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Studied by the Anthraquinone as a Probe Molecule**

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Received November 18, 2006

Revised January 17, 2007

Accepted January 29, 2007



*Volume 9, No. 1,
pages 13-17, 2007*

<http://mrsej.ksu.ru>

**Electron-acceptor Centers of Alkali Metal Modified Alumina
Studied by the Anthraquinone as a Probe Molecule**

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Anthraquinone paramagnetic complexes have been used to study electron-acceptor centers on the surface of alumina modified with alkali metal ions (Li^+ , Na^+ , K^+). Complexes have been characterized by CW EPR, ENDOR and pulse EPR (HYSCORE) techniques. It has been shown that alkali metal ions decreased the strength of electron-acceptor centers due to the inductive effect. As a result the concentration of anthraquinone complex with two Lewis acid sites (LAS) decreased, but the concentration of complex with one LAS increased with the increasing of alkali metal content. At large alkali metal concentration other kinds of anthraquinone paramagnetic complexes are formed, that are anthrasemiquinone weakly bound with LAS as well as anthrasemiquinone ion pair with alkali metal cation (lithium).

PACS: 68.47.Gh, 33.35.+r, 33.40.+f, 31.30.Gs

Keywords: EPR, ENDOR, HYSCORE, electron-acceptor centers, paramagnetic complexes of anthraquinone, alumina, aluminates

1. Introduction

Alkali metals are often used for the modification of alumina catalysts, and also of Al_2O_3 -based catalysts [1-2]. Their presence on the surface could strongly affect the acid-base properties and, hence, the catalytic properties. The main goal of this work was to study how a modifying with alkali Li^+ , Na^+ , K^+ cations can influence the electron-acceptor sites on the surface of alumina. We applied the method of paramagnetic complexes of probe molecules for investigation. We chose 9,10-anthraquinone as a probe molecule.

2. Results and Discussion

After the adsorption of anthraquinone on the surface of studied samples the EPR spectra appeared (Fig. 1). Three different types of spectra have been found:

1. The 11-component spectrum with line intensities 1:2:3:4:5:6:5:4:3:2:1, $g = 2.0036$, average splitting between components 7.4 ± 0.2 G. This spectrum was analogous to those observed previously on the alumina [3] and alumina modified by LiAl_5O_8 , MgAl_2O_4 and boric acid [4,5], and corresponded to the paramagnetic anthraquinone complex with two equivalent aluminum ions (spin of ^{27}Al is $5/2$).
2. The 6-component spectrum with equal intensities, $g = 2.0036$, average splitting between components 9.0 ± 0.2 G. This spectrum was analogous to those observed previously on the various aluminas [3], Al_2O_3 - ZrO_2 system [6], and corresponded to the paramagnetic anthraquinone complex with one aluminum ion.
3. The narrow spectrum, $g = 2.0036$, peak to peak line width 8.0 ± 0.2 G. The nature of this spectrum was not clear before because of the absence of hyperfine splitting (h.f.s). The nature of this spectrum is discussed in the present investigation.

In the row of modifying cations Li^+ , Na^+ , K^+ in the equal concentration (0.9 mmol/g Al_2O_3) the shape of the spectra noticeably changed. The contribution of 11-component spectrum decreased in this row, while the contribution of narrow spectrum increased. Thus, the spectra of complexes on the surface of γ - Al_2O_3 and of Li-modified sample were mainly similar and exhibit h.f.s. of 11-component, for a sample with Na the contribution of the 6-component spectrum and of narrow spectrum in the middle appeared, and for K-modified sample these two spectra became dominant. The same changes in the spectrum shapes took place, when the Li^+ concentration increased up to the 4 mmol/g [7]. Taking into account the mechanism of formation of the paramagnetic anthraquinone complex [4], the appearance of the 6-component EPR spectrum is explained, most likely by a considerable enhancement of the basicity of alkali metal modified alumina. In this case, it can be assumed that the interaction of anthraquinone with Lewis acid sites (LAS) affords only a complex with one coordinatively unsaturated Al^{3+} cation, because the strength of electron-acceptor sites is not strong enough for an interaction of this complex with an additional Al^{3+} cation. The decrease of the strength of the LAS is also responsible, probably, for the appearance of a narrow spectrum, which could be attributed to anthraquinone weakly bounded with the LAS.

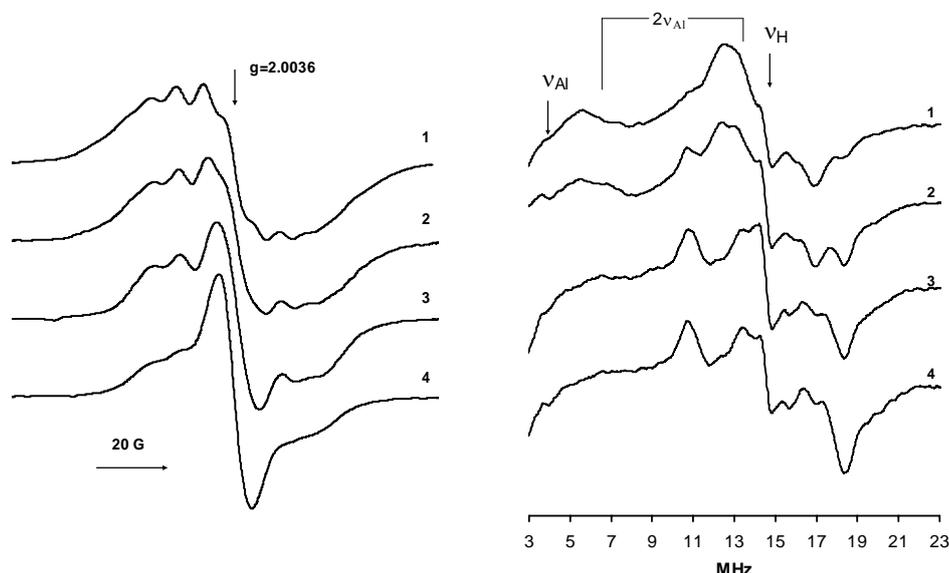


Fig. 1 EPR spectra of anthraquinone adsorbed on the surface of the: 1- γ - Al_2O_3 ; 2- $\text{Li}^+/\text{Al}_2\text{O}_3$; 3- $\text{Na}^+/\text{Al}_2\text{O}_3$; 4- $\text{K}^+/\text{Al}_2\text{O}_3$.

Fig. 2 ENDOR spectra of anthraquinone adsorbed on the surface of the: 1- γ - Al_2O_3 ; 2- $\text{Li}^+/\text{Al}_2\text{O}_3$; 3- $\text{Na}^+/\text{Al}_2\text{O}_3$; 4- $\text{K}^+/\text{Al}_2\text{O}_3$.

The ENDOR spectra of the anthraquinone complexes of the samples, modified with alkali metal ions were in good agreement with EPR spectra (Fig. 2). The two broad lines, denoted by $^{27}\text{Al}_a$, split by twice the ^{27}Al Zeeman frequency $2\nu_1 = 7.8$ MHz in the applied magnetic field and centered at 10.5 MHz, attributed to the 11-line EPR spectra and were observed for complexes with γ - Al_2O_3 and with $\text{Li}^+/\text{Al}_2\text{O}_3$. In the same row of modifiers (Li^+ , Na^+ , K^+) the intensity of lines corresponding to the large proton coupling about 8-9 MHz (two broad lines centered at 14,9 MHz –

Zeeman frequency of ^1H) increased. As it was shown earlier [5] this pair of lines was attributed to the anthraquinone radical, which gave narrow spectrum. According to the obtained data it has been shown that modification with alkali metal led to decrease of the strength of electron-acceptor sites because of their inductive effect (electronic influence) and did not block the acid centers.

For more detailed investigation of the alkali metal influence on the electron-acceptor centers we studied aluminates LiAl_5O_8 and $\alpha\text{-LiAlO}_2$, as a model compounds with known structure. LiAl_5O_8 has a spinel-like structure with aluminum ions distributed between octahedral and tetrahedral positions. The three-coordinated aluminum ions formation is possible after the removal of the terminal OH-groups from tetrahedral coordinated aluminum ions (they seem to play a role of Lewis acid sites on the alumina surface). In the structure of $\alpha\text{-LiAlO}_2$ there are only octahedral aluminum ions. The spectra of the complexes on the surface of aluminates were similar to the spectra of the complexes on alumina with large lithium concentration (4 mmol/g) [7] and consisted of 6-component spectrum and of a narrow spectrum (Fig. 3). When the temperature of anthraquinone adsorption increased from 120°C to 200°C the concentration of single line spectrum decreased and the contribution of 6-component spectrum rose. This fact means that the complex with narrow spectrum is less stable, than the complex with one aluminum. In the ENDOR spectra of aluminates (Fig. 4) a matrix line from lithium revealed. The intensity of this line was higher for the complexes with $\alpha\text{-LiAlO}_2$ samples due to higher lithium content. With the help of Q-band EPR it was shown, that narrow spectrum for aluminates was a superposition of two spectra, one of them could be attributed to anthrasemiquinone weakly bound with the LAS and another was supposed to be concerned with anthrasemiquinone ion pair with lithium cation.

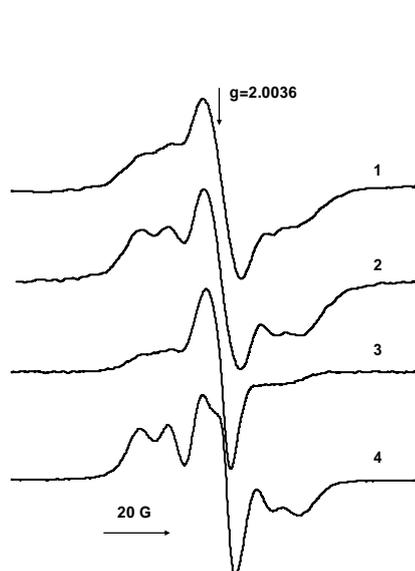


Fig. 3 EPR spectra of anthraquinone adsorbed on the surface of the: 1- LiAl_5O_8 at 120°C ; 2- LiAl_5O_8 at 200°C ; 3- $\alpha\text{-LiAlO}_2$ at 120°C ; 4- $\alpha\text{-LiAlO}_2$ at 200°C .

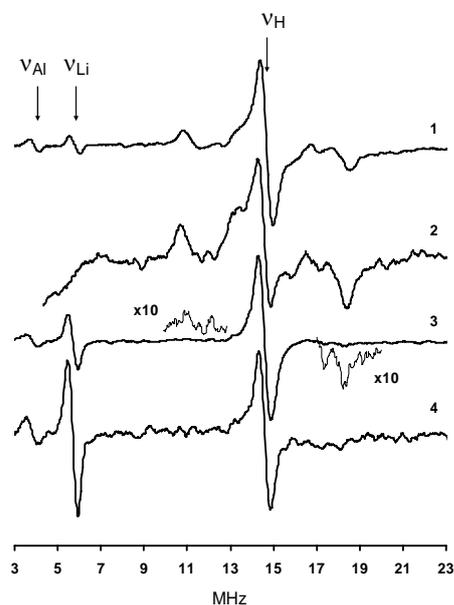


Fig. 4 ENDOR spectra of anthraquinone adsorbed on the surface of the: 1- LiAl_5O_8 at 120°C ; 2- LiAl_5O_8 at 200°C ; 3- $\alpha\text{-LiAlO}_2$ at 120°C ; 4- $\alpha\text{-LiAlO}_2$ at 200°C .

We managed to obtain distinct HYSORE spectra of anthraquinone complexes on the surface of lithium aluminates. The HYSORE spectra of anthraquinone adsorbed on $\alpha\text{-LiAlO}_2$ are depicted on the Fig. 5-6. They both clearly showed the presence of the pair of cross-peaks, centered on the Zeeman frequency of ^7Li (5.7 MHz in the field of 3450 G). Thus with the help of HYSORE technique we showed the presence of h.f.s. from the lithium in the spectra, that was not revealed in the X-band EPR. Thus in the case of aluminates one of the narrow spectra (detected by Q-band EPR) could be attributed to the anthrasemiquinone ion pair with lithium.

It has been shown that alkali metal ions decreased the strength of electron-acceptor centers due to the inductive effect. As a result the concentration of anthraquinone complex with two Lewis acid sites (LAS) decreased, when the concentration of complex with one LAS increased with the increasing of alkali metal content. At large alkali metal concentration other kinds of anthraquinone paramagnetic complexes are formed, that are anthrasemiquinone weakly bound with LAS as well as anthrasemiquinone ion pair with alkali metal cation (lithium).

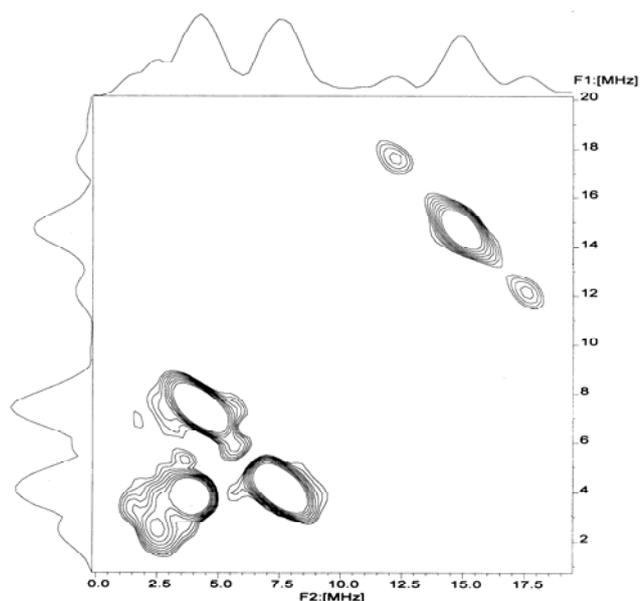


Fig. 5 HYSCORE spectra of anthraquinone adsorbed on α -LiAlO₂, obtained at the maximum of the EPR signal at $\tau = 180$ ns. signal at $\tau = 200$ ns.

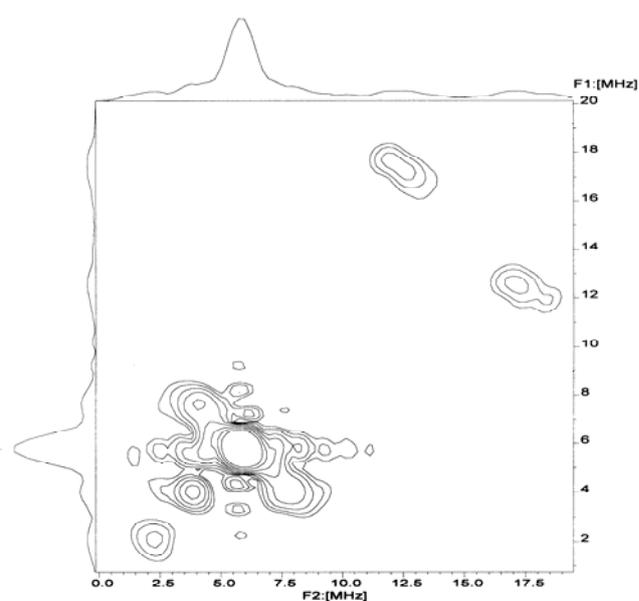


Fig. 6 HYSCORE spectra of anthraquinone adsorbed on α -LiAlO₂, obtained at the maximum of the EPR

Acknowledgement

This work was supported by the Federal Agency on the Science and Innovations (State Contract 02.451.11.7012 of August 29, 2005), the Concil on Grants of the President Of the Russian Federation (Program of State Support for Leading Scientific Schools of the Russian Federation, Grant RI-112/001/056) and the Russian Foundation for Basic Research (Project No. 06-03-32830a).

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