Differential heats of water adsorption on rutile Doliev G.¹, Rakhmatkariev G.² (Republic of Uzbekistan) Дифференциальные теплоты адсорбции воды на рутиле Долиев Г. А.¹, Рахматкариев Г. У.² (Республика Узбекистан)

¹Долиев Голиб Алишерович / Doliev Golib – младший научный сотрудник; ²Рахматкариев Гайрат Убайдуллаевич / Rakhmatkariev Gayrat – заведующий лабораторией, лаборатория элементного анализа, Институт общей и неорганической химии Академии наук Республики Узбекистан, г. Ташкент, Республика Узбекистан

Abstract: the full thermodynamic characteristics of adsorption of water on rutile were studied in detail in the paper. The correlation between the adsorption-power characteristics and crystal-chemical structure of rutile was found and the molecular mechanism of adsorption of water on rutile in the whole areas of fillings were identified.

Аннотация: в работе детально изучены полные термодинамические характеристики адсорбции воды на рутиле. Найдена корреляция между адсорбционно-энергетическими характеристиками и кристаллохимическим строением рутила и выявлен молекулярный механизм адсорбции воды на рутиле во всей области заполнений.

Keywords: titan dioxide, isotherm, heat, entropy and thermokinetics of adsorption, water, adsoption calorimetry. **Ключевые слова:** диоксид титана, изотерма, теплота, энтропия и термокинетика адсорбции, вода, адсорбционная калориметрия.

Knowledge of the structure of oxide surface is important for understanding of chemical reactions at the interface. In order to describe the reactions occurring on the surface, it is necessary to have detailed information about the nature, number, strength and distribution of the surface centers involved in the adsorption and catalytic processes. This information is necessary for modeling of chemical processes at the surface and for determining the stoichiometry and mechanism of surface reaction [1-7].

More complete description of the physical, chemical, crystal-chemical nature of the surface of the adsorbent provides differential heat of adsorption with other differential adsorption-power characteristics - entropy, free energy and heat capacity.

The purpose of this presentation is the study of the surface chemistry of rutile and mechanism of adsorption of water using a high-precision adsorption calorimeter installation built in the laboratory. An attempt to study this system was undertaken by us earlier [2]. However, we decided to go back to it as to obtain more accurate results in the experiment [2] adsorbent dosage was carried out in large amounts to increase the accuracy of measurements and therefore some of the fine details in the heat of adsorption curve at high occupancies were not identified, moreover over the years the accuracy of measuring the differential heat significantly increased.

Rutile is obtained using hydrolysis $TiCl_4$ and processed by acid steam treatment at 523 K. XRD analysis did not reveal any foreign matter in the contents of the adsorbents. The curves of differential thermal analysis were typical for rutile.

The differential molar adsorption calorimetric studies on rutile water adsorption were conducted on the instrument described in [3, 4]. Employing the compensation method of heat flows by Peltier effect allowed to increase the accuracy of measuring the heat of adsorption for more than one order. Adsorption measurements were carried out on a universal high-vacuum volume setting, allowing adsorption measurement and dosage of adsorbent with high accuracy.



Differential heat adsorption of H_2O on T_2O at 303K. Dashed line refers to condensation heat of H_2O at 303K.

The entropy of liquid n-heptane is chosen for zero. The horizontal dashed line – is integral mean molar entropy.

Fig. 1. The differential heat of adsorption (Q_d) of water on rutile

De-hydroxylated surface of the adsorbent was obtained by treating it with thermal vacuum at 720 K. In order to avoid the changes in surface properties during the de-hydroxylation, the sample was further oxidized in the hot state.

Before the water steam inlet, sample was heated and processed by high vacuum pumping at 720° K for 10 hours. Before measuring, water was carefully cleaned and degassed.

Figure 1 shows the differential heat of adsorption (Q_d) of water on rutile. The curve has a complicated step form. In accordance with the steps we have identified 7 sections: section 1 – from 0 to 40 µmole/g (40 µmole/g); 2 – 40 – 80 (40 µmole/g); 3 – 80 – 93 (13 µmole/g); 4 – 106 (13 µmole/g); 5 – 106 – 126 (20 µmole/g); 6 – 126 – 136 (10 µmole/g); and finally, 7 – 136 – 146 (10 µmole/g).

According to Jones and Hock [5], 5- coordinated ions Ti^{4+} of A series [110] are more accessible to the adsorbed molecules and have different high energy activity compared to the 4-coordinated (series B), which are tightly screened by two oxygen ions (O²) and are therefore not active in the act of adsorption molecules with adsorbent.

The data obtained on a specially assembled high vacuum infrared spectroscopic cell [13], which allows taking spectra at strictly controlled surface coverage, revealed adsorption mechanism implemented in the sections 1 and 2. In section 1, the increase of the absorption of hydroxyl groups' growth was observed and in the section 2, the increase of the absorption bands of molecular adsorbed water and simultaneously a sharp decline in the intensity of the absorption bands of hydroxyl groups as the adsorption of water. Consequently, unit 1 is responsible for the dissociative adsorption of water to form a 2-hydroxyl groups on the coordinative unsaturated ions Ti^{4+} , and section 2 for a solid, but still molecular adsorption of water by ions Ti^{4+} while the adsorbed water implements additional hydrogen bond with the hydroxyl groups.

Additionally, the verges of [110] present the verge of a lower index of [100] [101]. These verges have been well identified in [6], and clearly visible during the water adsorption (sections 3 and 4, 13 μ mol / g each). In these faces there are no hydroxyl groups [7] and water molecules are adsorbed molecularly. At this stage it is difficult to identify exactly in which of these two sides the adsorption is occurring or it is simultaneously occurring on one or the other, so we refer these 2 steps to the sequential adsorption of water on the verge of titanium ions [100] and / or [101].

As for sections 5, 6 and 7 (20, 10 and 10 μ mol / g, respectively), they add up to 40 μ mol / g. On the brink of the [110] there are still present centers capable to accept water molecules and they are the basic oxygen ions O²⁻, OH group and the coordinated water protons, with which water can form hydrogen bonds. On the IR spectra of

the region of these sections, reversibly by hydrogen bonds, adsorbed water is detected. It shows the dependence of the molar differential entropy of adsorption of water on rutile. The molar differential entropy of the adsorption $(\Box S_d)$ of water is calculated by the isotherms and differential heats of the adsorption according to the Gibbs – Helmholtz equation (zero as the entropy of liquid water):

The differential entropy of the adsorption of water on rutile at 303 K. The entropy of liquid water is taken as zero. The horizontal dashed line - average molar integral entropy.

$$\Delta S_a = \frac{\Delta H - \Delta G}{T} = \frac{-(Q_a - \lambda) + A}{T}$$

where λ is steam-heat, \Box H and \Box G are enthalpy and the free energy change in the process of adsorption from the standard sate to the adsorbed state.

The entropy of the adsorption of water on rutile is generally located in the negative range. At low fillings, it has low negative ranges and reaches ~ 90 J / mol * K, then sharply increases approaching the entropy of liquid water. Average molar cumulative entropy is -60 J / K * mol, which indicates the state of the ice-like adsorbed water on rutile.

References

- 1. Fujishima A., Honda K., Nature, 1972. V. 238. P. 37-38.
- 2. Huruta M., Yamada N., Kobayashi T. and Iijima S. J., 1989. Catal. V. 115. Pp. 301-309.
- 3. Klabunde K. J., Erickson L., Koper O. and Richards R. Naboscale Mater. In Chem.: Env. App. American Chemical Society, 2010.
- 4. Zhu Y., Shi J., Zhang Z., Zhang. C. and Zhang X. Anal. Chem., 2002. V. 74. Hh. 120-124.
- 5. Fujishima A., Rao T. N. and Tryk D. A. J. Photoch. Photobio. C. 2000. V. 1. Pp. 1-21.
- 6. *Rakhmatkariev G. U.* Mechanism of Adsorption of Water Vapor by Muscovite: A Model Based on Adsorption Calorimetry // Clays and Clay Minerals, 2006. Vol. 54. P. 423-430.
- 7. *Mentzen B. F., Rakhmatkariev G. U.* Host/Guest interactions in zeolitic nonostructured MFI type materials: Complementarity of X-ray Powder Diffraction, NMR spectroscopy, Adsorption calorimetry and Computer Simulations // Узб. хим. журн., 2007. № 6. Р. 10-31.