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Surface Electrical Potential of ZrO₂-SiO₂ Binary Xerogels by EPR pH-sensitive Spin Probes

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Abstract. In this paper, we performed a qualitative assessment of the surface electrical potential for individual and binary xerogels based on silica and zirconia which were synthesized by hydrolysis in aqua ammonia medium. The effect of surface charge on near surface local acidity of solid-phase compositions was studied.

INTRODUCTION

Binary systems ZrO₂-SiO₂ are of interest as thin-film coatings, selective sorbents, catalysts, and their carriers [1–4].

Previously [5], it was shown that the materials based on silica and zirconia synthesized by the sol - gel technology in a water-ammonia atmosphere are highly porous, have a developed specific surface, and also exist in these materials as individual phases ZrO₂ and SiO₂, and the mixed phase Zr-O-Si.

Also, for catalysis, the acidity of the medium plays an important role, but the pH of the external solution may differ from the pH of the solution inside the pores and near the surface of the catalyst. The reasons for these differences can serve as their own surface charge, as well as a change in the properties of water located near the surface.

Therefore, the purpose of this work is to assess the electric potential of the surface of mixed ZrO₂-SiO₂ xerogels and to study the changes in the acidity near these surfaces.

EXPERIMENTAL

The samples were synthesized by hydrolysis of tetraethoxysilane and tetrabutoxytitanium in an aqueous ammonia atmosphere [5]. The content of ZrO₂ in the samples was 0, 11, 42, and 100 mole %.

The studies were carried out using the EPR method. A stable nitroxyl radical (HP) was used as a pH-sensitive paramagnetic probe: 4 - dimethylamine-2-ethyl-5.5-dimethyl-2-pyridine-4 -yl-2.5-dihydro-1H imidazole - 1 - oxyl, which was synthesized at the Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences (Novosibirsk), according to the procedure described in [6]

The titration curves of NR used as the dependences of a , % (hyperfine splitting constant, found from isotropic EPR signal) and f , % (the fraction of slow motional NR molecules in a non-protonated form, calculated from an

anisotropic signal allowing to evaluate the surface electric potential) as a function of pH of the external solution, were plotted using OriginPro 2015 software package.

The best fits to the modified Henderson-Hasselbalch equation are shown as solid lines of the same color as the corresponding symbols.

RESULTS

From the dependence $a, \% = F(\text{pH of external solution})$ (Fig. 1), one can see that the titration curve for pure silica is significantly shifted to the right about the calibration curve of the NR in bulk solution in the range pH of external solution 1.7-4. This shift indicates that the pH value near the surface and inside the pores of silica is significantly higher than that for external solution.

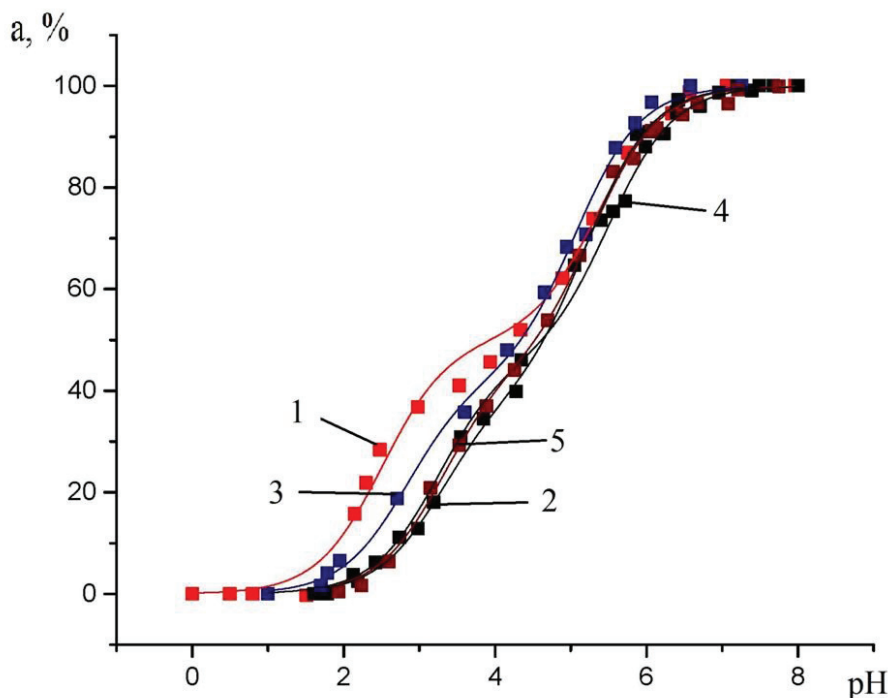


FIGURE 1 Titration curves for the fast motional NR near the surface: 1- bulk solution, 2- SiO₂, 3- ZrO₂, 4- ZrO₂-SiO₂-11%, 5- ZrO₂-SiO₂- 42%. $a, \% = (a - a_{\text{NRH}^{++}})/(a_{\text{NR}} - a_{\text{NRH}^{++}}) \times 100\%$, where $a_{\text{NRH}^{++}}$ and a_{NR} are the hyperfine splitting constants of NR R1 in the double protonated and unprotonated forms; a is the current hyperfine splitting constant of NR R1.

The titration curve of NR for ZrO₂ is also shifted to the right, but is much closer to the calibration curve, whereas the titration curves for the mixed ZrO₂-SiO₂ systems are positioned between those for individual dioxides. From Fig.1, we can conclude that the incorporation of ZrO₂ silica in a system matrix decreases pH value near its surface and inside of pores. Also, such a run of titration curves for mixed samples indicates the mixed Zr-O-Si phase does not affect the acidity near the surface.

From the titration curves for slow motional NR plotted from anisotropic spectra simulations (Fig. 2), the titration curve for SiO₂ sample was shown to be shifted to the right about the calibration curve in the range of higher pH of external solution indicating a negative charge of the SiO₂ surface in a neutral and slightly acidic medium [6]. Then, with a decrease in the pH of external solution, the titration curve for SiO₂ approaches the calibration curve and crosses it (shifted to the left about the calibration curve) in the range below pH 3. It is known [7] that the hydroxylated surface of silica has a point of zero charge (PZC) at pH $\sim 2 \div 3$ and less. It charges positively. The

horizontal plateaus on the titration curves for SiO_2 and $\text{ZrO}_2 - \text{SiO}_2$ mixtures reflect the constancy of the fraction of the non-protonated form of the radical when the pH of external solution changes.

The horizontal plateaus correspond to the titration process of silanol groups of silica [6]. In this paper it was previously shown that by projecting $f, \%$ parameter on the horizontal plateau onto the calibration curve, we obtain the pK_a value of the titrated functional groups on pH axis.

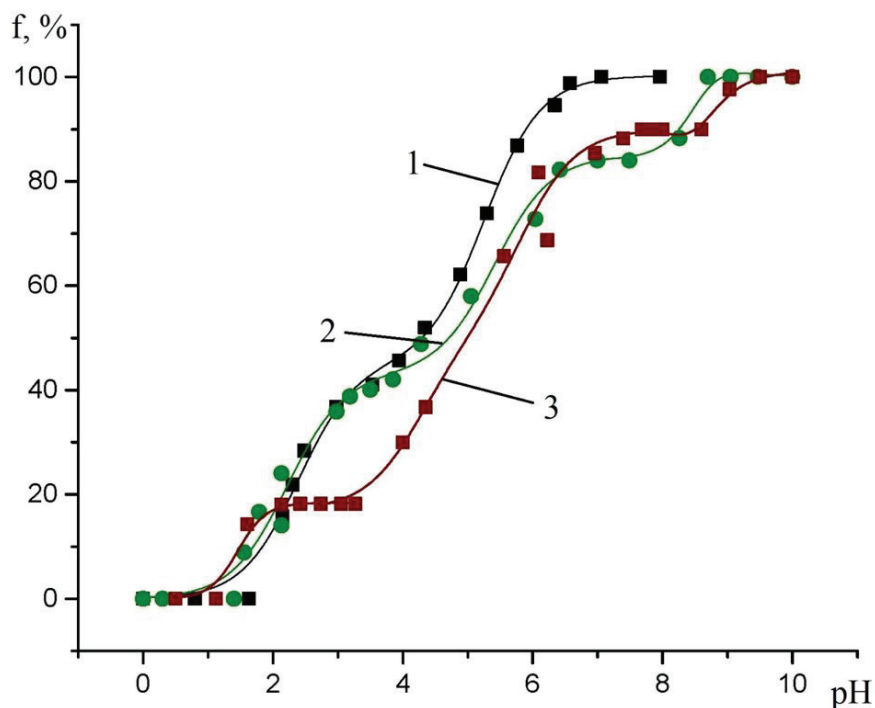


FIGURE 2. Titration curves for NR in the pores of the samples plotted from anisotropic spectra simulations : 1-bulk solution, 2- SiO_2 , 3- $\text{ZrO}_2\text{-SiO}_2\text{-11}\%$.

The titration curve of the mixed sample is shifted to the right about the calibration curve greater than that for pure silica. There is also the second horizontal plateau in the range of $\text{pH} \sim 1.5 \div 3.5$. It reflects the process of titration of more acidic functional groups belonging to the mixed phase Zr-O-Si .

CONCLUSIONS

As a result of this work, it was found that the pH values near the surface of individual and mixed xerogels based on ZrO_2 and SiO_2 are higher than those in the external solution. But the acidity values near the surface of mixed oxides have intermediate values between pH values for individual ZrO_2 and SiO_2 .

ACKNOWLEDGEMENTS

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