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ESR probe study of acid sites on the silica surface modified by organotin compounds

A. A. Kudrinsky, P. G. Mingalyov,★ A. V. Fionov, and G. V. Lisichkin

Department of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie Gory, 119992 Moscow, Russian Federation.
Tel.: +7 (095) 939 4638. E-mail: glo@petrol.chem.msu.ru

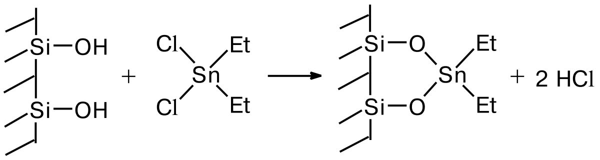
Brönsted acid sites formed due to the interaction of coordinately unsaturated tin atoms with water on the silica surface modified by organotin compounds were found and studied using an ESR spin probe technique. The half-life period of a probe at room temperature can serve as an additional characteristic of the acidity of the surface.

Key words: silica, organotin compounds, acid sites, spin probe technique, ESR spectroscopy.

Materials based on oxides chemically modified by organic compounds are successfully used in chemistry and technology.[1] Organosilicon compounds are usually used as modifiers for syntheses. However, modifiers containing no silicon, in particular, organotin compounds, have aroused increasing interest in recent years.[2]

Tin(IV) is a strong Lewis acid[3] and, therefore, silicas modified by organotin compounds (Scheme 1) can gain ion-exchange properties due to complexation with solvents. The complexing ability of grafted tin atoms and the properties of the formed complexes have been little studied as yet. Therefore, the purpose of this work is to study silica modified by organotin compounds.

Scheme 1



Experimental

Synthesis of modifiers and modified supports. Diethyltin dicaprylate and tetraethyltin (both purchased from the Redkinskii Pilot Plant, Russia), as well as tin tetrachloride (Merck), were used for the synthesis of organotin modifiers. Silasorb Si-600 (Merck) with a specific surface of 580 $m^2 g^{-1}$ and an average pore diameter of 5.4 nm served as the initial matrix. Silicas were modified by triethyltin chloride, diethyltin dichloride, and ethyltin trichloride. Procedures for the synthesis of the modifiers have previously been described in detail.[2] Silica was modified as follows: anhydrous toluene (100 mL), Silasorb (5 g), and anhydrous morpholine (1.25-fold molar excess over hydrogen chloride evolved upon modification) were placed in a three-neck flask with a stirrer and a reflux condenser. The mixture was heated to boiling, and a modifier (0.003 moles per 1 g of silica) was added. Then the mixture was stored for 24 h at 110 °C.

Then the modified sample was successively washed with toluene, acetonitrile, a water—acetonitrile (1 : 1) mixture, acetonitrile, and dichloromethane and dried on a Büchner funnel at room temperature. According to the elemental analysis data, the tin content in the resulting samples was 4.5 wt.% for SiO_2/Et_3SnCl, 7.8 wt.% for SiO_2/Et_2SnCl_2, and 6.0 wt.% for $SiO_2/EtSnCl_3$.[2] Before experiments, the samples were additionally dried at 20 Torr to remove physically adsorbed water.

Adsorption of a paramagnetic probe. Di-*tert*-butyl nitroxide (DTBN) was adsorbed from a dilute solution followed by the complete (to a residual pressure of 0.01 Torr) or partial evaporation of the solvent at room temperature and a pressure of 20 Torr. The amount of adsorbed radicals was varied from 0.01 to 0.05 group/nm^2.

ESR measurements. A sample was placed in a glass ampule, which was evacuated to 0.01 Torr at 77 K and sealed. ESR spectra were recorded on an RE-1306 radiospectrometer (working frequency 9300 MHz). The anisotropic hyperfine splitting (HFS) constant $A^{N}{}_{\parallel}$ was determined[4] as a halved distance between the external extremes of the ESR spectrum recorded at 77 K, and the g factor was measured in the intersection point of the central component and zero line (Fig. 1) using diphenylpicrylhydrazyl as the external standard ($g = 2.0036$).

Results and Discussion

The paramagnetic probe technique[4—6] is successful in detecting aprotic (Lewis) acid sites on the surface of oxide systems using ESR spectra of adsorbed nitroxyl radicals (probes). The ESR spectrum of nitroxyl radicals contains three hyperfine (HFS) components arising from one nucleus ^{14}N (natural abundance 99.6 at.%; $I = +1$[7]). The reaction of a nitroxyl radical with Brönsted acids affords

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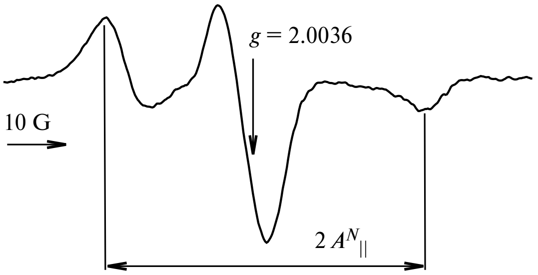
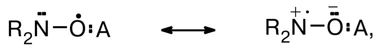


Fig. 1. ESR spectrum of di-*tert*-butyl nitroxide (77 K) adsorbed on the silica surface modified by organotin compounds.

the corresponding complexes,[5] ESR spectra of which contain an additional HFS caused by the interaction with ^{1}H. However, if a nitroxyl radical interacts with Brönsted acid sites on the solid support surface, then this HFS does not appear because of the low rotational mobility of the radical and, as a consequence, anisotropy of the ESR spectrum.[5]

The nature of interaction of the $R_2NO^\bullet$ fragment with the environment can be envisaged from the value of the $A^N_{||}$ constant characterizing the anisotropic hyperfine splitting of an unpaired electron with the ^{14}N nucleus.[6]

The interaction of a nitroxyl molecule with an acid site results in the redistribution of the π-electron density, which is equivalent to an increase in the contribution of resonance structure II



$$\mathrm{R_2\overset{-}{N}{-}\overset{\bullet}{O}{:}A} \longleftrightarrow \mathrm{R_2\overset{+\bullet}{N}{-}\overset{-}{O}{:}A},$$

I II

where A is the acid site.

For example, in toluene that interacts nonspecifically with the $R_2NO^\bullet$ group, $A^N_{||} \approx 35$ G; upon the interaction with hydroxyl groups of the SiO_2 surface, $A^N_{||}$ increases to ~38 G and can achieve higher values when the interaction with strong acid sites occurs.[5]

The anisotropic ESR spectrum of adsorbed molecules (see Fig. 1) is observed when DTBN was adsorbed on the surface of the modified silica samples at 77 K in the absence of solvent. The resulting spectra exhibit an HFS ascribed to the ^{14}N nucleus and no additional hyperfine structure from the interaction of the unpaired electron with the ^{117}Sn ($I = +1/2$) and ^{119}Sn ($I = +1/2$) nuclei. This suggests that Lewis acid sites are absent from the surface of the samples under study. At the same time, the $A^N_{||}$ values (Table 1) observed for the spectra of adsorbed DTBN are higher than those for solutions of the radical in nonpolar solvents[5] and for DTBN adsorbed on the initial silica. The $A^N_{||}$ values decrease regularly on going from silica modified by $EtSnCl_3$ to the Et_2SnCl_2/SiO_2 systems and further to Et_3SnCl/SiO_2 (see Table 1). This can be explained by the interaction of the nitroxyl radical with Brönsted acid sites (complex acids of Sn^{IV}) formed by the reactions of grafted coordinately unsaturated tin compounds with water or adjacent OH groups (Fig. 2). Based on the assumed structure of the acid sites, the observed decrease in the HFS constant can be explained by a decrease in the strength of the complex acids due to an increase in the electron-donor effect of the substituents on going from $EtSnCl_3$ to Et_3SnCl.

Table 1. Properties of DTBN solutions and DTBN complexes adsorbed on the modified silica surfaces

Solvent	$g\pm0.0002$	τ[a]/min	$A^N_{||}\pm0.2$ G	K[b]/V[8]
		Di-*tert*-butyl nitroxide		
Hexane	—	—	34.1[c]	0
Toluene	—	—	34.6[c]	58
		Di-*tert*-butyl nitroxide/silica		
—[d]	2.0051	—	38.0[c]	—
		Triethyltin chloride/silica		
—[d]	2.0052	100	36.5	—
Hexane	2.0051	~150	36.5	0
		Diethyltin chloride/silica		
—[d]	2.0051	<5	41.0	—
Hexane	2.0056	26	40.0	0
Chloroform	2.0065	~150	38.5	14
Benzene	2.0059	108	40.5	48
Ether	2.0066	~150	36.0	280
		Ethyltin trichloride/silica		
—[d]	2.0051	<5	44.8	
Hexane	2.0055	17	40.0	0
Chloroform	2.0054	65	39.5	14
Benzene	2.0063	60	38.5	48
Ether	2.0057	95	36.0	280

[a] Half-life period of the probe.

[b] General basicity (nucleophilicity) constant of solvent.

[c] According to Ref. 4.

[d] No solvent.

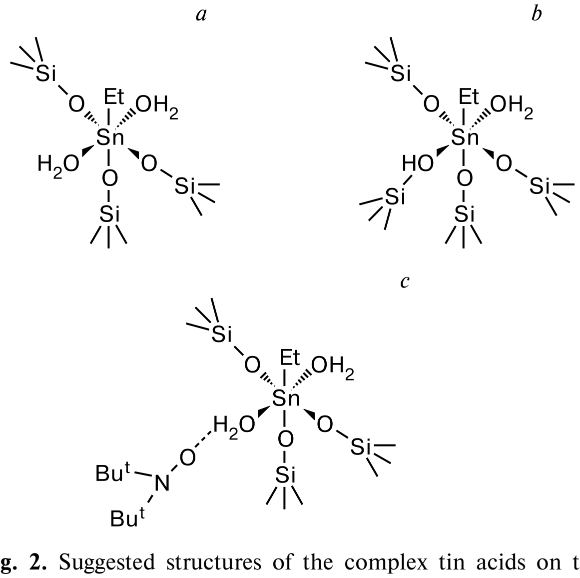
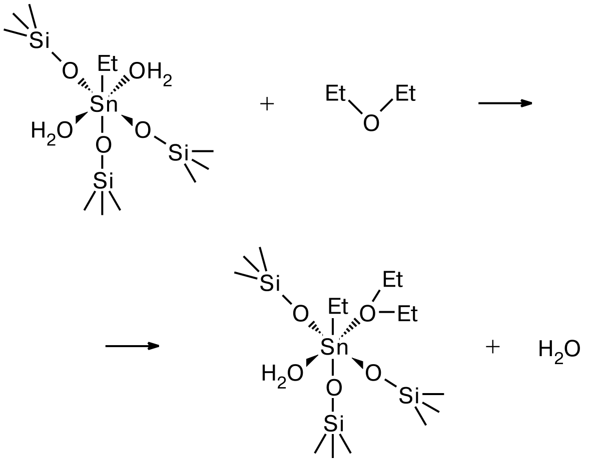


Fig. 2. Suggested structures of the complex tin acids on the modified silica surface (*a*, *b*) and the di-*tert*-butyl nitroxide complex with Brönsted acid sites (*c*).

To characterize the composition of the Brönsted acid sites containing Sn^{IV} atoms, we studied the solvent effect on the acidity of organotin compounds grafted on the silica surface. When the solvent is partially removed, the shape of the ESR spectrum of adsorbed DTBN remains virtually unchanged and the HFS constants decrease with an increase in the Lewis basicity of the solvent (see Table 1). These effects suggest that the Brönsted acid sites contain both proton-donor species (water or surface OH groups) and solvent molecules (Scheme 2). An increase in the basicity of the solvent used should decrease the strength of the complex tin acids and HFS constant and that was indeed observed in the experiments.

Scheme 2



When the samples containing adsorbed DTBN was warmed from 77 to 295 K, the paramagnetic probe decayed. The half-life period of adsorbed DTBN was chosen as the quantitative characteristic of the decay rate (see Table 1). It is known that the decomposition of nitroxyl radicals can proceed *via* different mechanisms: radical: redox, or acid-base.**[9]** Since compounds capable of oxidizing, reducing, or forming radical species under the experimental conditions are absent, we can assume that the transformations of the protonated form of the nitroxyl radical on the Brönsted acid sites contribute mainly to DTBN decomposition. In this case, the strength of the acid sites should affect the decay rate of the probe. Indeed, the HFS constants in the spectra of adsorbed DTBN correlate with the half-life period of the probe (see Table 1). Therefore, its complexes formed by stronger acid sites on the surface decompose more rapidly than the complexes containing weaker sites. Thus, the half-life period of the probe at room temperature can serve as an additional characteristic of the acidity of the surface along with the spectral parameters that can be determined only at reduced temperature.

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