Properties of surface acid sites of ZrO_2 and SO_4/ZrO_2-based systems studied by diffuse-reflectance Fourier-transform IR spectroscopy: adsorption of acetonitrile-d_3

A. V. Ivanov and L. M. Kustov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: aivanov@ioc.ac.ru

The properties of acid sites of ZrO_2 and SO_4/ZrO_2-based systems modified by metal ions were studied by DRIFT spectroscopy using acetonitrile-d_3 as a probe molecule. In the case of ZrO_2, CD_3CN interacts with the Lewis acid sites (LAS) with moderate strength. Adsorption on the Brönsted acid sites (BAS) is very weak, which indicates the absence of strong BAS on the surface of ZrO_2. Modification of the surface by SO_4 groups results in the appearance of a new type of BAS that are capable of adsorbing CD_3CN in the polycoordinated form, *i.e.*, stronger complexes with the adsorbate. Addition of metal ions (Fe, Ga, Zn, or Co) leads to the formation of a new type of LAS connected with Fe^{3+}, Ga^{3+}, Zn^{2+}, and Co^{2+} promoter ions.

Key words: superacids, zirconia, sulfated zirconia, adsorption, acetonitrile, DRIFT spectroscopy.

Investigation of the properties and nature of acid sites in SO_4/ZrO_2-based systems enables establishing the relationship between the activity of SO_4/ZrO_2 in the conversion of low alkanes and the chemistry of the catalyst surface.[1,2] Two types of Lewis acid sites (LAS) and several types of the Brönsted acid sites (BAS) have been found on the SO_4/ZrO_2 surface.[3,4] The use of various probe molecules (CO, C_6H_6, CH_4, *etc.*) made it possible to conclude that BAS connected with bridged OH groups are less active than BAS in H-ZSM-5 type zeolites, which possess strong acid properties.[5,6] However, catalysts based on SO_4/ZrO_2 systems reveal higher activity in *n*-butane isomerization, as compared to zeolite catalysts.[7—9] The hypothesis about protons forming multicenter bonds with oxygen atoms belonging to the lattice or to SO_4 groups[5] was put forward in order to explain this effect. However, there is no reliable method for studying such BAS. The investigation of the properties of the SO_4/ZrO_2-based system using spectroscopic probe molecules such as acetonitrile-d_3 is of particular interest for gaining new information about the structure and properties of surface active sites.

The BAS and LAS of oxides and zeolites as well as acid sites connected with modifying metal ions have previously been tested using CD_3CN.[10—17] The active sites in ZrO_2, SO_4/ZrO_2, and sulfated systems modified by metal ions were studied in the present work using CD_3CN as a probe molecule.

Experimental

The SO_4/ZrO_2 system was prepared according to the procedure described earlier.[1—5] The catalyst was dried at 120 °C for 6 h and then calcined in an air flow at 625 °C for 2 h.

Catalysts containing Fe^{3+} ions were prepared by impregnation of $Zr(OH)_4$ with a mixture of 1 *N* H_2SO_4 and 0.3 *N* $Fe(NO_3)_3$ aqueous solutions. The concentration of SO_4^{2-} anions was 5 wt.%, and the metal concentration was 1 wt.%. Catalysts containing Ga^{3+}, Zn^{2+}, and Co^{2+} ions were prepared by the same method. $Ga(NO_3)_3$, $Zn(NO_3)_2$, and $Co(NO_3)_3$ were used as precursors of metal ions. The samples were dried at 120 °C for 6 h and then calcined in a dry air flow at 650 °C for 2 h.

IR spectra were registered on a Nicolet Protégé 460 spectrometer equipped with a diffuse-reflectance unit with a resolution of 8 cm^{-1}.[18] Quantitative analysis of spectra was made using the Kubelka—Munk equation and the OMNIC® program according to the method described elsewhere.[19,20] Computer spectra processing includes also spectra smoothing, background subtraction, and spectra deconvolution by their approximation with the mixed Gauss—Lorentz function combination (the correlation coefficient, 0.999; root-mean-square deviation, 0.0015).

Results and Discussion

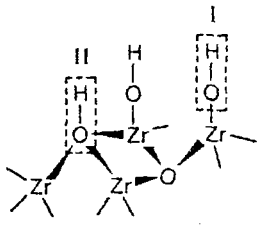
ZrO_2 system

IR spectra of ZrO_2 contain two absorption bands at 3770 and 3660 cm^{-1} in the region of stretching vibra-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 38—44, January, 2000.

1066-5285/00/4901-0039 $25.00

tions of OH groups, which are attributed to terminal and three-fold bridged OH groups existing on the surface of both tetragonal and monoclinic ZrO_2 modifications, respectively.[5,21] According to the literature data, these spectral features can indicate the presence of a mixture of the tetragonal and monoclinic modifications, and the fragment of such a surface can be described by structure **A**.



A

The band at 3770 cm^{-1} for this structure corresponds to OH groups of type I, whereas that at 3660 cm^{-1} is ascribed to OH groups of type II.

Absorption bands in the range of 2400—2200 cm^{-1} indicate the presence of surface carbonates formed at the pretreatment stage.[22]

After CD_3CN adsorption, the bands of OH groups in the spectra of ZrO_2 are shifted to low frequencies and are observed as broad bands with maxima at 3555 and 3360 cm^{-1}, which are characteristic of terminal and bridged OH groups that are hydrogen-bonded with CD_3CN, respectively (see Fig. 1, *a*, *b*).

Such a shift of the band of bridged OH groups with $\nu(OH) = 3660$ cm^{-1} is equal to 300 cm^{-1} only. This fact as well as the low thermal stability of the complexes indicate insufficiently strong acidic properties of BAS. The low intensity of the band of the disturbed bridged OH groups testifies to the low concentration of BAS capable of coordinating CD_3CN. This is consistent with the results obtained earlier in studying acidic properties of ZrO_2-based systems using bases stronger than CD_3CN, such as ammonia[3] and pyridine.[4]

Bands at 2650 and 2460 cm^{-1} were also observed in the spectra. These bands indicate the occurrence of H—D exchange between CD_3CN molecules and the surface OH groups yielding OD groups disturbed by H-bonding with acetonitrile. Evacuation of the sample with a stepwise increase in temperature leads to the removal of the weakly bound physically adsorbed molecules and to the appearance of free OD groups with absorption bands at 2780 and 2705 cm^{-1} corresponding to the bands of OH groups at 3770 and 3660 cm^{-1} in the spectrum of the initial ZrO_2 sample.

The considerable decrease in the intensity of the band at 3770 cm^{-1} after adsorption indicates that less strong acidic terminal OH groups readily react with CD_3CN molecules.

Absorption bands at 2114 and 2250 cm^{-1} found in the spectrum of liquid CD_3CN are characteristic of symmetric (ν_s) and antisymmetric (ν_{as}) vibrations of the CD_3 groups, respectively, whereas the band at 2264 cm^{-1} is ascribed to stretching vibrations of the C≡N bond.[13] The two low-frequency bands do not change after CD_3CN adsorption on the oxide or zeolite systems. On the contrary, the value of ν(C≡N) depends on the nature

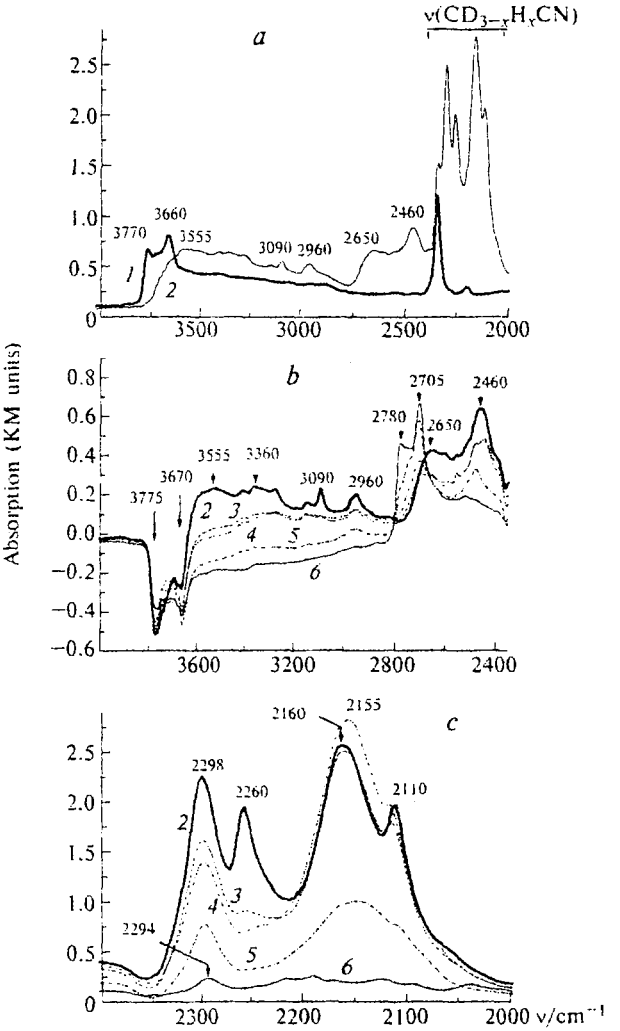


Fig. 1. CD_3CN adsorption on ZrO_2: (*a*) IR spectra of ZrO_2 before (*1*) and after CD_3CN adsorption (*2*); difference spectra in the region of OH and OD group vibrations (*b*) and CN bond vibrations (*c*) after CD_3CN adsorption (*2*) and evacuation at 20 (*3*), 100 (*4*), 200 (*5*), and 300 °C (*6*).

of the adsorption site. In the complex with BAS, the value of ν(C≡N) is typically equal to 2290—2300 cm^{-1}, whereas the range of ν(C≡N) after adsorption on LAS or metal ions is wider: 2270—2340 cm^{-1} (see Refs. 10—16).

Bands at 2298, 2260, 2160, and 2110 cm^{-1} (see Fig. 1, *c*) appear in the region of the stretching vibrations of the C—D and C≡N bonds after CD_3CN adsorption on ZrO_2. The band at 2260 cm^{-1} vanishes after evacuation at 20 °C and, consequently, could be assigned to vibrations of the C≡N bond in physically adsorbed CD_3CN. The band at 2110 cm^{-1} corresponds to $\nu_s(CD_3)$. The absorption band at 2298 cm^{-1} is close to the bands for CD_3CN adsorbed on BAS in zeolites,[10—12] but the high stability of this band under evacuation and insufficiently

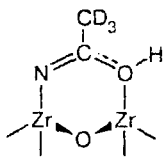
strong perturbation of the OH groups after CD_3CN adsorption allow us to ascribe this band to the molecules adsorbed on LAS of ZrO_2. It was shown earlier[23] that the frequency of the C≡N bond vibrations in the adsorption CD_3CN complex with Zr^{4+} ions of the oxide lattice depends on the ionization potential of the cation (I^{n+}) and on the radius of its highest orbital (r^{n+}_{orb}) by the following equation:

$$\nu(C{\equiv}N) = 2255 + 6.88\sqrt{\frac{I^{n+}}{r^{n+}_{orb}}}. \qquad (1)$$

Substituting I^{n+} = 33.97 and 24.8 eV and r^{n+}_{orb} = 0.603 and 0.600 Å for Zr^{4+} and Zr^{3+} ions, respectively,[24] one can derive the ν(C≡N) value in the range of 2298–2305 cm^{-1}. This is in agreement with the assignment made.

Complexes of LAS with CD_3CN molecules are stable under heating up to 200 °C. Only the band with a very low intensity at 2294 cm^{-1} is observed in the spectra after evacuation at 300 °C. This band can be ascribed to CD_3CN molecules adsorbed on Zr^{3+} sites. It has been found that such sites are present in ZrO_2 in a low concentration.[25]

The appearance of an absorption band at 2160 cm^{-1} is a peculiar feature of CD_3CN adsorption on ZrO_2. This band was not observed in the spectra of zeolite or aluminophosphate systems. It has been shown[26] that the formation of nitrile complexes with Lewis acids results in an increase in the activity of the carbon atom of the nitrile group in reactions with electrophilic agents. The appearance of the band at 2160 cm^{-1} and simultaneous changes in the region of OH group vibrations indicate the possibility of a reaction between the terminal surface OH groups possessing weak basic properties and CD_3CN molecules with the formation of NCO fragments (structure **B**) characterized by frequencies in the range of 2000–2273 cm^{-1} (see Ref. 27).



B

This hypothesis is confirmed by the appearance of new absorption bands in the range of 1440–1570 cm^{-1} corresponding to the NCO and C=N fragments.

SO_4/ZrO_2 system

An absorption band at 3640 cm^{-1} characteristic of the bridging tricoordinated OH groups of the tetragonal modification was observed in the range of stretching vibrations in the IR spectra of the SO_4/ZrO_2 system (Fig. 2, *a*). The high-frequency shoulder indicates the presence of residual terminal OH groups. The shift of the maximum to lower frequencies with respect to the corresponding band in the spectrum of ZrO_2 testifies to the enhancement of the strength of the acid sites.[5] According to the data obtained previously,[28] introduction of SO_4^{2-} anions at the concentration 5 wt.% corresponds to a nearly monolayer surface coverage. The decrease in the intensity of the absorption band assigned to the terminal OH groups, which are the stronger basic sites in the SO_4^{2-}/ZrO_2 system as compared to ZrO_2, can result from their interaction with H_2SO_4 molecules to form the surface $HO_3S{-}O{-}$ groups.

A broad absorption maximum in the region 3200–3400 cm^{-1}, which is characteristic of sulfated oxides, was also observed in the spectra. This absorption has been ascribed to protons forming multicenter bonds with the surface oxygen atoms and SO_4 groups.[5,29]

The bands at 2760–2765 and 2040 cm^{-1} in the spectra of SO_4/ZrO_2 belong to the first overtones of stretching vibrations of the S=O and S–O bonds, respectively.

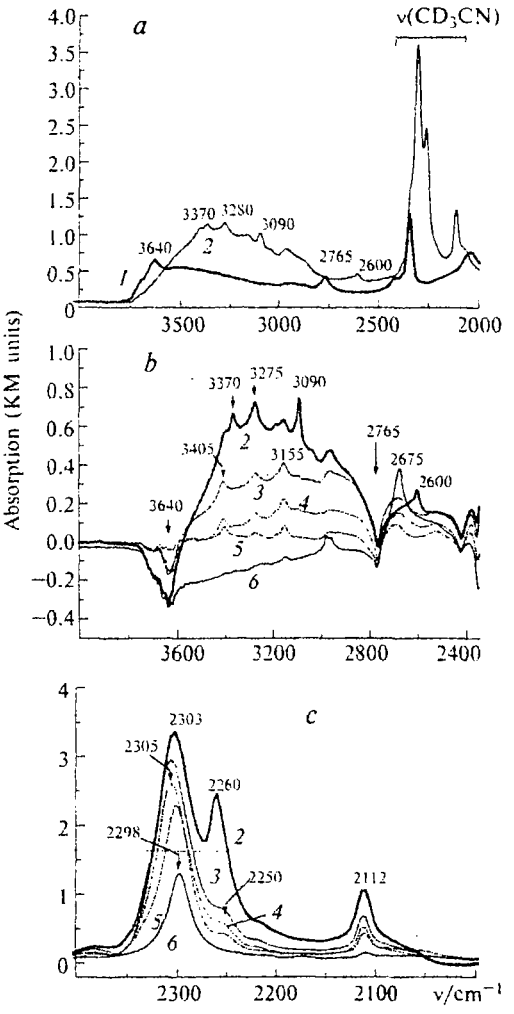
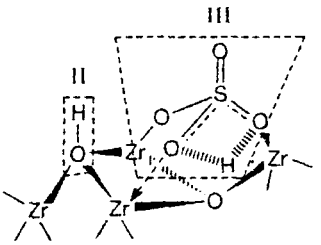


Fig. 2. CD_3CN adsorption on ZrO_2: (*a*) IR spectra of ZrO_2 before (*1*) and after CD_3CN adsorption (*2*); difference spectra in the region of OH and OD group vibrations (*b*) and CN group vibrations (*c*) after CD_3CN adsorption (*2*) and evacuation at 20 (*3*), 100 (*4*), 200 (*5*), and 300 °C (*6*).

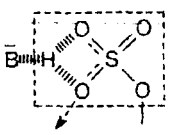
The spectral data obtained confirm the formation of the tetragonal modification of ZrO_2 with the terminal OH groups being partially substituted by HO_3S—O— groups. The fragment of such a surface could be described by structure **C**.



C

The OH groups of type II in this structure are responsible for the band at 3640 cm^{-1}, shifted toward low frequencies with respect to the corresponding band of ZrO_2 as a result of structural and electronic effects. The frequency of the band corresponding to O—H bond vibrations in fragment III is close to that in free H_2SO_4 molecules (2900—3200 cm^{-1})[30] and implies strong hydrogen bond formation.

After CD_3CN adsorption on SO_4/ZrO_2 (see Fig. 2, *a*, *b*), the band at 3640 cm^{-1} is shifted toward low frequencies, while the bridging OH groups participating in the formation of hydrogen bonds were found as a broad absorption peak with the maximum at 3190 cm^{-1}. The shift of the band at 3640 cm^{-1} reaches 450 cm^{-1}, which testifies to enhancement of the strength of BAS connected with the bridged OH groups with respect to those in ZrO_2. Comparison of the available data on CD_3CN adsorption on different zeolites and aluminophosphate systems (Table 1) shows that BAS of type II in SO_4/ZrO_2 are weaker than BAS in H-ZSM-5, H-Y, and H-MOR zeolites, despite the increase in their strength as compared to ZrO_2. The acidity of these BAS is moderate and close to those in $AlPO_4$-5 aluminophosphate systems. Consequently, centers of this type cannot be responsible for the superacidic properties of SO_4/ZrO_2 revealed in various catalytic reactions, for example, in *n*-butane isomerization. Unfortunately, this method, as well as adsorption of strong bases,[5] does not allow one to estimate the acidity of BAS of type III responsible for the broad absorption band. The H-bond formation with adsorbed acetonitrile results in further line broadening, which makes it hardly possible to determine precisely the position of the band of the perturbed OH groups. Furthermore, adsorption of a basic molecule on a site of type III may cause the transformation of the active center structure, leading to the formation of hydrogen-bound adduct **D**. In this case, the formation of an additional H-bond may not considerably affect the frequency of the OH group stretching vibrations, no matter how strong the acid site or the basic adsorbate.



D
(B is the base)

Table 1. The shifts of the absorption bands corresponding to the bridged OH groups after CD_3CN adsorption at 100 °C

Catalyst[a]	ν(OH)/cm^{-1}		Δν(OH) /cm^{-1}	Reference
	before adsorption	after adsorption		
ZrO_2	3660	3360	300	[b]
SO_4/ZrO_2	3640	3190	450	
	3630	3200	430	6
$Ga/SO_4/ZrO_2$	3640	3195	445	[b]
$Fe/SO_4/ZrO_2$	3640	3190	450	[b]
$Zn/SO_4/ZrO_2$	3640	3315	325	[b]
$Co/SO_4/ZrO_2$	3640	3400	240	[b]
H-ZSM-5 (80)	3610	2480	1130	12
H-ZSM-5 (50)	3610	2470	1140	31
1.2Cu-H-ZSM-5 (50)	3610	2635	975	31
H-Y (5)	3630	2680	950	12
H-MOR (10)	3609	2540	1069	14
$AlPO_4$-5	3680	3100	580	14
SAPO-5	3630	2850	780	14
SAPO-34	3625	2850	775	14

[a] The SiO_2/Al_2O_3 ratio is indicated in the parentheses.
[b] The data from the present work.

Evacuation of the sample with a stepwise temperature increase results in the appearance of a band at 2675 cm^{-1} assigned to vibrations of bridged OD groups. Noticeable H—D exchange is observed, however, only at high temperatures.

The changes in the region of OH group vibrations are accompanied by shifts of the bands in the region of S=O bond vibrations (Fig. 3). An absorption band at 1400 cm^{-1}, which is probably a superposition of two bands at 1410 and 1385 cm^{-1}, was observed in the spectra of the starting SO_4/ZrO_2 system. These bands can be ascribed either to the ν(S=O) mode in SO_4 groups with different configuration[3] or to S=O bond vibrations in mono- or disulfated surface fragments.[32] Nevertheless, a different interpretation of this band is quite possible. The frequency of S=O bonds vibrations is known to increase with an increase in the bond order. Thus, the bands at 1410 and 1385 cm^{-1} could correspond to two S=O bond with different bond orders in the same acid site. Analysis of structure **C** shows that these bands can be assigned to the terminal S=O group ($S=O_{term}$) and to the S=O group coordinated to the surface ($S=O_{coord}$). The order of the $S=O_{coord}$ bond is decreased due to interaction with Zr^{4+} ions.

These two bands are shifted to low frequencies after CD_3CN adsorption, and two poorly resolved bands at 1350 and 1310 cm^{-1} were found in the spectra. Analysis of the intensities of these bands showed that they correspond to the $S=O_{coord}$ and $S=O_{term}$ bond vibrations

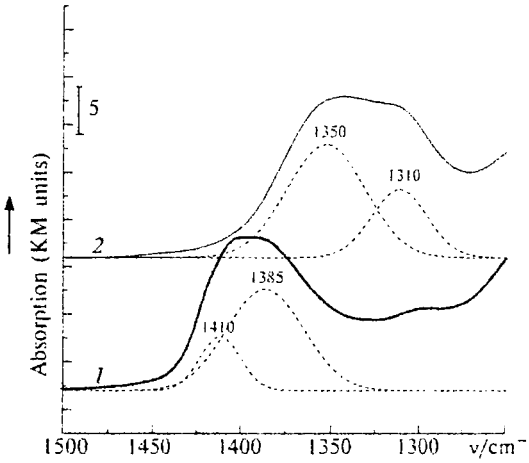


Fig. 3. IR spectra in the region of S=O bond vibrations for SO_4/ZrO_2 before (*1*) and after CD_3CN adsorption (*2*). The dotted line corresponds to spectra deconvolution.

perturbed by the adsorbed CD_3CN molecules. The dependence of the shift $\Delta\nu$(S=O) on the evacuation temperature is presented in Fig. 4. Analogous shifts of the S=O bond frequency have been observed previously[3] in studying adsorption on the SO_4/ZrO_2 surface of other probe molecules suitable for identification of both BAS and LAS such as CO. The shift of the band is the result of a decrease in the S=O bond order due to interaction with adsorbed molecules. The stronger such an interaction between the adsorption site and the adsorbate, the larger the shift of the absorption band. Therefore, the $S{=}O_{term}$ group should interact with adsorbed CD_3CN molecules to a greater extent as compared to the $S{=}O_{coord}$ group. On the other hand, the interaction between CD_3CN and $S{=}O_{coord}$ groups is kept at elevated temperatures.

Spectra of CD_3CN adsorbed on the SO_4/ZrO_2 surface reveal absorption bands at 2303, 2260, and 2112 cm^{-1} (see. Fig. 2, *c*). The two latter bands are similar to those observed upon CD_3CN adsorption on ZrO_2. The band at 2260 cm^{-1} is assigned to C≡N bond vibrations in physically adsorbed CD_3CN molecules, and that at 2212 cm^{-1} belongs to $\nu_s(CD_3)$ vibations.

Evacuation at 20 and 100 °C leads to the shift of the band at 2303 cm^{-1} to 2305 cm^{-1}, probably because of a decrease in dipole interaction upon removal of weakly bound physically adsorbed CD_3CN molecules. This phenomenon has earlier been observed[31] in the course of the formation of acetonitrile complexes with BAS of zeolites.

An increase in the evacuation temperature up to 300 °C results in shift of the band of C≡N stretches toward lower frequencies (from 2305 to 2298 cm^{-1}). This effect cannot be explained by weakening of the dipole—dipole interaction causing the C≡N bond vibration frequency to increase. We could only suggest that the band at 2305 cm^{-1} is a complex superposition and consists of two maxima at 2298 and 2308 cm^{-1}. The dependence of the intensity of these bands on the evacuation temperature is presented in Fig. 5.

The band at 2298 cm^{-1} is close to that of CD_3CN adsorbed on LAS in the ZrO_2 system. This band can be observed even after evacuation at 300 °C. The higher frequency ν(C≡N) for the CD_3CN—SO_4/ZrO_2 system as compared to the CD_3CN—ZrO_2 sample demonstrates the stronger acidity of LAS due to the electron-acceptor influence of the HO_3SO groups.

The high-frequency band at 2308 cm^{-1} is less stable and disappears after evacuation at temperatures higher than 200 °C. This band probably corresponds to weak complexes. The intensity of this band decreases simultaneously with a decrease in the intensity of the band of

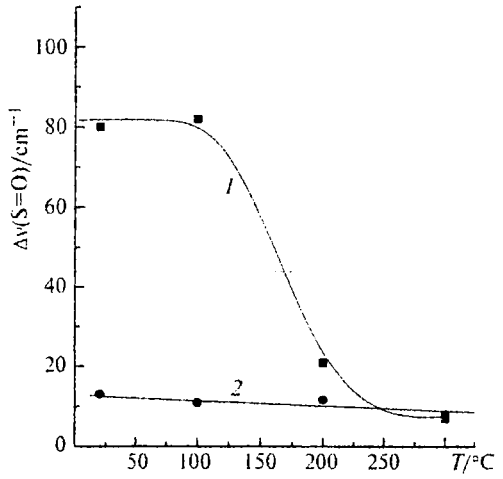


Fig. 4. Dependence of the S=O bond vibration frequency ($\Delta\nu$(S=O)) for the SO_4/ZrO_2 system after CD_3CN adsorption on the evacuation temperature (*T*): absorption bands at 1410 (*1*) and 1385 cm^{-1} (*2*).

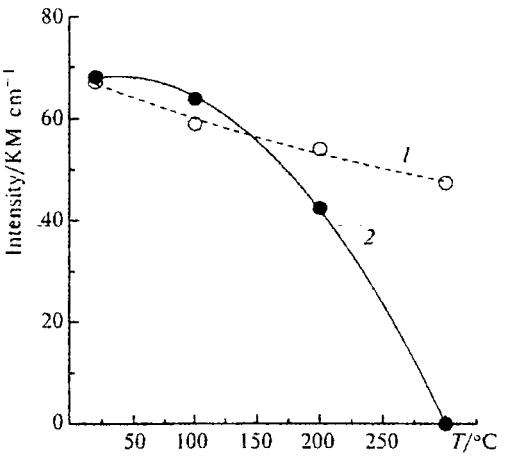
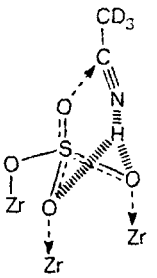


Fig. 5. Dependence of the intensity of the absorption bands at 2298 (*1*) and 2308 cm^{-1} (*2*) in the spectra of CD_3CN adsorbed on SO_4/ZrO_2 on the evacuation temperature (*T*).

OH groups perturbed by hydrogen bond formation and with the disappearance of the low-frequency band at 1315 cm^{-1}, which is characteristic of the $S=O_{term}$ bond vibrations in the $HOSO_3$ groups interacting with the adsorbate. Thus, the band at 2308 cm^{-1} most likely corresponds to $\nu(C\equiv N)$ of CD_3CN adsorbed on BAS that are formed by the surface SO_4 groups. Strong interaction of the $S=O_{term}$ bonds indicates that they participate in the formation of the adsorption complex with CD_3CN. In addition, absorption bands at 3405, 3275, and 3155 cm^{-1}, characteristic of the vibrations of N—H bonds in free or bound NH or NH_2 fragments, have been also observed in the spectra of CD_3CN adsorbed on the SO_4/ZrO_2 surface.[27] The appearance of such bands is quite unexpected for spectra of acetonitrile adsorbed on the oxide or zeolite systems under investigation and thus could be a specific feature of CD_3CN adsorption on the SO_4/ZrO_2 surface. The N—H bond could be formed only on BAS having acidity close to that of liquid superacids,[26] for example, on the protons of type III in the $HOSO_3$ surface groups (structure **C**). On the other hand, the absence of bands in the range of 1450—1600 cm^{-1} indicates that the C≡N triple bond is preserved and no C=N or NCO bonds are formed. Thus, the formation of a complex of type **E** due to the interaction of CD_3CN and SO_4/ZrO_2 can be speculated.

In this case, the bond order in the $S=O_{coord}$ fragments would be lowered due to acetonitrile interaction with BAS and due to the inductive effect of the CD_3CN molecules adsorbed on neighboring LAS.



E

Unlike zeolite systems in which the adsorption—desorption process is reversible, acetonitrile desorption from active sites in SO_4/ZrO_2 may lead to chemical transformations of CD_3CN molecules.[2,6] The reason behind this effect may be the activation of the adsorbate molecule bonds in the case of multi-center CD_3CN adsorption on the HO_3SO fragments due to addition of the conjugated base ^-O_3SO and a proton to the C≡N bond.[26] The complex could decompose simultaneously with sulfur reduction in the SO_4 group accompanied by the evolution of SO_2 and other destruction products (CO, N_2, *etc.*).[6]

SO_4/ZrO_2-based systems modified by metal ions

Addition of Ga, Fe, Zn, and Co ions into the SO_4/ZrO_2 system hardly changes the spectra in the region of stretching vibrations of OH groups. The bands that could have been assigned to new OH groups bound to metal ions are probably masked by the OH group vibrations in the original SO_4/ZrO_2 system.

Table 2. Frequencies of the C≡N bond vibrations (ν/cm^{-1}) for ZrO_2 and $M/SO_4/ZrO_2$ systems (M = Ga, Fe, Zn, and Co)

Catalyst	BAS	LAS_M	LAS
ZrO_2	—	—	2294
SO_4/ZrO_2	2308	—	2298
$Ga/SO_4/ZrO_2$	2305	2324	2298
$Fe/SO_4/ZrO_2$	2305	2319	2298
$Zn/SO_4/ZrO_2$	2306	2316	2298
$Co/SO_4/ZrO_2$	2305	2314	2299

The spectra in the region of OH groups obtained after CD_3CN adsorption are quite similar to those for SO_4/ZrO_2 (see Table 1). However, analysis of the region of C≡N bond vibrations shows that additional LAS that can strongly adsorb acetonitrile (LAS_M) are formed due to the presence of metal ions. These sites are characterized by the appearance of new absorption bands AB at 2330—2300 cm^{-1} (Table 2), indicating the ability of LAS_M to adsorb acetonitrile firmly.

The addition of Fe^{3+} and Ga^{3+} ions does not alter the spectra at low evacuation temperatures but does so at higher temperatures. A weak AB at 2330 cm^{-1} was observed in the $\nu(C\equiv N)$ area of the spectra after removal of the physically adsorbed CD_3CN molecules (at 100 °C). The maximum location of this band was shifted after evacuation at 300 °C up to 2320 and 2324 cm^{-1} for Fe and Ga ions, respectively, indicating new sites involving metal ion formation.

After Zn or Co addition a new band at 2322 or 2320 cm^{-1}, respectively, appears in the region of $\nu(C\equiv N)$. The maximums of these bands shift to 2316 and 2314 cm^{-1}, respectively, after evacuation at temperature higher then 100 °C. These bands are situated close to the $\nu(C\equiv N)$ band in the Zn^{2+} complex in the spectra of the ZnAPO-18 system (2316 cm^{-1}),[13] but the values of these frequencies are somewhat higher than those in the case of Co^{2+} ions in CoAPO-18 or CoY zeolite (2312—2308 cm^{-1}).[15,16]

Thus, the results obtained enable the following conclusions.

The CD_3CN molecule is not an effective probe molecule for testing BAS in oxide-based systems, because the spectra obtained are complicated by side reactions between adsorbate and basic sites of oxides.

In case of the ZrO_2-based system, the CD_3CN molecule reacts with mild LAS of only one type. The interaction with BAS is complicated by interaction with basic terminal OH groups and is insignificant, which indicates the weak acidity of BAS in ZrO_2.

Surface promotion with HO_3SO groups results in the formation of a new type of active BAS. These new BAS are able to adsorb CD_3CN molecules with formation of polycoordinated species, thus forming rigid complexes.

The addition of Fe^{3+}, Ga^{3+}, Zn^{2+}, and Co^{2+} ions results in new LAS connected with metal ion formation.

References

1. A. Corma, *Chem. Rev.*, 1995, **95**, 559.
2. X. Song and A. Sayari, *Catal. Rev.-Sci. Eng.*, 1996, **38**, 329.
3. D. Spielbauer, G. A. H. Mekhemer, M. I. Zaki, and H. Knözinger, *Catal. Lett.*, 1996, **40**, 71.
4. C. Morterra, G. Cerrato, V. Bolis, S. DiCiero, and M. Signoretto, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 1179.
5. L. M. Kustov, V. B. Kazansky, F. Figueras, and D. Tichit, *J. Catal.*, 1994, **150**, 143.
6. V. Adeeva, J. W. de Haan, J. Jänchen, G. D. Lei, V. Schünemann, L. J. M. van de Ven, W. M. H. Sachtler, and R. A. van Santen, *J. Catal.*, 1995, **151**, 364.
7. J. C. Yori, J. C. Luy, and J. M. Parera, *Appl. Catal.*, 1989, **46**, 103.
8. H. Liu, G. D. Lei, and W. M. H. Sachtler, *Appl. Catal. A*, 1996, **137**, 167.
9. L. M. Kustov, T. V. Vasina, O. V. Masloboishchikova, A. V. Ivanov, E. G. Khelkovskaya-Sergeeva, and P. Zeuthen, *12th Int. Zeolite Conf., Abstrs. of Papers*, Baltimore (USA), 1998, A-22.
10. J. Kotrla, L. Kubelkova, C.-C. Lee, and R. J. Gorte, *J. Phys. Chem. B*, 1998, **102**, 1437.
11. A. G. Pelmenshchikov, R. A. van Santen, J. Jänchen, and E. Meijer, *J. Phys. Chem.*, 1993, **97**, 11071.
12. J. Jänchen, J. H. M. C. van Wolput, L. J. M. van de Ven, J. W. de Haan, and R. A. van Santen, *Catal. Lett.*, 1996, **39**, 147.
13. J. Chen, J. M. Thomas, and G. Sankar, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 3455.
14. S. A. Zubkov, L. M. Kustov, and V. B. Kazansky, *Kinet. Katal.*, 1993, **34**, 750 [*Kinet. Catal.*, 1993, **34** (Engl. Transl.)].
15. S. A. Zubkov, G. A. Dvoretskov, L. M. Kustov, and V. B. Kazansky, *Kinet. Katal.*, 1994, **35**, 155 [*Kinet. Catal.*, 1994, **35** (Engl. Transl.)].
16. C. L. Angell and M. V. Howell, *J. Phys. Chem.*, 1969, **73**, 2551.
17. S. G. Yim, D. H. Son, and K. Kim, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 837.
18. L. M. Kustov, A. A. Alekseev, V. Yu. Borovkov, and V. B. Kazansky, *Dokl. Akad. Nauk SSSR*, 1981, **261**, 1374 [*Dokl. Chem.*, 1981, **261** (Engl. Transl.)].
19. V. Yu. Borovkov, Doct. Sci. (Chem.) Thesis, Inst. Organic Chemistry, Moscow, 1989 (in Russian).
20. A. S. Medin, Ph. D. (Phys.-Math.) Thesis, Inst. Organic Chemistry, Moscow, 1990 (in Russian).
21. A. N. Kharlanov, E. V. Lunina, and V. V. Lunin, *Zh. Fiz. Khim.*, 1997, **71**, 1672 [*Russ. J. Phys. Chem.*, 1997, **71** (Engl. Transl.)].
22. C. Morterra, R. Aschieri, and M. Volante, *Mater. Chem. Phys.*, 1988, **20**, 539.
23. R. I. Soltanov, E. A. Paukshtis, and E. N. Yurchenko, *React. Kinet. Catal. Lett.*, 1987, **34**, 421.
24. A. A. Godovikov, in *Periodicheskaya sistema D. I. Mendeleeva i silovye kharakteristiki elementov* [*D. I. Mendeleev Periodic System and Force Constants of Elements*], Novosibirsk, Nauka, 1981, 95 (in Russian).
25. F. R. Chen, G. Coudurier, J.-F. Joly, and J. C. Vedrine, *J. Catal.*, 1993, **143**, 616.
26. I. D. Gridnev and N. A. Gridneva, *Usp. Khim.*, 1995, **64**, 11 [*Russ. Chem. Rev.*, 1995, **64** (Engl. Transl.)].
27. L. Bellamy, *The Infra-Red Spectra of Complex Molecules*, Methuen, London, 1954.
28. P. Nascimento, Ç. Akratopoulou, M. Oszagyan, G. Coudurier, C. Travers, J.-F. Joly, and J. C. Vedrine, *New Frontiers in Catalysis, Proc. 10th Int. Congr. Catal.*, Akademiai Kiado, Budapest, 1993, 1185.
29. A. G. Panov, A. V. Ivanov, L. M. Kustov, and V. B. Kazansky, *Kinet. Katal.*, 1997, **38**, 410 [*Kinet. Catal.*, 1997, **38** (Engl. Transl.)].
30. P. A. Giguère and R. Savoie, *Can. J. Chem.*, 1960, **38**, 2467.
31. A. V. Ivanov, G. W. Graham, and M. Shelef, *Appl. Catal., B, Env.*, 1999, **21**, 243.
32. M. Bensitel, O. Saur, J.-C. Lavalley, and B. A. Morrow, *Mater. Chem. Phys.*, 1988, **19**, 147.

Received May 14, 1999