Surface Acidity and Basicity of Oxide Catalysts: From Aqueous Suspensions to In Situ Measurements

T. S. Glazneva, N. S. Kotsarenko, and E. A. Paukshtis

Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia
e-mail: glazn@catalysis.ru
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Abstract—Our review covers the achievements of recent decades in the investigation of the acid–base properties of oxide catalyst surfaces. Both conventional and new investigation techniques are reviewed, including SSITKA for H/D exchange.

The catalytic activity of many oxides in various petrochemical and petroleum-refining processes, such as isomerization, alkylation, cracking, aromatization, and many others [1], is due to their Lewis and Brønsted acidities [2].

The research concerning the acid–base properties of inorganic solid surfaces is extensive and has resulted in the modeling of the chemistry of acid–base catalysis and the appearance of new fields, such as catalysis by superacids, heteropoly acids, and zeolites. The development of a scientific basis for heterogeneous acid–base catalysis was considerably provided by physical methods of investigation. IR spectroscopy revealed a number of fundamental features of acid catalysis; primarily, Lewis and Brønsted acid sites (hereafter, LAS's and BAS's, respectively) were discovered and characterization techniques for acid–base surface properties were developed.

DEVELOPMENT OF METHODS OF CHARACTERIZING SURFACE ACIDITY AND BASICITY

The fundamentals of acid–base catalysis were first developed as applied to solution reactions and then transferred to solid acid–base catalysis. This strategy made it possible to expand the terminology of homogeneous acid catalysis to solid acid catalysts and promoted rapid proliferation of general views on the nature of their catalytic effect. The following feature of solid acids arising from the absence of solvents is, however, important and notable. The role of solvation, i.e., nonspecific (van der Waals and electrostatic) acid–solvent interaction, in the dissociation of an acids in solutions is known to be at least equal to the role of the chemical composition and structure of the acid. In gas-phase acid–base interactions, there is no solvation; in the interaction of a base with an acidic surface site, solvation become apparent only on the pore wall on which

the acid site is located, being insignificant on the other wall [3]. Another important feature of solid acids is the occurrence of both BAS's and LAS's on their surfaces, with the properties of one type of site varying only in association with the properties of the other. In this context, the characterization of a catalyst should include the determination of the strength and concentration of all types of sites, the investigation of acid–base interactions of reagents with these sites, and comparison of the characteristics obtained in this way with catalytic properties.

Ion exchange was initially used to determine the acidity of solids. The underlying idea of this method is that the surface acidity is determined by the hydrogen mobility of surface OH groups, characterized by their ability to exchange for other ions [4–9]. To determine the concentration of sites, an aqueous suspension of the catalyst is titrated with aqueous salts or alkalis. The site concentration is determined by potentiometric or conductometric titration; their strength is characterized by solution pH. However, water is not an inert medium; adsorption of water molecules on Lewis sites generates extra BAS's (which were absent in the initial catalyst), and it remains disputable whether the measured quantities can be applied to catalytic reactions of hydrocarbons (which occur without water).

The acidity function, initially proposed by Hammett and Deyrup [10] for solutions (the *indicator method*) is used for the characterization of solid acids. For heterogeneous acid–base catalysts, the H_0 scale is considered as a concentration-independent measure of the strength of acid sites.

The strength of a BAS is characterized by the Hammett acidity function

$$H_0 = pK_a - \log \frac{[BH^+]}{[B]},$$

where $pK_a = pK_{BH^+}$ is the ionization constant exponent for the indicator base B. The indicator method requires

Table 1. Probe molecules most frequently used in the identification of acid sites

Probe molecule	BAS feature in IR spectra, cm^{-1}	LAS feature in IR spectra, cm^{-1}	Reference
Ammonia	1400–1500	1150–1300	[34, 35]
Pyridine	1540–1550	1450–1460	[34, 36]
		1600–1630	
Benzonitrile	H-bond	2245–2300	[37]
Acetonitrile and deuterated acetonitrile	H-bond	2270–2350	[38]
Carbon oxide	H-bond	2155–2250	[39, 40]
Dihydrogen	H-bond	3900–4150	[41–43]

(1) the existence of equilibrium between the basic and protonated species of the indicator on the surface, (2) a small indicator concentration compared to the BAS concentration, (3) and equal pK_a of the indicator in the solution and on the catalyst surface [3].

The strength of acid sites is derived from the change in the color of an adsorbed base indicator [11], observed either visually or using **UV–Vis spectroscopy** [12–14]. A number of indicators are used to determine the range where an indicator with p$K_a^{(1)}$ changes color, whereas an indicator with p$K_a^{(2)}$ does not (p$K_a^{(1)} \leq H_0 \leq$ p$K_a^{(2)}$) on the assumption that H_0 is the strength of the BAS. The BAS concentration is determined by titrating the catalyst suspended in hexane by n-butylamine in the presence of various indicators. Sequentially varying indicators, one obtains the acidic-site strength distribution with $H_0 \leq$ pK_a [15].

Take et al. [16] and Balikova [17] outlined the problem of achieving equilibrium between the basic and protonated indicator species on the surface. Later, Deeba and Hall [18] proved that this equilibrium cannot be reached. However, the indicator technique gives adequate sequences for the strengths of acid sites. The inconsistency with the nonequilibration is explained as follows. A molecule is protonated in two stages: an H-bonded complex is first formed, and then an ion pair is. In the absence of adsorption equilibrium, the change in color of the indicator is determined by the fraction of indicator base molecules adsorbed on acid sites in the form of ion pairs. Equilibrium between H-bonded complexes and ion pairs is acquired on account of the rapid and reversible transfer of a proton from the acid moiety of the BAS to a base molecule and has nothing in common with adsorption equilibrium.

To estimate the concentration of acid sites involved in reactions, *deactivation (poisoning)* of acid catalysts with bases is employed [19–23]. Presumably, the poi-

son is primarily adsorbed on acid sites. The active site concentration is determined from the activity versus poison concentration dependence. The weakness of this method is that poisons are adsorbed not only on active sites but also on inactive ones [19].

Adsorption of volatile amines, such as ammonia, pyridine, n-butylamine, quinoline, and some others, is used to determine the acid site concentration of solid catalysts. The amount of the base remaining on the surface after evacuation is considered chemisorbed and serves as a measure of the acid site concentration. The adsorbed base concentration as a function of evacuation temperature gives the site strength distribution. Another way to determine the site strength distribution is calorimetry [24] or the temperature-programmed desorption (TPD) of the preadsorbed base [25–27]. Ammonia is widely used in TPD [28]. However, one should keep in mind that ammonia is strongly adsorbed on both BAS's and LAS's and can also dissociate into NH$_2^-$ and H$^+$. In particular, it is strongly adsorbed (likely, in a dissociative form) on solid bases such as CaO [29].

The use of amines as adsorbates in TPD is better for measurements of the catalyst acidity [29–31]. In TPD, alkylammonium ions generated by amine protonation on BAS's (except for methylamine) are converted by the Hofman reaction within a very narrow temperature range [32]. In H-MFI samples with various aluminum contents, there is one reacting amine molecule per framework aluminum atom [30, 33].

IR spectroscopy with various probe molecules, in particular, ammonia, pyridine, carbon oxide, acetonitrile, and benzonitrile, is widely used to identify adsorption sites [3]. Table 1 displays the spectral characteristics of the probe molecules most frequently used for identifying acid sites. There is some trouble with using ammonia as a probe molecule. First, surface amination occurs on alumina and phosphates [44, 45]. Second, ammonia cannot be used to study LAS's in silicate systems where the IR transparency window is above 1300 cm^{-1}. For pyridine, the recognition of weak LAS's is complicated by the overlap of coordination-sensitive bands with the bands of pyridinium ions and physisorbed pyridine. Acetonitrile and benzonitrile form only hydrogen bonds with BAS's [46]; therefore, they can only be used to identify LAS's. For identification of basic surface sites, deuterochloroform is used [46].

The term *strength of an acid site* is frequently used as an acidity parameter, meaning that the strength of the site is a certain quantity characterizing the degree of its interaction with molecules (probe molecules and reagents). The question is how to quantify the degree of this interaction.

The strength of a protic acid or base in solution is determined by the thermodynamic constant of the reactions AH $\rightleftarrows$ A$^-$ + H$^+$ and BH$^+$ $\rightleftarrows$ B + H$^+$ (pK_a) [47, 48]; in the gas phase, this strength is measured by the enthalpies of these reactions [48], referred to as proton

affinity (PA). Because reagent molecules in heterogeneous catalysis interact with surface sites from the gas phase, the PA scale was proposed as a characteristic of the strength of BAS's [3]. The convenience of this scale is due to the possibility of quantum-chemical calculations of PA [49–52].

Paukshtis and Yurchenko [46, 53] were the first to propose correlation techniques for measuring the PA of Brønsted acids. These techniques study the spectral characteristics of complexes of acids and bases as a function of their PAs. The adsorption of a weak base (in particular, CO) proceeds via the formation of an H-bond between the surface acid OH group and a probe molecule. This interaction is manifested as low-frequency shifts of the absorption bands of OH groups ($\Delta\nu_{OH}$). The stronger the acid site, the greater the $\Delta\nu_{OH}$. The strength of a proton site is derived from experimentally determined $\Delta\nu_{OH}$ relative to a reference. $\Delta\nu_{SiOH}$ for OH groups of Aerosil is used as a reference. The following equation is proposed to determine the PA of the BAS:

$$PA_{OH} = 1390 - 0.00226^{-1}\log(\Delta\nu_{OH}/\Delta\nu_{SiOH}).$$

Here, 1390 kJ/mol corresponds to the PA of surface OH groups of Aerosil (for CO adsorption, $\Delta\nu_{SiOH} = 90$ cm^{-1}) [3].

The interaction of strong bases with acid sites generates ion pairs. The properties of ion pairs are used to measure the BAS strength in cases where Brønsted sites as isolated OH groups do not appear in IR spectra (in supported heteropoly acids, V_2O_5/Al_2O_3) [54–56].

A special case is the investigation of the strength of LAS's. We know that the interaction of each Lewis acid–base pair has some specificity, and the acid strength sequences for two bases usually do not coincide. Therefore, a single strength scale for Lewis acids is nonexistent. The specifics of acid–base interactions were formulated by Pearson [57] in his theory of hard and soft acids and bases. In terms of this theory, hard acids prefer to interact with hard bases, whereas soft acids prefer soft bases. For the detailed investigation of surface Lewis sites on catalysts, Paukshtis [3] recommended to use at least one hard base probe and one soft base probe.

Acids are used as probe molecules for the identification and determination of the strength of basic sites. Many of these acids interact with surface LAS's (these are oxygen- and nitrogen-containing compounds) or are adsorbed on catalysts in the dissociative form (hydrogen sulfide and mercaptans) [3]. Deuterochloroform, having weak basicity, is a CH-acid [58]. Paukshtis et al. [59] used the shift of deuterochloroform frequencies (ν_{CD}) to find the strength of basic sites. Later, the equation

$$\log\Delta\nu_{CD} = 0.0066PA - 4.36$$

was used, where $\Delta\nu_{CD}$ is the shift of deuterochloroform frequencies ν_{CD}, to characterize the strength of surface sites on the PA scale.

The *IR-spectroscopic determination of the concentrations of acidic and basic sites* is based on the validity of the Bouguer–Lambert–Beer law as applied to some bands in the spectra of adsorbed probe molecules. For adsorbed probe molecules, this law reads

$$A = 10^{-3}A_0C_s\rho,$$

where A is the observed integrated absorption of the band, cm^{-1}; A_0 is the integrated absorbance coefficient of the band, cm/µmol; C_s is the adsorbed probe molecule concentration, µmol/g; and ρ is the amount of the catalysts per 1 cm^2 of the luminous flux cross section, mg [3]. The integrated absorbance coefficients of bands (A_0) for a number of probe molecules determined by volumetric or gravimetric methods can be found in the literature. There are two strategies to determine the BAS concentration on catalysts: one is to measure the OH group concentration directly from the ν_{OH} intensity [60]; the other is to measure them from the spectra of protonated bases. The LAS concentration can only be found from absorption intensities in the probe molecule spectra.

Thus, the availability of integrated absorbance data for some probe molecules makes IR spectroscopy usable for routine analyses of surface characteristics of catalysts.

In situ determination of Brønsted acidity is possible with the use of steady-state isotopic transient kinetic analysis (SSITKA) [61] in the situation close to the performance of real catalysts. The underlying idea of this method, which studies the isotope transfer dynamics in steady-state reaction conditions, is as follows: under steady-state reaction conditions, the isotopic composition of one reagent is changed abruptly, and the change in isotope label concentration in reaction products is analyzed using a mass spectrometer (isotopic response curves are obtained in this way) [62]. This method is unique: while being itself non-steady-state, it studies the kinetics of steady-state processes, where the rates of all reactions and the state of the catalyst remain unchanged. Analysis of isotopic response curves in terms of various mathematical models gives the average residence time for the reaction, the concentrations of the most active intermediates, and surface coverage [62].

Isotope exchange as a means for characterization of the Brønsted acidity of zeolites was pioneered by Olindo et al. [63] and Louis et al. [64]. This method was based on the H/D exchange between D_2O molecules and OH groups of zeolites with subsequent back titration of O–D exchange sites by water vapor. The isotope-kinetic determination of the Brønsted acidity proposed by Keller, Koehl, et al. [65, 66] was based on the quantitative analysis of the H/D exchange rate between solid acids and D_2O in the gas phase with the mass-
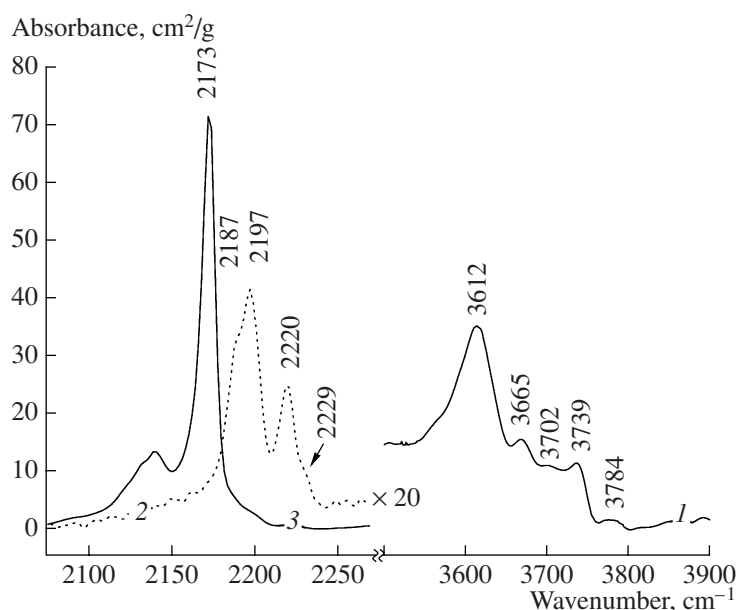
Fig. 1. (*1*) Initial IR spectrum of OH groups and (*2, 3*) IR spectra of CO absorbed on zeolite HZSM-5 under (*2*) 0.1 and (*3*) 10 Torr.

spectrometric analysis of the concentrations of isotopic water molecules in the gas phase. The BAS strength was characterized by the rate constant of exchange between D_2O molecules and surface OH groups of the catalyst (this is the rate constant of proton detachment, which is directly proportional to the strength of the site). To determine the rate constants for sites of different strengths, the overall rate curve was decomposed into components using the algorithm described in [67]. The integrated intensities of these components were used to determine the concentrations of various types of BAS's.

In our studies of H/D exchange on a series of catalysts (zeolite HZSM-5, SiO_2, and fiberglass materials with various aluminum percentages), we used deuterium, as in SSITKA: H_2 was replaced by D_2 under steady-state adsorption–desorption equilibrium. Using the numerical analysis of H/D exchange dynamics at 500°C (for fiberglass materials, the transfer of the isotope label in the bulk of the catalyst was taken into account), we revealed the different rates of deuterium exchange (characterized by the constant k) with the acid sites of catalysts and estimated the concentrations of these sites. We found that the aluminum sulfate modification of fiberglass materials generates extra acid sites, some of them being located in the subsurface layers of the catalyst and some on its external surface. Comparing the deuterium exchange results obtained on fiberglass catalysts ($k = 5 \times 10^{-3}$ s^{-1}) with those on zeolite HZSM-5 ($k = 2 \times 10^{-3}$ s^{-1}) and SiO_2 ($k = 2 \times 10^{-5}$ s^{-1}), we showed that the BAS's of zeolite HZSM-5 and fiberglass materials have comparable strengths and, therefore, the PAs of the fiberglass materials are close to 1170–1190 kJ/mol.

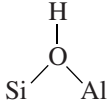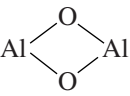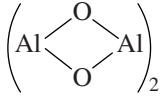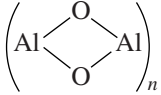## STRENGTH AND STRUCTURE OF ACIDIC AND BASIC SURFACE SITES
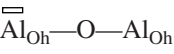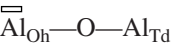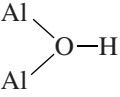
Probe molecule spectroscopy now can give us the most complete data on the surface acidity (the nature of sites and their concentration, strength, and strength distribution). Probe molecules are used in two versions. In the first, a probe molecule perturbs an adsorption site, and the properties of the site are characterized by this perturbation. This application of probe molecules is exemplified by studies of H-bonded com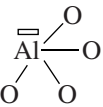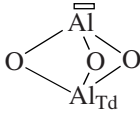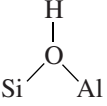plexes [46, 60, 68]. In the second version, the properties of sites are studied from the evolution of the spectra of the probe molecule itself. This version is widely used for studying Lewis sites [37, 38, 69–71].

Surface Acidity

We believe that low-temperature carbon oxide adsorption is the most efficient tool for studying BAS's and LAS's. Its efficiency is due to the small size of the CO molecule and to the simplicity of its spectral pattern (one site has one absorption band in the IR spectrum).

Table 2 compiles the properties of various acid catalysts obtained at the Boreskov Institute of Catalysis using the IR spectroscopy of adsorbed probe molecules (primarily, low-temperature CO adsorption). Figure 1 exemplifies an IR spectrum obtained upon low-temperature CO adsorption on zeolite HZSM-5. The IR spectra of zeolites contain absorption bands due to bridging OH groups (at 3612 cm^{-1}) and SiOH groups (3739 cm^{-1}) positioned on the external surface and on defects of zeolite crystals. Bands are also observed at 3665, 3702, and 3784 cm^{-1}, conventionally assigned to the OH groups located at extraframework aluminum

Table 2. Strength and structure of acid sites on oxide surfaces*

Catalyst	BAS		LAS	
	PA, kJ/mol	structure	band position, cm^{-1}	structure
Zeolites and amorphous aluminosilicates	1170–1240; strength increases with increasing ratio Si/Al	H–O bridging Si and Al	2229	Al–O/O–Al ring
			2220	(Al–O/O–Al ring)$_2$
			2210	(Al–O/O–Al ring)$_n$
			2200	A nucleus of the Al_2O_3 phase anchored to BAS
			2190	Al_2O_3 nucleus
Alumina	1550–1590	–Al–OH	2175–2178	$\overline{Al}_{Oh}$—O—Al_{Oh}
			2185–2195	$\overline{Al}_{Oh}$—O—Al_{Td}
	1380–1440	Al–O–H with Al, Al	2203–2235	$\overline{Al}$ with O, O, O
			2238–2242	$\overline{Al}$, O, O, O, Al_{Td}
SO_4/ZrO_2	1260–1300	?	2208	O_3S–O–Zr–O–SO_3
	1170–1190**		2202	Zr–O–SO_3
			2198	Zr–O–Zr–O–SO_3
			2190	Zr–O–Zr–O–Zr
HPA/support	1120–1130**	?	No	–
V_2O_5/Al_2O_3	1140**	?	No	O, O, O, O around V
			1250*** [72]	
Fiberglass materials	1170–1240 (isotope exchange)	H–O bridging Si and Al	1590–1610***	?

*CO was used as the probe molecule.
**Pyridine was the probe molecule.
***NH_3 was the probe molecule.

Table 3. Strength of basic surface sites of oxides

Catalyst	$\Delta\nu_{CD}$, cm^{-1}	PA, kJ/mol	Reference
BeO	55	925	[46, 59]
	15	810	
MgO	60	930	[46, 59]
	20	870	
CaO	95	970	[46, 59]
	30	890	
ZnO	55	925	[3]
Al$_2$O$_3$	40–45	900	[73]
	25	860	
	15	810	
Ga$_2$O$_3$	50	920	[3]
Y$_2$O$_3$	60	930	[3]
La$_2$O$_3$	60	930	[3]
SiO$_2$	<5	≤750	[46, 59]
TiO$_2$	25	860	[74]
	15	840	
ZrO$_2$	40	900	[3]

atoms (spectrum *1*). The position of the high-frequency band coincides with that for terminal OH groups. The pair of low-frequency bands is characteristic of bridging Al–OH–Al groups of extraframework aluminum oxide clusters. For all zeolites, regardless of their structure, up to five ν_{CO} bands can appear in low-temperature CO desorption spectra (Table 2). In the spectrum in Fig. 1, four ν_{CO} band appear. The bands at 2229, 2220, and 2210 cm^{-1} are assigned to CO absorbed on aluminum cations in hydroxoaluminum complexes (including polynuclear complexes). The appearance of bands at 2190 and 2200 cm^{-1} is assigned to CO adsorbed on Al^{3+} cations in alumina nuclei [3].

For various aluminas, absorption bands associated with terminal and bridging OH groups appear in the IR spectra of adsorbed CO; seven to nine types of OH groups are distinguished [3]. Four types of LAS's associated with variously coordinated aluminum cations (CN = 6, 5, and 4) are identified from CO spectra. The first two LAS's most likely arise from octahedral aluminum (Al$_{Oh}$). A neighboring tetrahedral aluminum (Al$_{Td}$) in the coordination sphere can be assumed, and so on. The third type of LAS, absorbing at 2203–2235 cm^{-1}, is associated with CO adsorbed on the aluminum atom that is linked to four oxygen atoms. This suggested structure can be realized at the edge of oxide crystallites. The fourth type of site is of great interest,

being among the strongest known LAS. We think that this site is generated by a tricoordinate aluminum atom located above a tetrahedral aluminum atom in the bulk of the oxide. This site corresponds to a structure defect where two tetrahedral metal atoms are linked with each other; this is a forbidden structure. The concentration of this type of site does not exceed 2–3 μmol/g.

The low-temperature adsorption measurements of the BAS strength in sulfated zirconium oxides reveals only rather weak sites with PAs of about 1300 kJ/mol. The IR spectra of pyridinium ions are the only means for discovering sites with strengths close to zeolitic OH groups. The discrepancy between CO and pyridine data is due to the fact that the strongest BAS's of sulfated oxide form H-bonds with neighboring basic sites (possibly, O–H…O=S); these bonds can be broken by pyridine but not CO. The different LAS types are generated by the inductive effect of sulfate groups, either bound to the zirconium ion or located in the second coordination sphere of zirconium.

Supported heteropoly acids (HPAs) have strong Brønsted sites (PA = 1120–1130 kJ/mol); the strength of these sites considerably exceeds that for other acid catalysts. The high acidity is possibly the result of the generation of a P–O–Mo bridge in which phosphoric or silicic acid enhances the overall acidity of peripheral molybdenum–oxygen fragments [3].

The Brønsted sites of alumina-supported vanadium(V) oxide (V$_2$O$_5$/Al$_2$O$_3$) are also rather strong (PA = 1140 kJ/mol). The nature of these sites remains unclear; presumably, these are the OH groups of dissociated water molecules.

The examination of IR spectra of chemisorbed ammonia showed that fiberglass silicas used as catalyst supports contain considerable amounts of Brønsted sites in the bulk of fibers. The strength of the BAS structure in fiberglass materials was determined by isotope exchange; this strength is commensurate to the strength of BAS's in zeolites. In this context, we think that BAS's in fiberglass materials are the same as in zeolites (bridging Si–OH–Al groups).

Surface Basicity

Table 3 lists the properties of a set of oxides studied by means of IR spectroscopy of adsorbed deuterochloroform. For basic sites, we easily trace ordinary Mendeleev periodicities: the basicity increases in the Be–Mg–Ca series, as well as in the Al–Ga–Y–La and Si–Ti–Zr series. Some oxides having rather strong basic sites also have weak sites. The effect of acid dopants on basic sites can be traced using the IR spectra of adsorbed deuterochloroform. For titania, for example (Fig. 2), the strength of basic sites is decreased by sulfation; stronger sites (with PA = 860 kJ/mol) completely disappear from the surface when 3.8% sulfate ions is introduced, whereas the concentration of weak basic sites increases.
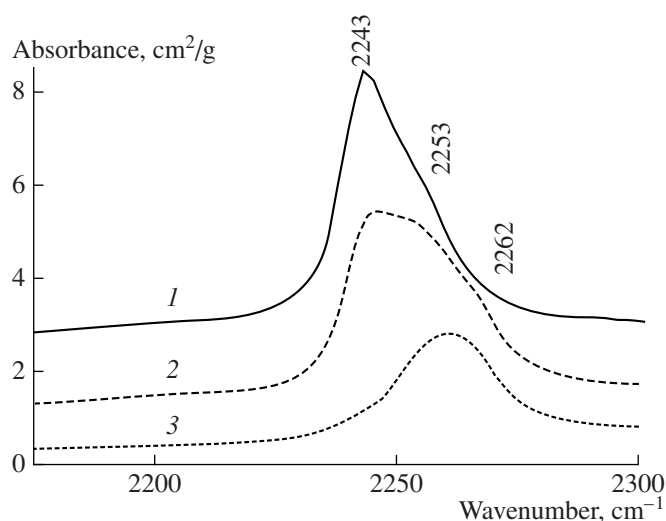
Fig. 2. IR spectra of $CDCl_3$ adsorbed on (*1*) unmodified and (*2, 3*) sulfated titania samples containing (*2*) 2 wt % SO_4^{2-} and (*3*) 14 wt % SO_4^{2-} .

CONCLUSIONS

The five-decade-long history of investigations of the acid–base surface properties of catalysts at the Boreskov Institute of Catalysis passed through several stages, starting with the use of aqueous and nonaqueous titration and finishing with in situ measurements. New tools of investigation, including physical methods, were always sought for solving topical problems; a number of new methods developed at the Boreskov Institute of Catalysis later found wide use. For example, the indicator method for the identification of LAS's and BAS's brought into use diffuse reflectance UV-Vis spectroscopy for analysis of the nature of adsorbate indicator base complexes. The need to match the acidity and catalytic properties led to the proposition and development of Brønsted acidity measurements on the proton affinity scale; this scale is now widely used for characterization of BAS's. Quantitative low-temperature IR spectroscopy of adsorbed CO molecules helped to solve problems associated with the heterogeneity of acid sites; the relevant procedures have become routine at the Boreskov Institute of Catalysis. The need to quantify the acidity of fiberglass materials gave impetus to the development of high-temperature H/D exchange kinetic measurements of the strength of Brønsted sites. This method is the only one to which the term in situ can actually be applied.

In situ acidity studies require more discussion. The measurability of the Brønsted acidity in H/D exchange for deuterium (H_2/D_2) is undoubted. Here, the probe molecule is the reagent molecule itself; for catalysts without reducible components, this reagent does not alter their surface properties. However, this method cannot be used for acidity determination in transition metal catalysts. Adsorption of base probe molecules evidently cannot be used for in situ acidity measurements. First, adsorption equilibrium is necessary for basic probe molecules, whose acquisition temperature can differ from the temperature at which acidity should be measured. Second, a basic probe (such as ammonia) can alter the surface chemistry because of chemical reactions. Third, probe molecules do not coincide in size with reagent molecules, and the problem of matching acidity and catalytic activity measurements will always exist. Thus, reagent molecules themselves can exclusively be used for in situ acidity measurements; SSITKA is the base for the further development of in situ acidity measurements, and we expect rapid progress in this field.

Regarding acidity measurement techniques in relation to the structure of acid sites, we should note that probe molecule spectroscopy cannot determine the structure of these sites, only providing us with a base for suggestions. For example, the discovery of various types of surface ammonia complexes on aluminosilicate catalysts implied the existence of LAS's and BAS's. However, the inference that the BAS's of aluminosilicate structures are bridge SiOHAl groups was made possible by x-ray powder diffraction and neutron scattering studies of zeolites. The first studies where CO was used for identifying LAS's of alumina (and later for zeolites) usually employed a simplified model. This model assumed the existence of two types of sites, one formed by a tricoordinate surface aluminum ion and the other by a pentacoordinate surface aluminum ion. More precise FTIR spectrometer measurements showed three to five types of LAS's. The tandem of quantum chemistry and spectroscopy is now the only means for recognizing the structure of sites. There are two constraints: (1) probe molecules should not distort the surface structure severely (optimal probes are H_2, CO, and N_2), and (2) the spectra of adsorbed probe molecules should be calculated by quantum chemistry with accuracies of at least 2–3 cm^{-1}. The second constraint arises from the fact that minor structural perturbations in the second and third coordination spheres of the site can give rise to continuum spectra of site types in quantum-chemical calculations, and thus, comparison with experimental results will not substantiate the choice of the site structure.

Thus, there are two techniques that seem most promising for developing heterogeneous acid catalysts: (1) in situ acidity measurements using reagent molecules as probes and (2) high-accuracy quantum-chemical calculations of acid site structures.

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