Surface Acid Sites of Light Olefins Oligomerization Catalysts B_2O_3−Al_2O_3 and NiO/B_2O_3−Al_2O_3 by the ESR Spin Probe Method

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Abstract

The study results of acidity in a series of borate-containing aluminium oxide with the B_2O_3 content from 2.0 to 31.4 mass % (butenes oligomerisation catalyst) and a nickel-containing ethane oligomerisation catalyst obtained on its base were presented using the ESR spin probe method. The correlations between catalytic properties and the amount of nickel adsorbed with the concentration of Brønsted acid sites (BAS) determined using the probe molecules perylene were found: an increase in the concentration of BAS determined with perylene in systems leads to a rise in the butenes conversion degree, the yield of oligomerisation products, and also to an increase in the amount of nickel adsorbed.

Key words: borate-containing aluminium oxide, Solid State NMR, Brønsted acid sites

INTRODUCTION

Aluminium oxide-based systems are widely used in modern catalytic processes and technologies that require acid sites participation. The amount and the ratio of various nature acid sites on their surface is important for such catalysts that are Brønsted acid sites (BAS) and Lewis acid sites (LAS) determining the yields, the selectivity of the formation of the target and side products under conditions of catalytic processes. Surface modification of aluminium oxide with various anions is usually applied for regulating acid properties of the original Al_2O_3 to obtain systems containing the required number of LAS or BAS of a certain strength on the surface. It is known that boric acid modification of aluminium oxide allows obtaining catalysts showing a high catalytic activity in acid-controllable reactions of butenes oligomerisation [1], alcohols dehydratation [2], olefins isomerisation [3, 4] *etc.* However, the existing contradictions relatively to acid properties including LAS and BAS ratios [5, 6], borate-containing aluminum oxide lead to the need to study surface acid sites and their role in catalysis.

Spin Probe ESR Spectroscopy is a convenient method to study the surface of heterogeneous catalysts and allows obtaining qualititative and quantitative information about acid sites of various nature [7−9]. The relative experimental rapidity and a high ESR method sensitivity allow studying numerous series of catalytic samples used for a broad range of processes in catalysis. Thus, in the framework of this work, the ESR Spin Probe Method is assumed to be used for obtaining information about the effect of boron oxide content in borate-containing aluminum oxide on the type and the concentration of acid sites of obtainable systems using the nitrosyl radical TEMPO and also anthracene and perylene as probe molecules.

EXPERIMENTAL

Synthesis and sample preparation for spectroscopic studies

To prepare $B_2O_3-Al_2O_3$ borate-containing complex (BA) samples (Table 1) pseudoboehmite was treated with orthoboric acid water solutions at a temperature of 90 °C, then dried at 120 °C and calcined at 550 °C. The preparation of $NiO/B_2O_3-Al_2O_3$ (NiO/BA) samples by the adsorption method (see Table 1) was carried out on media with the B_2O_3 content of 0–30 mass % under conditions of the excess of an aqueous $Ni(NO_3)_2$ solution. After washing samples with water until the negative reaction for Ni^{2+}, they were dried at 120 °C and calcined at 500 °C. The detailed techniques for the preparation of BA and NiO/BA samples were described in work [10].

Before the start of spectroscopic studies, the samples were previously activated by calcining a series of sample weights on air in quartz ampules at 500 °C and after cooling in a desiccator were treated with a probe solution: 2,2,6,6-tetramethylpyridine-1-oxide (TEMPO) in hexane (probe concentration of $5 \cdot 10^{-4}$ mol/L), as well as with anthracene or perylene in toluene (concentration of probes of $5 \cdot 10^{-2}$ and $2 \cdot 10^{-2}$ mol/L, respectively).

The treatment procedure included the addition of a 0.5 mL probe solution followed by purging vials with dry nitrogen. Ampules with TEMPO were aged at room temperature for 6 h and ESR spectra were recorded. In case of anthracene and perylene, the concentration of cation radicals formed during the first hour after the addition of the probe solution were determined.

Spectroscopic studies

ESR measurements were performed at a temperature of 25 °C using a Bruker Employ spectrometer (Germany), operating in the X-range (~9.7 GHz) using an ER 4105 DR dual resonator at microwave power of 2.0 mW with a modulation frequency of 100 kHz and modulation amplitude of 1.0 G. Standards in ESR spectroscopy based on ultradispersed diamond (UDA) with a number of spins of $1.44 \cdot 10^{16}$ and $1.35 \cdot 10^{18}$ were used for quantitative analysis. To determine the *g*-factors a Bruker ER 4119 HS-2100 marker with a passport value $g = 1.9800 \pm 0.0006$ was used. The resulting ESR spectra were processed using the WinEPR program. Processing, simulation of spectra was performed in the WinEPRSimFonia program.

^{1}H NMR spectra were recorded using a Bruker Avances 400 spectrometer (400 MHz) with a solid-state detector for samples calcined at 500 °C with rotating the ampule under the magic angle with a frequency of ~10 kHz.

The studies were performed on the instrumental base of the Omsk Regional Center for Collective Use of the SB RAS.

RESULTS AND DISCUSSION

Types of acid sites in BA and NiO/Ba systems using the nitroxyl radical TEMPO

Peculiarities of behaviour of classic EPS probes to study LAS and BAS that are nitroxyl radicals of the piperidine series were studied

TABLE 1

Chemical composition and specific surface of the studied samples of borate-containing aluminium oxide (BA) and a nickel based catalyst (NiO/BA)

Samples	B_2O_3 content, mass %		S_{sp}, m²/g	Samples	Ni content, mass %
	Nominal	Actual			
BA-0	–	–	219±4	NiO/BA-0	0.54
BA-2	2	2.0	254±5	NiO/BA-2	0.93
BA-5	5	4.6	292±6	NiO/BA-5	1.47
BA-10	10	9.7	257±5	NiO/BA-10	1.85
BA-15	15	13.6	228±5	NiO/BA-15	3.12
BA-20	20	18.8	210±4	NiO/BA-20	2.73
BA-30	30	31.4	168±3	NiO/BA-30	1.71

by us in detail in works [11, 12] in systems with similar chemical compositions of borate-containing aluminium oxide in a range of 0–30 mass % B_2O_5 synthesized by mixing pseudoboehmite in solid orthoboric acid [13]. Based on analysis of the results obtained using modeling ESR spectra of TEMPO-LAS and TEMPO-BAS complexes it was found that for the entire series, from pure aluminium oxide to BA with the boron oxide content of 27.5 mass %, the gradual increase in the contribution of BAS at with B_2O_3 content increase is typical.

Having applied a similar approach to the BA series studied in this work a similarity of the results obtained with the works described above was found. Thus, a way of introduction of boric acid (aqueous solution or solid powder) affects acid properties of the obtainable samples in a similar way leading to the formation of almost only BAS at boron oxide contents of over 15 mass %.

It is noteworthy that at applying nickel cations to the surface of BA, the appearance of the obtainable TEMPO spectra after its adsorption on the surface does not change in comparison with the initial BA. However, a free radical (broad triplet with A_N = 15.6 G) greatly contributed into ESR spectra in the system for various samples from 6 to 20 h after introducing the probe, while the entire radical in the initial BA already during the first hour were bound to LAS or BAS. Apparently, such behaviour is associated with a significantly lower number of acid sites in NiO/BA and their predominant localization on the inner surface of samples, which in total, complicates the access of probe molecules to them.

Determination of Brønsted acid sites in BA and Ni/BA systems by the ESR Spin Probe Method with anthracene and perylene molecules

Anthracene and perylene molecules form stable cation radicals at adsorption on the surface of oxide catalysts [14] similar to permanganate molecules observable at the action of concentrated sulphuric acid on perylene [14]. The formation of perylene cation radicals at adsorption on the surface of clean and modified aluminium oxide is associated with the processes of the interaction of these molecules with surface acceptor sites; in particular, with Lewis

(LAS) and Brønsted acid sites (BAS) [8]. It is known that a molecular probe reaction is grounded on the single-electron transfer (SET), as well as requires the availability of oxygen molecules in the system [8, 15, 16]. At the same time, there is no consensus now regarding the participation of primarily LAS or BAS in the interaction with aromatic probe molecules. However, the works results of recent years [9, 11, 12] supported by data of additional physical methods, as well as correlations with known catalytic reactions allow suggesting that precisely surfaces of BAS are responsible for the formation of cation radicals of these aromatic molecules. Thus, the use of anthracene and perylene as ESR probes can become a convenient method of assessing the strength and the concentration of BAS in catalytic systems.

Experimental ESR spectra of perylene and anthracene adsorbed on BA-30 and spectra obtained upon the action on probe molecules of 90 % H_2SO_4 were similar (Fig. 1). However, spectral lines of the cation radical adsorbed at the surface of the BA solid phase of the cation radical are significantly broadened, by more than an order of magnitude in comparison with a homogeneous system due to the availability of the anisotropy of the magnetic moment of an unpaired electron, as well as the dipole-dipole interaction between neighboring radicals. If in case of a homogeneous system spectral parameters (g-factor, superfine interaction constant (SIC) with protons) concur well with those calculated and obtained by other researches for perylene [17] and anthracene [18], then in case of a heterogeneous system analysis of the superfine structure (SFS) of the spectrum is complicated by line broadening. Partly, one managed to solve the problem in case of perylene in work [17], where method of electron nuclear double resonance (ENDOR) was used to determine the SIC of the protons. The current work presents theoretical spectra based on constants (g-factor, SIC) calculated from spectra in sulphuric acid using modelling that concur with experimental for BA-30 (Fig. 2) and literature data for both perylene and anthracene.

Determining the concentrations of perylene and anthracene radical cations generated because of the interaction with the surface of BAS of each of the BA and NiO/BA samples
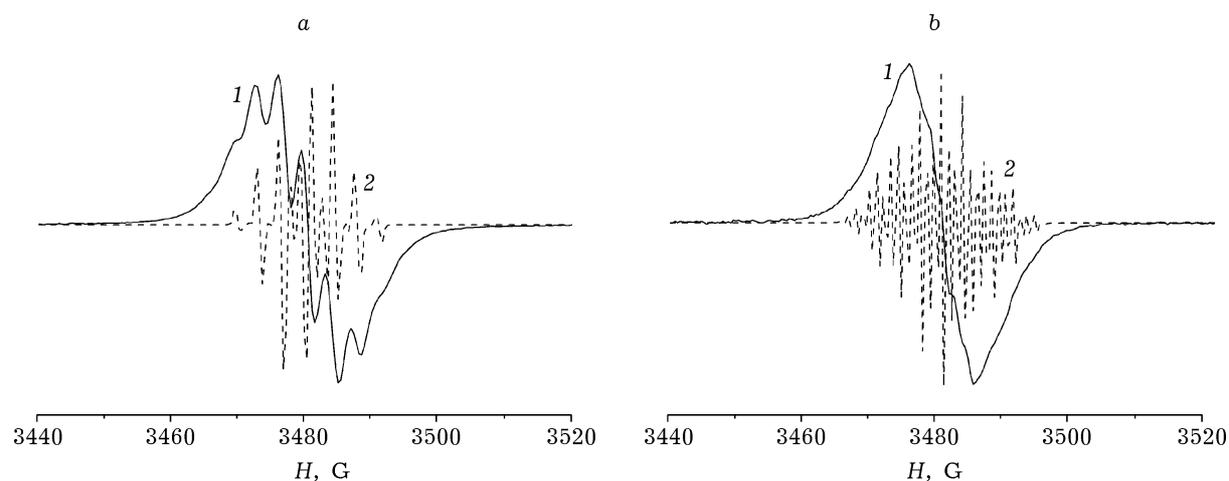
Fig. 1. ESR spectra of perylene (*a*) and anthracene (*b*) cation radicals formed during adsorption from toluene solutions over BA-30, calcined at 500 °C (*1*), and in 90 % H_2SO_4 (*2*).

studied demonstrated that their dependence on the B_2O_3 content in each case is of extreme character (Fig. 3) with the maximum in the region of 20 mass % boron oxide content.

An almost linear increase in the concentrations of both perylene and anthracene cation radicals (see Fig. 3), is observed for the contents of less than 20 mass % B_2O_3 in BA, which is probably due to an increase in the number of generated structures that is BAS on the surface. A decrease in the concentration of radical cations for BA-30 can be explained by the formation on the surface of condensed borate structures that already do not possess Brønsted acidity [10].

It is noteworthy that the concentration of BAS determined with perylene and anthracene (see Fig. 3, curves *2*) in samples with applied

nickel (NiO/BA) is significantly lower than in the initial BA. This is obvious that this is due to the participation of the determinable BAS in the adsorption of nickel cations according to the ion exchange mechanism [10]. ^1H NMR data (Fig. 4) also demonstrate that the intensity of acid proton signals in the region of 1−5 ppm in samples with applied nickel is significantly reduced in comparison with the initial BA, which also confirms the suggestion of the participation of BAS in the ion exchange.

Comparison of the amount of adsorbed nickel with the concentration of perylene radical cations in the initial BA (Fig. 5) reflecting the concentration of BAS also demonstrated the availability of an almost linear correlation.
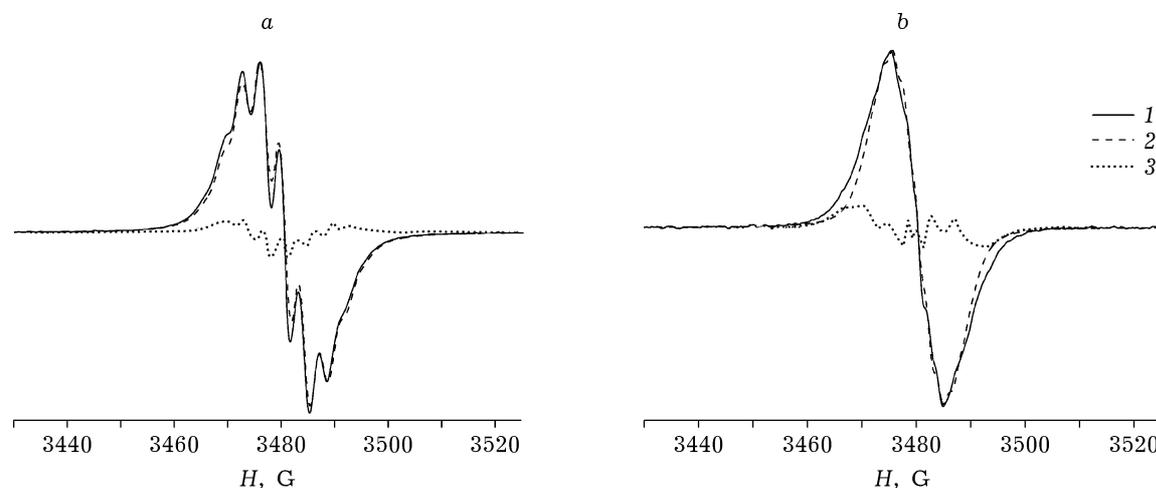

Fig. 2. Experimental (*1*) and calculated (*2*) ESR spectra of perylene (*a*) and anthracene (*b*) cation radicals formed during adsorption in a BA-30 system calcined at 500 °C: *1* − experimental, *2* − calculated, and *3* − difference of spectra.
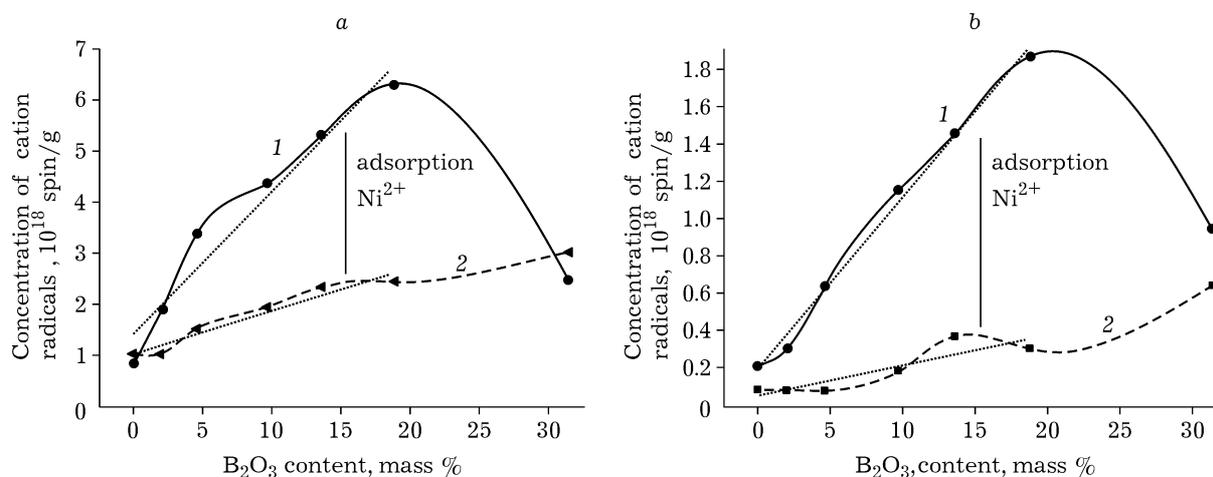
Fig. 3.Concentration of cation radicals formed during adsorption of perylene (*a*) and anthracene (*b*) from toluene solutions on the surface of BA (*1*) and NiO/BA (*2*) samples calcined at 500 °C depending on boron oxide content.

Comparison of the BAS concentration determined using perylene in the BA system with results of catalytic experiments in the butenes oligomerisation reaction

Brønsted acid catalysts are active in olefins oligomerization reactions according to the cationic mechanism with the participation of protons that are BAS [19, 20]. The most suitable active centres for processes are medium and average strength BAS, while strong BAS and LAS lead to undesirable side processes, for example, to cracking of the original reactants or oligomeric products. Thus, one may expect that samples with the largest concentration of radical cations will exhibit a higher activity.

To determine the role of average and weak strength BAS catalytic experimental results of the BA system obtained and described in detail in work [1] in the butenes oligomerisation reaction were compared with the results of determining the concentration of BAS using perylene as a probe. It was found that the butene conversion degree increased with an increase in the concentration of perylene radical cations (Fig. 6, curve *1*), the conversion degree for the values of over $6 \cdot 10^{18}$ spin/g reaches 80−90 %. The yield of the target products of hydrocarbons C_{9+} (curve *2*) and C_8 (curve *3*) oligomerization products also increases with a rise in the concentration of perylene radical cations. Herewith, the yield of cracking products of C_5 (curve *4*) remains at the level of no
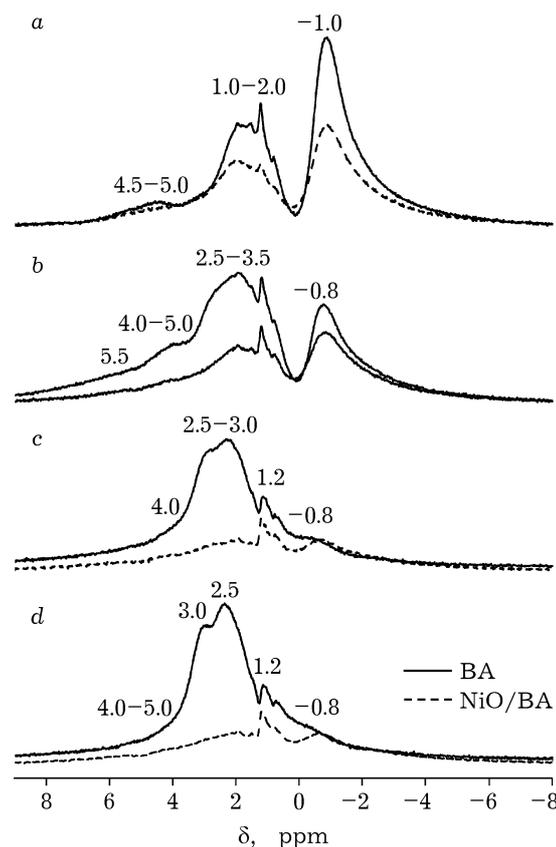

Fig. 4. ^1H NMR spectra of BA-0 (*a*), BA-5 (*b*), BA-15 (*c*) and BA-20 (*d*) samples calcined at 500 °C before and after application of Ni²⁺ (NiO/BA).

more than 8 % and almost does not depend on the concentration of perylene radical cations.

It is obvious that BAS determined as the concentration of perylene radical cations par-
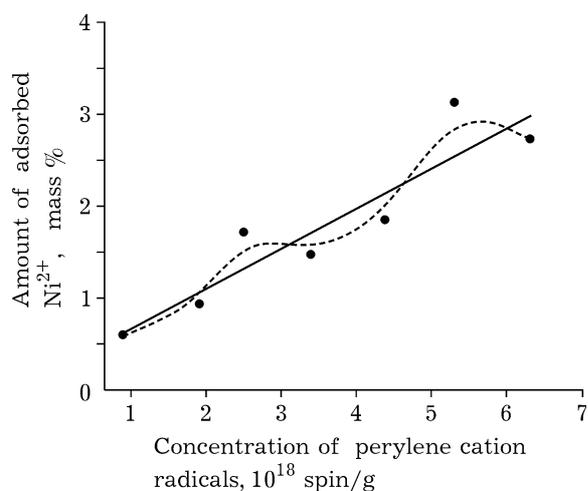
Fig. 5. Amount of Ni^{2+} adsorbed on the surface of BA samples depending on the concentration of perylene cation radicals in the initial BA.

Fig. 6. Conversion degree (*1*) of butenes and the yields of C_{9+} (*2*), C_8 (*3*) and C_1-C_4 (*4*) hydrocarbons in the oligomerisation reaction depending on the concentration of perylene cation radicals formed during adsorption over BA.

ticipates in the butenes oligomerization reaction. An increase in the concentration of determinable BAS in the systems contributes to the formation of a larger amount of active reaction sites, which ultimately results in an increase in the yield of target products.

CONCLUSION

Anthracene and perylene in the form of solutions are convenient spin probes for ESR spectroscopy at the study of acceptor centres of the borate-containing aluminium oxide surface and in the long term − other anion-containing systems based on aluminium oxide due to their ability to form cation radicals at the interaction with acid centres of various strengths.

It is obvious that acid centres registered using anthracene and perylene are of Brønsted nature, which is confirmed by the following facts: the symbate concentration dependence of cation radicals and the boron oxide content in systems, a decrease in the number of radical cations after nickel adsorption, the availability of SFS in perylene spectra, as well as a good agreement with the results at the use of TEMPO. The availability of concentration correlations of perylene cation radicals in the oligomerization reaction requiring the availability of BAS in catalysts is also an indirect confirmation of Brønsted character of determined ac-
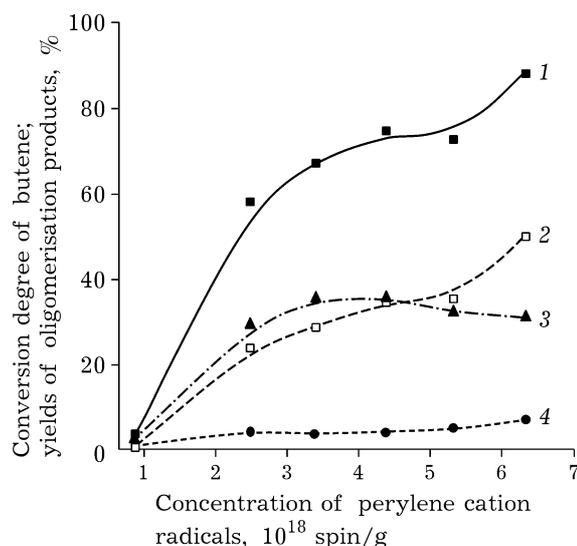
ceptor centres that are probably active centres in the reaction considered.

The resulting correlations of butenes conversion degree and yields of oligomerization products with the concentration of BAS determined as the number of perylene cation radicals may not only explain various catalytic activities in the series but also represent a method of express-evaluation of the activity of other systems based on aluminium oxide under conditions of this reaction.

Acknowledgments

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