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THERMOGRAVIMETRIC INVESTIGATION OF THE DEHYDRATION THERMODYNAMICS OF AMORPHOUS SILICA AFTER ITS HYDROTHERMAL AND THERMOVAPOROUS TREATMENT

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After hydrothermal and thermovaporous treatment of chemically pure amorphous aqueous silicic acid in solutions of NaOH and NH_4OH and in water vapour it is possible, using complex thermal analysis, to detect the weight loss and heat effects corresponding to evaporation of various forms of combined water, and to estimate the heats of evaporation of these forms. From the obtained data, the following water forms have been identified: (1) at 200 - 300° capillary-condensed water formations of the cluster type evaporate; ΔH_{deh} is about 8 kcal/mole H_2O; (2) at 250 - 400°, molecules of water linked by hydrogen bonds with hydroxyl groups on the surface and in the volume of the particles; ΔH_{deh} is about 5 kcal/mole H_2O; (3) at 350 600°, molecules of water coordinated to silicon atoms in the volume of the particles; ΔH_{deh} is approximately 1 kcal/mole H_2O. The total evaporation heat changes from 10 kcal/mole H_2O when water of form 1 predominates, to 5 kcal/mole H_2O when forms 2 and 3 predominate.

During an investigation of silica dehydration by TG, the weight losses caused by evaporation of free and combined water are recorded in the temperature range 100—1000°; at the same time, as a rule an endothermic effect is observed in the range 100—200° in the DTA curves, associated with evaporation of capillary-condensed water found in open pores [1—5]. Reference [6] is an exception, where the investigation of silica gel dehydration revealed four endothermic effects, at temperatures of 150, 200, 400 and 500° in the DTA curve, accompanied by discontinuities in the TG curve. It was assumed that three of the latter effects were caused by elimination of the hydroxyl groups bonded by hydrogen bonds, but the absence of numerical values relating to the thermal effects did not permit an unambiguous interpretation of the results. At the same time, it may be concluded on the basis of the present work that the non-observation of high-temperature thermal effects in most studies of silica gel dehydration results from the use of inaccurate equipment and measuring techniques.

The dehydration of silica gel subjected to hydrothermal and thermovaporous treatment was investigated thermogravimetrically in the present work. This preliminary treatment made it possible to record the thermal effects caused by water loss in the temperature range 200—600°, and to determine their magnitudes. The results are of considerable interest with regard to the nature and properties of the water in amorphous silica.

Experimental

As starting material, chemically pure aqueous silicic acid with a unit surface (by nitrogen) of 400 m^2/g and a total impurity content of 10^{-3} wt % was used. The acid was treated in autoclaves in water, in solutions of NaOH and NH_4OH, and in water vapour. Treatment conditions are shown in Table 1.

TG measurements were made using a MOM (Hungary) derivatograph, in the temperature range 20–1000°. The samples were put on a platinum multiplate sample holder. The heating rate was varied from 3 to 20 deg/min. The curves of the studied samples are shown in Fig. 1. For the starting silicic acid without treatment, one thermal effect is recorded [7], at a temperature of 160°, 5.0% of the water being lost in the process. The remaining 3.8% of the water is lost in the range 200–600°, this loss not being accompanied by thermal effects. Hydrothermal treatment in a 1% solution of NaOH at 185° for 70 hours leads to the appearance of an incompletely resolved peak at 210° in the DTA curve (curve 1). The weight loss is described by a smooth TG curve having no discontinuities; the dehydration range is 100–600°. After hydrothermal treatment at 350° for 6 hours, the endothermal effect in the range 150–200° disappears, but three fairly well-pronounced effects appear at 300, 400 and 500° (curve 2). The weight loss is described by an *S*-shaped TG curve, with three discontinuities corresponding to the three effects

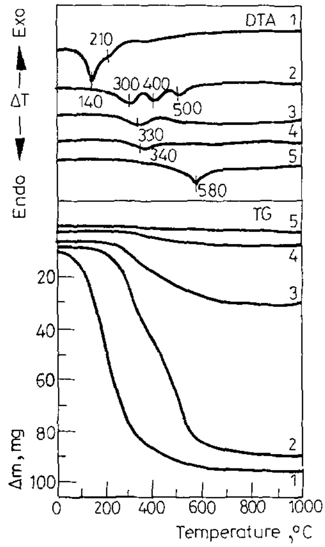

Fig. 1. TG and DTA curves of silica gel samples subjected to hydrothermal and thermovaporous treatment:
1. Autoclave treatment in 1% solution of NaOH, 185°, 70 hours;
2. Autoclave treatment in water, 350°, 170 atm, 6 hours;
3, 4. Sample No. 2 after autoclave treatment in water vapour, 440°, 6 hours;
5. Sample No. 2 after autoclave treatment in water vapour, 440°, 50 hours.

Table 1

No.	Initial sample and conditions of treatment	Total weight loss, wt. %	Temperature range of dehydration, °C	Number of dehydration heat effects	Temperature of effects, °C	Water loss accompanied by heat effects, wt. %	Water loss not accompanied by thermal effect, wt. %	Water evaporation heat, kcal/mole H_2O	
								total	for different forms of water
1.	$SiO_2 \cdot n\,H_2O$, chemically pure, after autoclave treatment in 1% solution of NaOH, 185°, 70 hr	9	60 – 700	2	140 210	6.5	2.5		
2.	$SiO_2 \cdot n\,H_2O$, chemically pure, after autoclave treatment in water, 350°, 170 atm, 6 hr	8.5	180 – 1000	3	300 400 500	8.0	0.5	5.3 ± 0.1	
3.	Sample No. 2 after autoclave treatment in water vapour, 440°, 6 hr	3.6	200 – 800	1	340	3.0	0.6		
4.	Sample No. 2 after autoclave treatment in water vapour, 440°, 24 hr	0.9	300 – 800						
5.	$SiO_2 \cdot n\,H_2O$, chem. pure, after autoclave treatment in NH_4OH, 350°, 180 atm, 6 hr	8.2	200 - 800	3	300 400 500	7.5	0.7	4.9 ± 0.3	~8 ~5 ~1

in the DTA curve. Dehydration starts at 250° and is practically over at 800°. Subsequent treatment of the specimen in water vapour in an autoclave at 440° and 400 atm for 6 hours or 24 hours (curves 3 and 4) results in the disappearance of the thermal effects at 400 and 500°. The temperature of the first thermal effect is shifted to 330 and 340°, respectively, the same shift being observed for the dehydration start temperature in the DTA curves. The total water losses for the three specimens are 8.5, 3.6 and 0.9%, respectively. Further thermovaporous treatment for 50 hours under similar conditions leads to the disappearance of the thermal effects of dehydration and the appearance of a thermal effect corresponding to the $\alpha \rightleftharpoons \beta$-quartz phase transition. The total water loss is 0.4 wt%.

Results

Numerical values relating to the dehydration thermal effects have been determined (Table 1) for silicic acid samples subjected to hydrothermal treatment in water and in an ammonia solution by the Berg and Anosov method [7, 8].

For the total thermal effect, in the two samples close values of the heat of dehydration, of about 5 kcal/mole evaporated water, were obtained. Determination of the individual thermal effects making up the total one is very difficult in view of their poor resolution, and for this reason these values may be regarded as very approximate. The best resolution during determination of the thermal effect was achieved for the silicic acid sample treated with a solution of NH_4OH at 350° for 6 hours. The thermal effect values at 300, 400 and 500° are ~ 8, ~ 5 and ~ 1 kcal/mole H_2O, respectively. The well-pronounced discontinuity points in the TG curve permitted the thermal effects relating to the evaporated water to be attributed to a certain form. The results make it possible to identify the various forms of combined water in silica gel, as well as to reveal their intertransitions and their part in the modification of the silica gel structure during its hydrothermal and thermovaporous treatment.

During hydrothermal treatment of silica gel, its globular structure is rearranged into a spongy, more massive one, the particle size increase reaching several tenths of a mm, and the surface decreasing to 1 – 10 m^2/g [9]. As compared to silica gel globules, the particles formed are less uniform and contain a great number of cavities filled with water. In the temperature range studied (200 – 600°) no noticeable dehydroxylation of the silica gel surface occurs [10], which may be regarded as the basis for the conclusion that all the effects observed are caused by the loss of water. The large size of the particles formed, as compared to the initial globules, allows the recording of effects which, for the small globules of silica gel, are beyond the sensitivity range of the equipment employed. Further, for large particles, of most importance are the kinetic factors, and more particularly the processes of water molecule diffusion. In the silica gel structure rearrangement caused by hydrothermal treatment, the determining part is played by the processes of recondensation of the silicic acid [9]. The spongy structure formed predetermines the formation of a large number of clusters included in the silica gel structure; as a result of the spongy structure, these clusters are in fact contained in the particle volume and communicate with the surrounding space *via* channels formed by irregularly-spaced siloxane bonds. Kinetic barriers to evaporation result in a shift of the temperature range of dehydration from 140–200° to 250–550°. The value of the first thermal effect of dehydration with a minimum at 250°, equal to 8 kcal/mole, is close to the water evaporation heat. This confirms the view point that in this case we are dealing with water clusters. As the temperature rises and the water formations disappear, the water molecules connected by hydrogen bonds with hydroxyl groups inside the volume of the particles formed during hydrothermal treatment also disappear the second effect in Fig. 1 (2) corresponding to 350°. The heat of evaporation amounts to 5 kcal/mole H_2O, which indicates that the water molecules are localized on one hydroxyl group. This form of water evaporates not only from the silica gel surface formed by open pores, but also from a closed volume; the water molecules escape to the surface, with subsequent evaporation being determined by diffusion, which results in a further shift of the dehydration thermal effect to 350°. As this form of water disappears, water molecules also disappear which are contained in the entire volume of the particles and are coordinated to silicon atoms. Kinetically, the elimination of this form of water is the most difficult process. The low value of the heat of evaporation and the high temperature of dehydration indicate that here we are dealing with a rather complicated kinetic process; the high energy of diffusion activation results in the fact that this form of water evaporates at the relatively high temperature of about 550°.

Conclusion

The thermogravimetric investigation of silica gel after hydrothermal treatment makes it possible to identify the forms of combined water characteristic of any silica-oxygen structure:

1. Capillary-condensed water formations of the cluster type; the evaporation heat is close to the water evaporation heat; the evaporation temperature range for non-treated silica gel is 140–200° while that for silica gel subjected to hydrothermal treatment is 200–300°.
2. Water molecules hydrogen-bonded to hydroxyl groups on the surface and in the volume of the particles. The heat of evaporation is about 5 kcal/mole H_2O, and the evaporation range for silica gel subjected to hydrothermal treatment is 250–350°.
3. Water molecules coordinated to silicon atoms in the particle volume. The heat of evaporation is about 1 kcal/mole; the evaporation range is 350–600°.

The correlation of the various forms of water in silica gel may be responsible for the value of the integral thermal effect: 10 kcal/mole H_2O when the capillary-condensed water predominates; and 5 kcal/mole H_2O when the hydrogen-bonded and coordinated water forms predominate. It is most probable that the presence of the third form of water makes the silica-oxygen structure most labile, facilitating the weakening of the siloxane bond and thereby the relaxation of the structure to a thermodynamically more favourable state.

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RÉSUMÉ — Après traitement hydrothermique et par la vapeur de l'acide silicique aqueux amorphe et pur en solution dans NaOH et NH_4OH ainsi que dans la vapeur d'eau, il est possible, en se servant de l'analyse thermique complexe, de déceler les pertes de poids et les effets thermiques qui correspondent à l'évaporation des formes diverses de l'eau combinée et de trouver les valeurs des chaleurs d'évaporation correspondantes. A partir des données obtenues, on a identifié les formes d'eau suivantes:

1. entre 200 et 300° les formations d'eau capillaire condensée du type inclusion s'évaporent, $\Delta H_{\text{déh}}$ est voisin de 8 kcal/mol d'H_2O;
2. entre 250 et 400° ce sont les molécules d'eau liées aux groupes hydroxyles par liaisons hydrogène qui se volatilisent à la surface et à l'intérieur des particules, $\Delta H_{\text{déh}}$ est voisin de 5 kcal/mol d'eau;
3. entre 350 et 600° ce sont les molécules d'eau liées par liaisons de coordination aux atomes de silicium qui se vaporisent à l'intérieur des particules, $\Delta H_{\text{déh}}$ étant d'I kcal/mol H_2O environ. La chaleur totale d'évaporation varie de 10 kcal/mol H_2O lors de la prédominance de la première forme d'eau à 5 kcal/mol d'eau lors de la prédominance des formes 2 et 3.

ZUSAMMENFASSUNG — Nach hydrothermaler und Thermodampfbehandlung chemisch reiner, amorpher wässeriger Kieselsäure in NaOH- und NH_4OH-Lösungen sowie in Wasserdampf ist es möglich, durch Einsatz der komplexen Thermoanalyse, den Gewichtsverlust und die der Verdampfung der verschiedenen Formen des gebundenen Wassers entsprechenden Wärmeeffekte nachzuweisen und die Verdampfungswärmen dieser Formen annähernd zu bestimmen. Aufgrund der erhaltenen Angaben wurden folgende Wasserformen identifiziert:

(i) bei 200 bis 300° entweicht kapillarkondensiertes Wasser vom Einschlußtyp, ΔH_{deh} beträgt etwa 8 kcal/mol H_2O.

ii) bei 250 bis 400° entweichen die durch Wasserstoffbindungen über Hydroxylgruppen gebundenen Wassermoleküle von der Oberfläche und dem Inneren der Partikel, ΔH_{deh} beträgt etwa 5 kcal/mol Wasser.

iii) bei 350 bis 600° entweichen die durch Koordinationsbindungen an Siliciumdioxid gebundenen Wassermoleküle aus dem Inneren der Teilchen, ΔH_{deh} beträgt annähernd 1 kcal/ /mol H_2O. Die Gesamtverdampfungswärme ändert sich von 10 kcal/mol H_2O bei überwiegender Form 1 von gebundenem Wasser, auf 5 kcal/mol Wasser bei Vorherrschen der Formen 2 und 3.

Резюме — После гидротермической и паротепловой обработки химически чистой аморфной водной кремневой кислоты в растворе NaOH и NH_4OH, а также в парах воды, представилось возможным, используя комплексный термический анализ, определить потерю веса и тепловые эффекты испарения различных форм связанной воды и оценить теплоту испарения этих форм. На основе полученных данных были идентифицированы следующие воды: 1) при 200—300° испаряется капиллярная конденсированная вода кластерного типа, $\Delta H_{\text{дег}}$ составляет около 8 ккал/моль H_2O. 2) при 250—400° испаряются молекулы воды, связанные водородными связями с гидроксильными группами как на поверхности, так и в объеме частиц, $\Delta H_{\text{дег}}$ — около 5 ккал/моль воды. 3) при 350—600° испаряются молекулы воды, связанные координационными связями с атомами кремния в объеме частиц, $\Delta H_{\text{дег}}$ составляет приблизительно 1 ккал/моль H_2O. Общая теплота испарения изменяется от 10 ккал/моль H_2O при преобладании первой формы воды до 5 ккал/моль воды при преобладании 2 и 3 форм воды.