THE PRACTICAL USE OF RADIOACTIVE WASTE FOR THE PROCESS OF RADIOACTIVE-CATALYTI PRODUCTION OF HYDROGEN FROM WATER AND ITS STORAGE IN SOLIDS

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Introduction

The heterogeneous processes of radiating-catalytic transformations of water and hydrocarbons represents a huge interest, because can be used for obtaining of ecological pure hydrogen.

The efficiency of decomposition reactions course and yield of radiolysis products is based on a choice of catalyst used in the process. As catalysts for heterogeneous transformations of water molecules under action of γ-radiation every possible oxides and oxide systems are applied.

Results and discussion

That moving from especially pure silicagel (SiO_2) up to Be-SiO_2, increases the speed of processes of accumulation of the radiating paramagnetic centers, and, respectively, increase in their radiating-chemical yields.

If to consider, that molecules of water possess electron-donor properties, it is possible to approve, that more probable channel of carry of energy from a firm body to the adsorbed molecules is interaction of these molecules with holes on a surface of a firm matrix.

The observed law is well combined with radiating-catalytic properties of silicates at the water radiolysis.

Accumulation regularities of the radiating paramagnetic centers in cationic-silicates can be explained by change of ionicity of cationic-oxygen groups and, accordingly, by polarizing action of cations.

Thus, by change of cationic composition in cationic-silicates it is possible to operate processes of accumulation of the radiating paramagnetic centers and radiating-catalytic activity of silicates.

Efficiency of radiating-chemical processes in silicates depends not only by cation's nature, but also on concentration of this or that cation in silicate.

Kinetic laws of accumulation of the radiating paramagnetic centers in borosilicate with various percentage of B_2O_3, which have formed under action of γ- quantum, have been investigated.

It has been revealed, that small concentration of ions of boron in structure of silicate led to increase in a radiating yield of the paramagnetic centers connected with additional places for localization of nonequilibrium holes. Thus the maximal output of the paramagnetic centers calculated on 100 эВ absorbed energy is observed at maintenance B_2O_3 in SiO_2 equal 1,5 %.

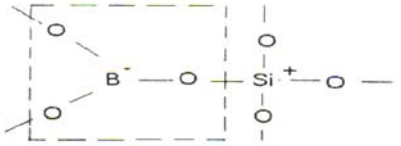
Fig.1. IR spectra of initial borosilicates with different contents of B_2O_3: a – 0,9%; b – 1,5%; c – 10%; d – irradiated by γ - radiation with the maintenance of B_2O_3 – 0,9%.

For revealing an interrelation between borosilicate composition and their catalytic activity, the borosilicate structural researches by a method of the repeated broken full internal reflection (RBFIR) at the IR range have been undertaken. The volumetric infra-red absorption spectra also have been investigated.

Apparently from figure 1, in spectra the intensive band is shown at 1060 cm^{-1}, corresponding antisymmetric valent fluctuations of bond Si-O. Frequency of this band noticeably differs from frequency of fluctuations of bond Si-O observable in volumetric spectra of absorption (1095 cm^{-1}). According to theoretical calculation, reduction of the resulted weight fluctuation atoms (that is possible at break of bonds)

conducts to reduction of frequency of antisymmetric valent fluctuations of bonds Si-O. According to it low-frequency displacement of fluctuations of bond Si-O in superficial spectra of absorption can be connected with superficial defects of structure and to carry to fluctuations of fragments a silicon-oxygen skeleton on a surface.

With increase in percentage B_2O_3 in SiO_2 intensity of a band of ties Si-O corresponding to antisymmetric valent vibration (1060 cm^{-1}) grows, its displacement aside high frequencies is simultaneously observed. Such behaviour of this band it is possible to explain introduction a boron oxide in a silicon-oxygen skeleton and reduction of deficiency of structure by surfaces. At parity B_2O_3 in SiO_2, equal 1,5 % intensity of a band reaches a maximum and at the further increase in concentration remains constant, that it is possible to connect with indemnification of deficiency a silicon-oxygen skeleton on a surface borosilicates at this concentration.



For revealing the mechanism of transfer of energy absorbed oxide to the adsorbed molecules of water spectra radiothermoluminescence in [B_2O_3 + SiO_2] with various maintenance B_2O_3 have been investigated:

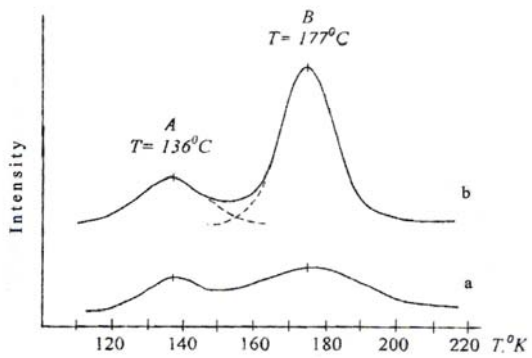


Fig.2. Thermoluminescence spectra of borosilicates with maintenance B_2O_3 equal: a - 0,9 mass %; b - 1,5 mass %.

The maximum thermalglow at 177°K has been carried to recombination holes with electrons localized on bridge atom of oxygen between trigonal-coordinated boron atoms and silicon atoms:

$$e^+ + B - O^- - Si \rightarrow (B - O^{-+} - Si)^* \rightarrow$$
$$\rightarrow B - O^- - Si + h\nu \rightarrow$$

The maximum at 130°K has been carried to recombination electrons with holes localized on oxygen vacancies:

$$e^- + V_0e^+ \rightarrow V_0e^-e^+ \rightarrow (V_0)^* \rightarrow V_0 + h\nu \rightarrow$$

Calculation of energy of activation of the centers of a luminescence lead on the basis of intensity and halfwidth peaks have shown prevalence of processes of capture of holes the centers of a luminescence in case of borosilicates with maintenance B_2O_3 of equal 1,5 %. That is, at given concentration B_2O_3 the hole mechanism of transfer of energy to the molecules of water adsorbed on a surface prevails.

Conclusions

Peak efficiency of borosilicates is reached at full indemnification of superficial deficiency silicon-oxygen skeleton by boron atoms.

References

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