above, related to the acid centers of the catalyst.

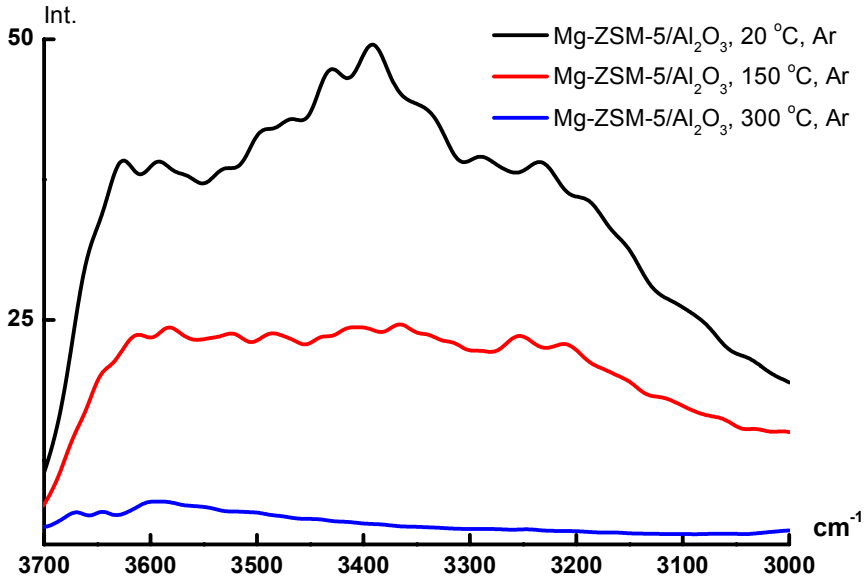


Fig. 4. DR spectra of the zeolite-based catalyst, modified by magnesium, at different temperatures

3.3 Comparison and features of the structure of zeolite-based catalysts, modified with Mg and Rh salts

When comparing the IR-spectra registered by the methods of ATR and transmission spectroscopy of zeolite-based catalysts, modified with magnesium nitrate and rhodium chloride, some interesting facts were also found. When zeolite is modified by a transition metal, one can see a shift of the maximum of absorption bands, corresponding to stretching vibrations of Si-O in the zeolite, in the short-wavelength range as compared to their original position in the spectrum of the basic zeolite (Fig. 5). When zeolite is modified by Rh this shift is demonstrated stronger than while modification by Mg.

According to the literature, such shift of the maximum of the absorption bands of Si-O stretching vibrations may be caused by an increase of Si-O-Si angle[iii], table 2.

For the full confirmation of the literature data and to avoid possible inaccuracies, we carried out quantum-chemical calculations, with bringing them to the vibrational spectrum, which have qualitatively completely agreed with the literature data (Fig. 6). Calculations were carried out by the Hartree-Fock method in the software package Gaussian03. As a basis for calculation, a basis of 6-31G was used.

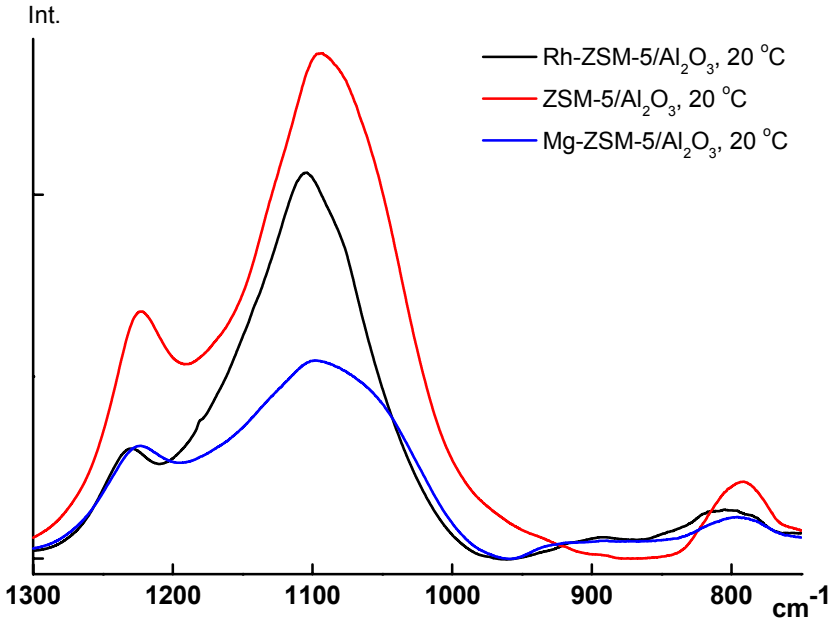


Fig. 5. Comparison of spectra of the catalysts based on zeolite, modified by Rh and Mg, in vaseline oil, registered in transmission mode, in the absorption region of Si-O stretching vibrations.

Table 2. The shift of the absorption band of Si-O stretching vibrations as a function of Si-O-Si angle.

	$(CH_3)_3SiOSi(CH_3)_3$ $[(CD_3)_3SiOSi(CD_3)_3]$	$H_3SiOSiH_3$ $[D_3SiOSiD_3]$	Cl_3SiOCl_3
ν_{as} SiOSi (IR, pairs)	1073 cm^{-1} [1065 cm^{-1}]	1107 cm^{-1} [1094 cm^{-1}]	1131
∠ SiOSi spectroscopy value	135÷140°	150°	160÷170°
Electrographic data ∠ SiOSi	130±10°	144.1±0.8°	175±5°

By this means, the displacement of the peak of antisymmetric Si-O-Si vibrations can be explained by increasing of surface Si-O-Si angles in zeolite structure under modification.

Changes into the region of OH- stretching vibrations are clearly visible in Diffuse Reflectance FTIR spectra. In figure 7 the DR-FTIR spectra in the region of hydroxyl groups absorption of three zeolites, that were heated to 300 °C, are presented.

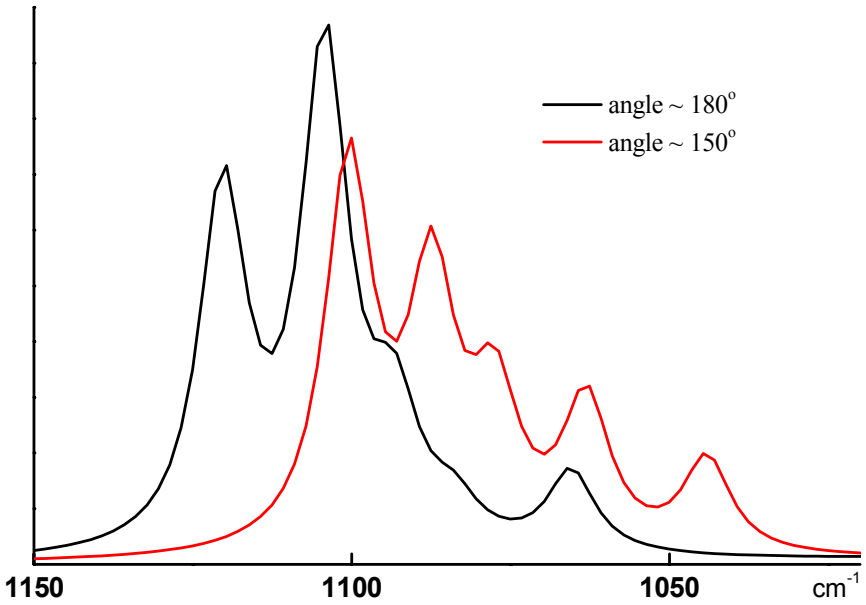


Fig. 6. Comparison of theoretical vibration spectra of zeolite models with different Si-O-Si angles in the region of Si-O stretching vibrations.

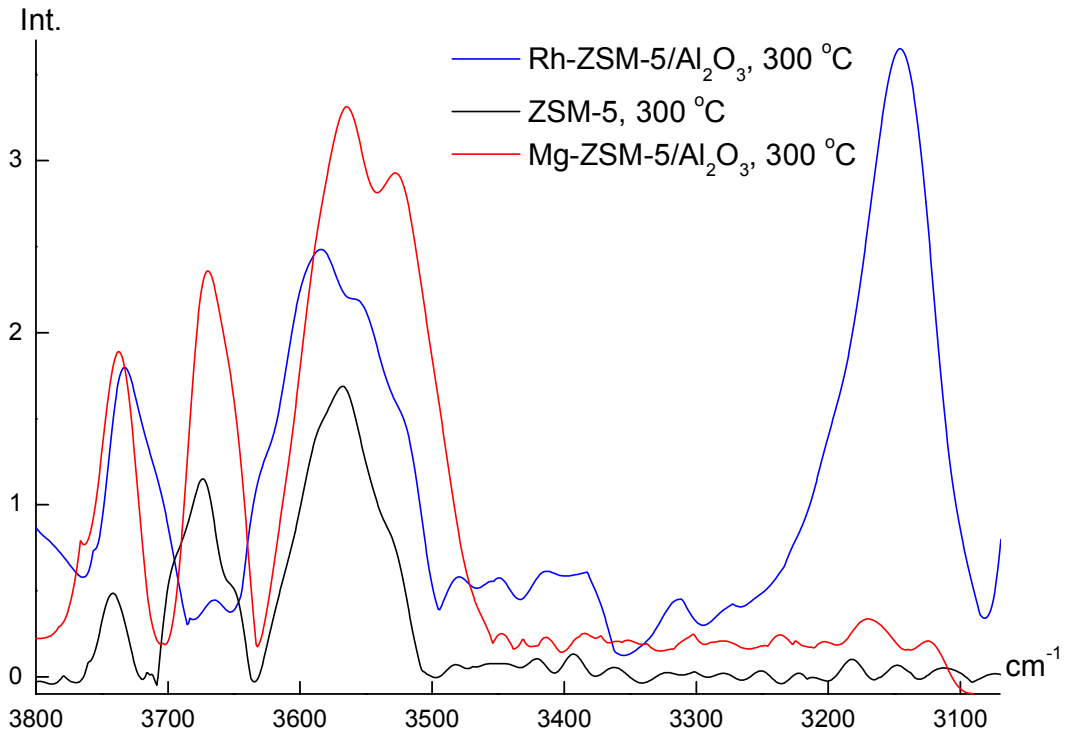


Fig. 7. The comparison of diffuse reflectance IR spectra in the region of hydroxyl groups stretching vibrations absorption of zeolite-based catalysts, that have been modified by different metals.

As seen in Figure 7, the spectral picture of the OH bonds in the catalysts that are based on zeolites modified with transition metals, are quite different. All objects do not contain water after annealing above 300 ° C, and in the spectrum of each sample the absorption band at 3750 cm^{-1} of isolated Si-OH bonds is observed. In the region of absorption from the associated-OH bonds (3550-3700 cm^{-1}) bands are observed in the spectra of all three samples, but they are wildly different in the position of the maxima, in number of bands and their intensity, bands of -OH stretching vibrations in the BAS at 3570, 3600 cm^{-1} one can observe in the spectra of all zeolites, but this bands intensity and maxima position strongly depend on the modifying metal nature (Fig.7). Weak bands in the 1580-1600 cm^{-1}, from deformation vibrations in the BAS can also be observed in the spectra of HZSM-5 modified by magnesium and rhodium (Fig. 8). So, we can conclude that the bands that characterize the BAS can be seen in the spectra of modified HZSM-5 zeolites, and their intensity and maxima position depend on the nature of the included in the zeolite metal. In addition, the spectrum of based on zeolite catalyst modified with rhodium (blue line), has a high-intensity absorption band at 3100 cm -1, characterize the strongly associated -OH bonds, in the IR spectrum of zeolite-based catalyst modified with magnesium, this band was not observed. In the spectrum of Rh-zeolite (Fig. 8) there is another absorption band (1558 cm-1), which is absent in the spectrum of unmodified zeolite HZSM-5 and the spectrum of a zeolite-based catalyst modified by Mg.

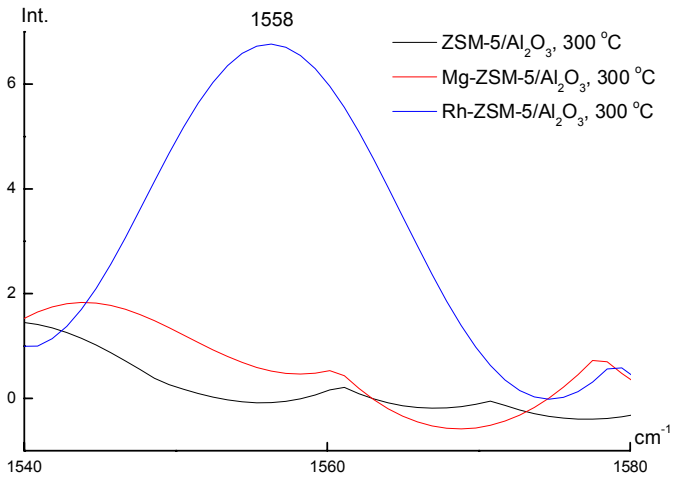
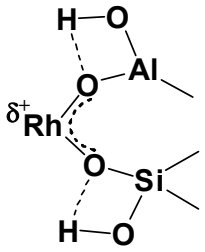


Fig. 8. The comparison of diffuse reflectance IR spectra in the region of 1550 cm-1 of zeolite-based catalysts, that have been modified by different metals.

It has been repeatedly pointed out in the spectral literature that under certain conditions in this region there is a highly delocalized absorption band of the O-M-O (where M is a transition metal atom)[iv]. The presence of absorption bands in this region of the IR spectrum of zeolite based catalyst modified by rhodium, allows us to assume the following structure of the active center:



This center has strongly associated OH- bonds, which may correspond to the absorption band at 3150 cm-1. Also this center has a strong electron density delocalization of between the two oxygen atoms and the atom of Rh, which may lead to the appearance of absorption band at 1558 cm-1. In this case, this structure belongs to the highly coordinatively unsaturated and electron-seeking center, i.e. corresponding to all the definitions of the LAS center.

4. CONCLUSIONS.

The possibility of detecting via the DR-FTIR spectroscopy in situ method of various types of acidic centers (Bronsted and Lewis) on the surface of pre-annealed up to complete removing of water from the surface of zeolite-based catalysts described. Очень тяжело написано, прямой перевод с русского, такие обороты – просто ы. Identification of the absorption bands of isolated and associated hydroxyl groups on the surface of zeolites using the spectral data and quantum-chemical calculations has been carried out. It has been determined that the sorption of water vapor on the surface of pre- annealed at 250 oC γ-Al_2O_3 leads to increasing of the BAS concentration on the surface. The results give the possibility of direct determination of the various active sites in zeolite catalysts, as well as to estimation of their partisipation in hydrocarbons catalytic conversion.

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