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Surface Properties of γ-Alumina Deposits on Highly Permeable Cellular Carriers

V. N. Antsiferov*, I. V. Filimonova*, and A. V. Fionov**

** Research Center of Powder Materials Science, Perm, Russia*
*** Department of Chemistry, Moscow State University, Moscow, 119899 Russia*

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Abstract—The electron–acceptor properties and the hydroxyl cover of the surface of a secondary support, γ-Al_2O_3 deposited on highly porous permeable cellular materials of corundum and Nichrome, were studied. The effect of lanthana additives on the acid–base properties of the surface of this support was also studied. The surface properties of the secondary support are typical of γ-Al_2O_3. The type of highly permeable porous cellular materials used and the modifying additives influence both the acidity of hydroxyl groups and the strength and concentration of electron-acceptor sites.

INTRODUCTION

Low-temperature modifications of alumina (especially γ-Al_2O_3) are widely used as catalysts and supports for catalytic compositions [1–3]. Much attention was drawn to the development of so-called block catalysts possessing high strength, thermal stability, and usability. Over the few past years, highly permeable porous cellular materials prepared by doubling a polymer matrix became widespread [4–7]. The efficiency of catalysts significantly increases due to the high permeability (10^{-9} m^2) and irregular structure of these materials, which is responsible for the turbulence of gas flows. Highly permeable porous cellular materials can be used as supports for catalytic compositions in the purification of industrial waste gases and vehicle emissions [8–11].

The aim of this work was to study the surface properties of γ-alumina deposited on highly permeable porous cellular materials of the Nichrome alloy and corundum (α-Al_2O_3).

As is known, the modification of γ-Al_2O_3 with the ions of rare-earth elements (in particular, lanthanum) enhances the thermal stability by 100–150 K [12, 13]. However, one can expect that such a modification also changes the adsorption and catalytic properties. Therefore, a sample of γ-Al_2O_3 modified with lanthana was also studied in this work.

The surface properties of γ-Al_2O_3 deposited on highly permeable porous cellular materials were investigated by IR and ESR spectroscopies using adsorbed probe molecules. Carbon monoxide, benzene, and anthraquinone, which were successfully used previously in studies of alumina and alumina-based catalysts [14–16], were used as the probe molecules.

EXPERIMENTAL

The deposition of γ-Al_2O_3 on highly permeable porous cellular materials was carried out according to a published procedure [17] by precipitation of aluminum hydroxide from a sodium aluminate solution followed by calcination of the hydroxide at 823 K. The effect of the preparation conditions on the structure of γ-Al_2O_3 has been studied in detail in [18, 19].

Three samples were studied in this work. The first sample was γ-Al_2O_3 deposited on a highly permeable porous cellular material of corundum, and the second and third samples were γ-Al_2O_3 deposited on a highly permeable porous cellular material of Nichrome. The third sample was additionally modified with lanthana by impregnation with an aqueous solution of lanthanum nitrate (4 wt % La_2O_3) followed by drying and calcination at 673 K.

The test samples were prepared as described below. The first sample (γ-Al_2O_3 deposited on corundum) was ground together with the support. The second and third samples (alumina deposited on Nichrome) were removed mechanically from the carrier.

The specific surface areas of the samples were measured chromatographically (from desorption peak areas) after the low-temperature (77 K) adsorption of nitrogen (with the use of a mixture of 6 mol % N_2 in helium) followed by desorption at room temperature.

The surface properties of the γ-Al_2O_3 samples were studied by diffuse-reflectance IR spectroscopy with the use of carbon monoxide and benzene as probe molecules and by electron spin resonance (ESR) with the use of adsorbed anthraquinone. Before the adsorption of indicator molecules, the samples were calcined in air for 2 h and in a vacuum of 5×10^{-5} torr for 2 h at a specified temperature. The samples studied by IR and ESR spectroscopy were calcined at 843 and 743 K, respectively.

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The adsorption of CO from a gas phase was performed at pressures of 5, 20, and 50 torr at room temperature, and the adsorption of benzene vapor was performed at 10 torr and room temperature. Anthraquinone was adsorbed according to a procedure described in [20]. Anthraquinone (3–5 mg) was placed in an ampule welded as a branch to an ampule with the sample (30–40 mg). After thermal vacuum treatment, the sample was transferred to the branch with anthraquinone, and the branch ampule was sealed off. Thus, the prepared ampule was thermostatted at 393 K for 10 h to attain a uniform distribution of anthraquinone over the sample surface. Then, the sample with anthraquinone was heated at 473–493 K for a long time (up to 200 h) to reach the limiting concentration of a paramagnetic anthraquinone complex with the surface electron-acceptor sites. An excess of anthraquinone was sublimed to the cold (upper) end of the ampule.

The diffuse-reflectance IR spectra of hydroxyl groups and adsorbed CO were recorded at room temperature on a Specord M80 spectrophotometer equipped with a special attachment. The intensity of diffusely reflected light was calculated using the Kubelka–Munk theory (in terms of the model of a semi-infinite layer) [21]. As is known, the intensities of absorption bands in Kubelka–Munk units is proportional to the concentration of adsorption sites (adsorbate molecules) in the region of low absorption [22].

The ESR spectra were recorded on a reflection radiospectrometer at a frequency of 9300 MHz. The concentration of paramagnetic sites in the sample was determined by double integration with the use of an intermediate standard (ruby crystal) and an absolute standard (sugar charcoal). The *g*-factor values were measured relative to diphenylpicrylhydrazyl as a reference substance ($g = 2.0036$).

RESULTS AND DISCUSSION

The specific surface areas of the test samples are given in Table 1. A great difference between the specific surface areas of samples 1 and 2 is due to the presence of a ceramic matrix (corundum, whose specific surface area is small as compared to that of γ-Al_2O_3) in sample 1.

Note that the specific surface area of alumina somewhat decreased upon modification with lanthanum ions. This is probably due to the partial blocking of alumina pores and the formation of solid solutions of La^{3+} in the structure of γ-Al_2O_3 upon this treatment [12].

Table 1. Characteristics of the alumina samples

No.	Sample	S_{sp}, m^2/g
1	21.25% γ-Al_2O_3/corundum	23
2	γ-Al_2O_3/nichrome*	201
3	4 wt % La_2O_3/γ-Al_2O_3/nichrome*	177

* Mechanically removed from the support.

Surface Hydroxyl Cover

The IR spectra of the hydroxyl covers of the samples γ-Al_2O_3/corundum (Fig. 1a, curve *1*) and γ-Al_2O_3/Nichrome (Fig. 1a, curve *2*) were the superpositions of the absorption bands of free hydroxyl groups with maximums at 3760, 3740–3745, and 3685–3690 cm^{-1}. According to published data [23], absorption bands in the region 3760–3800 cm^{-1} correspond to terminal OH groups, absorption bands in the region 3730–3745 cm^{-1} correspond to bridging OH groups bound to two aluminum cations, and bands at <3710 cm^{-1} are due to bridging OH groups bound to three aluminum cations. The introduction of lanthanum gave rise to a new absorption band with a maximum at 3645 cm^{-1} (Fig. 1a, curve *3*). This absorption band is probably due to the incorporation of lanthanum ions into the first coordination sphere of bridging hydroxyl groups bound to the three cations.

The acid–base properties of the surface OH groups were studied by measuring frequency shifts upon the formation of hydrogen bonds [14, 15]. Benzene was used as the adsorbate forming hydrogen bonds with the surface OH groups. According to published data [14], the most correct energy characteristics of the strength of Brønsted acids is proton affinity (*PA*), which is determined by a comparison of the frequency shifts of the absorption band maximums of hydroxyl groups in the test sample and a reference sample (SiO_2) upon the formation of hydrogen bonds (the frequency shift for OH groups of silica gel upon the formation of a hydrogen bond with benzene is $\Delta\nu(OH) = 110$ cm^{-1}). An increase in the acidity of hydroxyl groups is characterized by a great shift of the maximum of an absorption band due

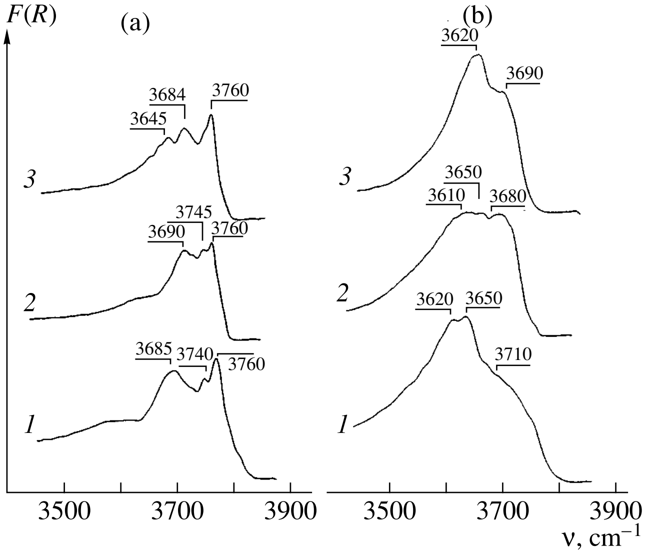

Fig. 1. IR spectra in the region of OH vibrations (a) before and (b) after benzene adsorption on samples (*1*) 1, (*2*) 2, and (*3*) 3.

Table 2. Acid–base properties of surface hydroxyl groups

No.	Sample	ν(OH), cm^{-1}	ν(OH)^B, cm^{-1}	Δν(OH), cm^{-1}	*PA*, kJ/mol
1	γ-Al_2O_3/corundum	3760	3710	50	1540
		3740	3650	90	1430
		3685	3620	65	1490
2	γ-Al_2O_3/Nichrome	3760	3680	80	1450
		3745	3650	95	1420
		3690	3610	80	1450
3	4% La_2O_3/γ-Al_2O_3/nichrome	3760	3690	70	1475
		3684	3620	64	1490

Note: ν(OH) is the absorption frequency of hydroxyl groups, ν(OH)^B is the absorption frequency of hydrogen-bonded OH groups after benzene adsorption, and *PA* is proton affinity (according to [14, 15]).

to OH groups to the low-frequency region and, correspondingly, by a decrease in the value of *PA* upon the formation of a hydrogen bond with a base. Table 2 summarizes the shifts of the absorption band maximums of hydroxyl groups and the corresponding values of *PA* upon the formation of hydrogen bonds with benzene.

The IR spectra of samples 1 and 2 are similar (Fig. 1a, curves *1* and *2*). However, an analysis of the spectra after benzene adsorption (Fig. 1b, curves *1* and *2*) allowed us to conclude that terminal hydroxyl groups on the surface of sample 2 are more acidic because they exhibited lower values of *PA* (Table 2). This can be due to the chemical effect of a carrier, which partially modifies the surface of alumina with nickel and (or) chromium ions. Sample 3 containing lanthana also possesses more acidic terminal hydroxyl groups (Fig. 1b, curve *3*) than those in sample 1; this can be due to the effect of the Nichrome carrier.

IR Spectra of Adsorbed CO

The electron-acceptor properties of surfaces were studied by IR spectroscopy with the use of adsorbed carbon monoxide. The adsorption and measurement of the IR spectra were carried out at room temperature.

A value that characterizes the strength of an electron-acceptor site is the frequency shift of the absorption band maximum of a CO : M complex relative to the absorption band maximum of gaseous CO (2143 cm^{-1}). The absorption bands corresponding to the complexes of CO bound to electron-acceptor sites (coordinatively unsaturated aluminum ions) appeared upon CO adsorption on the surface of the test samples dehydroxylated at 843 K (Fig. 2). The spectra of CO adsorbed on samples 1 and 2 were superpositions of two absorption bands: a band at 2235 cm^{-1} and a broad band at 2200–2210 cm^{-1}. During CO adsorption (5 torr), stronger electron-acceptor sites, which are associated with the absorption band at 2235 cm^{-1}, were initially filled.

As the pressure of CO was increased (up to 50 torr), the contribution of the second absorption band increased, and its maximum was shifted to lower wavenumbers (from 2210 to 2200 cm^{-1}). These findings are consistent with published data [24]. The intensity of the IR spectrum of CO adsorbed on the surface of sample 2 (γ-Al_2O_3/Nichrome) was higher than that of the spectrum of sample 1 (γ-Al_2O_3/α-Al_2O_3) by one order of magnitude. This is likely due to the smaller specific surface area of sample 1 as compared to sample 2 (Table 1).

The treatment of alumina with lanthanum ions (sample 3) led to a decrease in the contribution of the IR spectrum of the CO complex with the strongest electron-acceptor sites (absorption band at 2235 cm^{-1}). The absorption band with the maximum at 2210 cm^{-1} prevailed, and the maximum was shifted to 2205 cm^{-1} with increasing CO pressure up to 50 torr. The total intensity of the IR spectrum also significantly decreased as compared to sample 2.

Hence, the data suggest that samples 1 and 2 (γ-Al_2O_3 on different carriers) are characterized by equal (in strength) electron-acceptor properties. The modification with lanthanum ions resulted in a decrease in both the strength and concentration of electron-acceptor sites.

ESR Spectra of Adsorbed Anthraquinone

The concentration of electron-acceptor sites on the surface of alumina can be quantitatively estimated from the limiting concentration of a paramagnetic anthraquinone complex. The shape of the ESR spectrum of this complex corresponds to the interaction of an unpaired electron with one or two equivalent ^{27}Al nuclei, depending on the state of the oxide surface [16, 25–27].

According to published data, a paramagnetic complex is formed upon the adsorption of anthraquinone on the surface of pure γ-Al_2O_3. In this complex, one anthraquinone molecule interacts with two equivalent electron-acceptor sites, coordinatively unsaturated aluminum ions. The 11-component hyperfine structure

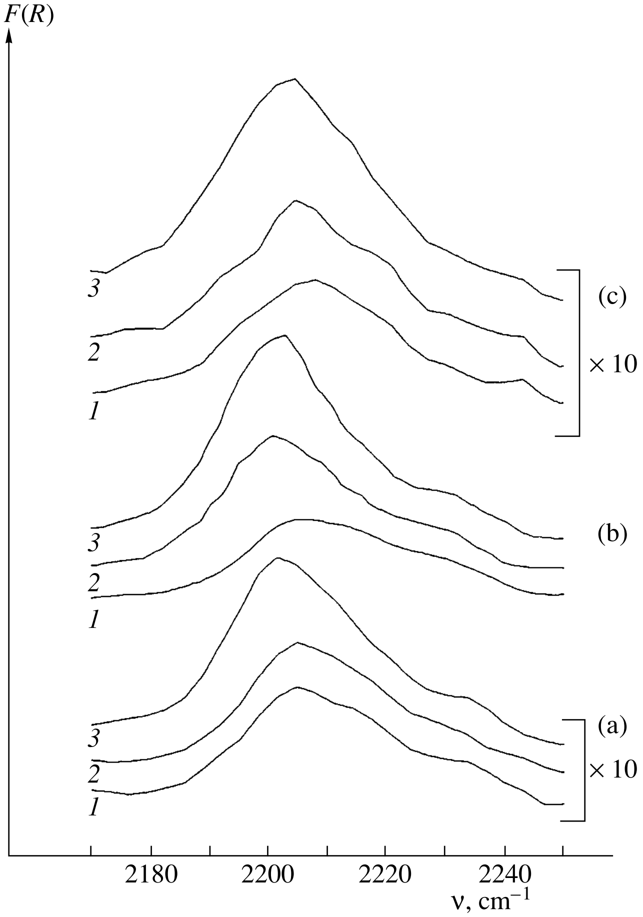

Fig. 2. IR spectra of CO adsorbed on the surface of samples (a) 1, (b) 2, and (c) 3 at room temperature and pressures of adsorbed CO (torr): (*1*) 5, (*2*) 20, and (*3*) 50. The intensity of the spectra of samples 1 and 3 is magnified tenfold.

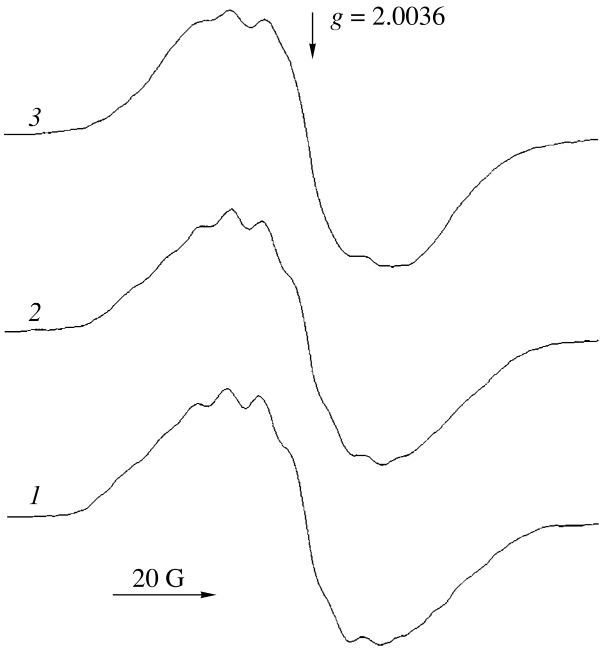

Fig. 3. ESR spectra of the paramagnetic complexes of anthraquinone with electron-acceptor sites on the surface of samples (*1*) 1, (*2*) 2, and (*3*) 3.

with an intensity ratio of 1 : 2 : 3 : 4 : 5 : 6 : 5 : 4 : 3 : 2 : 1 in the ESR spectrum gives evidence of the above structure of the complex. Significant dipole–dipole broadening of the spectra is indicative of high local concentrations of paramagnetic complexes and, hence, of coordinatively unsaturated aluminum ions. The concentration of electron-acceptor sites on the γ-Al_2O_3 surface can be calculated as the doubled concentration of a paramagnetic anthraquinone complex [16].

A similar 11-component ESR spectrum was observed upon the adsorption of anthraquinone on the surface of all the test samples (Fig. 3). The concentrations of electron-acceptor sites per unit surface are given in Table 3.

According to the above data, sample 1 exhibited the highest concentration of electron-acceptor sites per unit surface (2.4×10^{17} site/m^2), which is comparable to the reported value for γ-Al_2O_3 [16]. The concentration of electron-acceptor sites on sample 2 was about two times lower. It is believed that this effect was due to the impurity of nickel ions transferred from the block carrier. Indeed, initial samples 2 and 3 exhibited a broad ESR spectrum, whose parameters correspond to Ni^{2+} ions. The concentration of Ni^{2+} ions estimated from the ESR spectrum is $\sim 1 \times 10^{19}$ ion/g. It is well known [28] that the doping of alumina with nickel ions decreases the concentration of electron-acceptor sites. Hence, the type of carrier (highly permeable porous cellular materials) influences the concentration of electron-acceptor sites on the surface of γ-Al_2O_3.

The treatment with lanthanum ions resulted in a further decrease in the concentration of electron-acceptor sites. The observed ESR spectrum was somewhat broadened (Fig. 3, curve *3*). Taking into account that the nucleus of ^{139}La has a spin of 7/2 and a magnetic moment of 2.76 μB at a 99.9% concentration of this isotope, it is believed that the broadening of the ESR spectrum was due to the presence of La^{3+} ions in the vicinity of electron-acceptor sites.

Table 3. Concentrations of electron-acceptor sites (*N*) (coordinatively unsaturated aluminum ions) on the surface of test samples

No.	Sample	$N \times 10^{-16}$, site/m^2
1	γ-Al_2O_3/corundum	24
2	γ-Al_2O_3/Nichrome	14
3	4% La_2O_3/γ-Al_2O_3/nichrome	7.6

The data on electron-acceptor properties that were obtained by the ESR spectroscopy of paramagnetic anthraquinone complexes supplement the data of the IR spectroscopy of adsorbed CO and agree with them.

CONCLUSIONS

Thus, we found that the secondary support of γ-alumina on highly permeable cellular materials has a highly developed surface with electron-acceptor properties, which are typical of γ-Al_2O_3, and a hydroxyl cover. Both the carrier and modifying additives (lanthanum ions) influenced the surface properties of this alumina.

When Nichrome is used as the carrier, nickel ions partially modify γ-Al_2O_3, and the concentration of electron-acceptor sites per unit surface decreases as compared to alumina supported on corundum. In addition, the acidity of terminal hydroxyl groups on the Al_2O_3 surface somewhat increases with the use of Nichrome.

Modification with lanthanum ions decreases both the concentration and the strength of electron-acceptor sites. The supported lanthanum ions also influence the surface hydroxyl groups.

Generally, we conclude that systems based on highly permeable cellular materials with the use of γ-Al_2O_3 as a supported component can be used for the preparation of catalysts and catalyst supports, that combine both high construction characteristics (porosity, strength, thermal stability, and durability) and surface properties (electron-acceptor properties and a surface hydroxyl cover) typical of γ-Al_2O_3. Catalysts and supports with desired properties can be obtained by varying the types of carriers and modifying additives.

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