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THE MOLAR FORMATION ENTHALPY OF NANO-SiO_2 WITH DIFFERENT SURFACE AREA

L. Peng[*], *W. Qisui*, *L. Xi* and *Z. Chaocan*

School of Sciences, Wuhan University of Technology, Wuhan 430070, China

Three samples of silicon dioxide were syhthesized and their surface areas were measured. A thermo-chemical cycle was designed to calculate the molar formation enthalpy. The molar formation enthalpy, $\Delta_f H_m^\ominus$, for three amorphous silica with the Langmuir surface area 198.0854, 25.1108 and 11.9821 $m^2 g^{-1}$ gave –895.52, –910.86 and –915.67 kJ mol^{-1}, respectively. With the increasing surface area, the values of $\Delta_f H_m^\ominus$ increased accordingly.

The results suggest that the silica with larger surface area is more unstable. The wetting heat was also measured by adding the silica powder into water. With the rehydration of the more SiOH groups on the surface, the larger surface areas of silica lead to the more wetting heat. A smaller particle has the more unstable hydroxyl groups and surface energy.

Keywords: *calorimetry, enthalpy, silica, surface area, thermo-chemical cycle*

Introduction

Silicon dioxide is an amorphous inorganic polymer composed of siloxane groups (Si–O–Si) in the inward region and silanol groups (Si–OH) distributed on the surface [1, 2]. Silica powders are widely used in industry as fillers, catalysts, catalyst supports, adsorbents and chromatographic agents [3–5]. In each of these applications, knowledge of the surface properties is required in order to understand the physicochemical principles involved. As silanol groups can undergo various reactions (e.g., chlorination, ammoniation and esterification), it is important to control the surface nature of silica.

The standard enthalpy of formation of a compound, $\Delta_f H_m^\ominus$, is the change in enthalpy for the reaction that forms 1 mol of the compound from its elements. Usually, the $\Delta_f H_m^\ominus$ values were reported at 298.15 K. According to Hess's law, one can calculate the standard enthalpy change for any reaction by using $\Delta_f H_m^\ominus$ values for all reactants and products. As to most of inorganic substance and simple organic substance, there has been the reported data about $\Delta_f H_m^\ominus$ values by calorimetry which measuring the heat accompanying a reaction at constant pressure and temperature. In recent years, more and more new substances and materials were synthesized. $\Delta_f H_m^\ominus$ values of these substances are difficult to be determined, for example inorganic and organic polymers. One reason is that these substances exist in too many forms and molecular mass is varied. In some sense, they cannot be regarded as a pure substance. The other reason is that it is difficult for these substances to perform a chemical reaction at normal pressure and temperature. And the heat is difficult to be measured by calorimetry.

Although the standard enthalpy of formation of amorphous silica has been reported, the parameters about chemical and physical properties of silica were not mentioned, such as surface area, particle size and OH surface density. However, the parameters of these polymers are closely related to the standard enthalpy of formation. In the process of a chemical reaction of inorganic polymer, different surface area and particle size will be involved in different enthalpy. Thus, it is important to investigate the relationship between these physical properties and thermodynamics. In this study, a solution-reaction calorimetry was used to determine $\Delta_f H_m^\ominus$ values of amorphous silica with different surface area by designing a thermochemical cycle. Besides, the wetting heat and OH surface density were also obtained to analyze the relation between thermochemical properties and surface area of amorphous silica.

Experimental

Synthesis of amorphous silica particles

Tetraethoxysilane, ethanol, Na_2SiO_3, HF, KCl were purchased from Shenshi Chem. Ltd., All solutions were prepared with doubly distilled water. The pH values of the mixed solvent system were measured with a glass electrode in combination with an AgCl

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[*] Author for correspondence: liup567@163.com

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

reference electrode (Shanghai Precision and Scientific Instrument Co., Ltd.).

Silica particles were prepared by hydrolysis of tetraethoxysilane in a water-ethanol mixture at pH 7.5, 8.5 and 9.5, respectively. After filtration and purification, three samples were heated to 600°C and maintained for 4 h to obtain the dehydroxylated silica. The particle diameter was about 500 nm, evaluated by transmission electron microscopy (Jeol, JEM2100F).

Measurement of surface area of amorphous silica particles

The surface area of silica particles were measured by Micromeritics ASAP 2020. After the samples were degassed at 393 K, their surface areas were analyzed with N_2 at 78.025 K between 0.05 and 0.20 P^0, and the pore areas were analyzed at 0.995 P^0. Both BET surface area and Langmuir surface area were shown in Table 1.

Measurement of wetting heat

The isoperibol reaction calorimeter used for the study was constructed by Prof. Liu of Wuhan University and was adapted for measuring enthalpies of solid–liquid and liquid–liquid reaction [6, 7]. The precision temperature control and measurement are ±0.001 and ±0.0001 K, respectively. After KCl dried in a vacuum oven for 6 h at 408 K, the calorimeter was tested by dissolving KCl dried in a vacuum oven for 6 h at 408 K in water at 298 K. Three kinds of amorphous silica of 1.000 g were added into distilled water. After an electric calibration was performed, the heat of the process was calculated.

Measurement of reaction enthalpy of silica with HF

In experiment A, 2.840 g $Na_2SiO_3\cdot 9H_2O$ was added into 100 mL HF solution with 0.10 mol L^{-1}. The released heat was calculated after the reaction finished and an electric calibration was performed. 0.18 mL H_2O was added into the mixed solution. The other group (experiment B) was performed by adding 0.6000 g silica into 100 mL HF solution with 0.10 mol L^{-1}. Then 0.8000 g NaOH was added into the mixture. All the measurement experiment was performed for three times and the involved reactions were presented in Table 2.

Results and discussion

The properties of amorphous silica of high specific surface area, from the smallest colloidal particles to macroscopic gel, depends largely on the chemistry of the surface of the solid phase. It has practical importance in the technology of cracking catalysts, mineral processing, ceramics and adsorbers. It is also directly involved in the manufacture and use of siliceous fillers and thickening agents in organic systems. The thermodynamics should be related to the properties of the surface of the solid phase. However, the reported data of the thermodynamics for amorphous silica have nothing to do with the properties of the surface. It is difficult to determine the enthalpy

Table 1 The surface area of the three samples

Sample	BET surface area/ $m^2\ g^{-1}$	Langmuir surface area/ $m^2\ g^{-1}$	*t*-Plot micropore area/ $m^2\ g^{-1}$	*t*-Plot external surfac earea/ $m^2\ g^{-1}$
1	143.9455	198.0854	34.8017	109.1438
2	18.3707	25.1108	7.3888	10.9820
3	8.8217	11.9821	4.9098	3.9120

Table 2 The equations and enthalpy change for the experiment A and B

Reaction	Equation	$\Delta_r H_m^\Theta$
1	$8HF(aq)+Na_2SiO_3(s)=H_2SiF_6(aq)+2NaF(aq)+3H_2O(l)$	$\Delta_r H_1$
2	$H_2SiF_6(aq)+2NaF(aq)+3H_2O(l)+H_2O(l)=H_2SiF_6(aq)+2NaF(aq)+4H_2O(l)$	$\Delta_r H_2$
Overall reaction for experiment A	$8HF(aq)+Na_2SiO_3(s)+H_2O(l)=H_2SiF_6(aq)+2NaF(aq)+4H_2O(l)$	$\Delta_r H_4$
3	$6HF(aq)+SiO_2(s)=H_2SiF_6(aq)+2H_2O(l)$	$\Delta_r H_3$
4	$2HF(aq)+2NaOH(s)=2NaF(aq)+2H_2O(l)$	$\Delta_r H_4$
Overall reaction for experiment B	$8HF(aq)+SiO_2(s)+2NaOH(s)=H_2SiF_6(aq)+2NaF(aq)+4H_2O(l)$	$\Delta_r H_B$
Overall reaction	$SiO_2(s)+2NaOH(s)=Na_2SiO_3(s)+H_2O(l)$	$\Delta_r H_t$

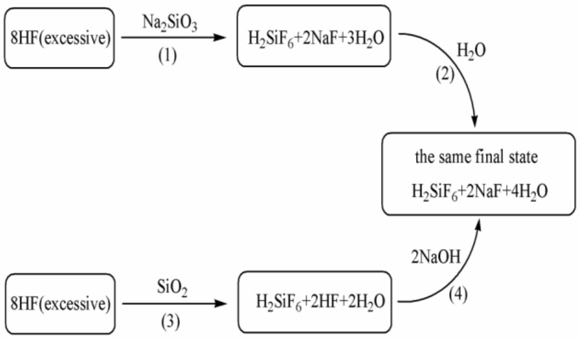

Fig. 1 Reaction scheme for determination of the standard molar enthalpy of formation

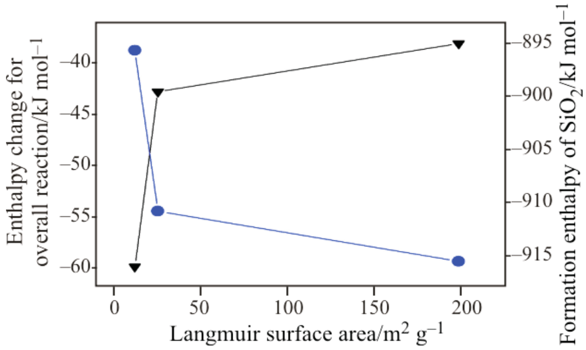

Fig. 2 Relationship between the standard molar enthalpy of formation and Langmuir surface areas for silica

change of solid-state reactions at ambient temperature because silicon dioxide is very unreactive and react only with hydrofluoric acid and sodium hydroxide [8]. A thermo-chemical cycle was designed in Fig. 1 to calculate the molar change of enthalpy of three amorphous silica.

From Fig. 1, it can be seen that the experiment A has the same products as experiment B. The total reactions for experiment A and B were presented in the Table 2. If equation A subtracts from equation B, the following equation can be obtained:

$$\Delta_r H_t = \Delta_r H_B - \Delta_r H_A = \Delta_r H_3 + \Delta_r H_4 - \Delta_r H_1 - \Delta_r H_2$$

According to Hess's law, the standard enthalpy change for the overall reaction can be written as the sum of the reactions 1–4 in Table 2.

$$\Delta_r H_t = \Delta_f H^{\ominus}_{Na_2SiO_3} + \Delta_f H^{\ominus}_{H_2O} - \Delta_f H^{\ominus}_{SiO_2} -$$

$$- 2\Delta_f H^{\ominus}_{NaOH}$$

$$\Delta_f H^{\ominus}_{SiO_2} = \Delta_f H^{\ominus}_{Na_2SiO_3} + \Delta_f H^{\ominus}_{H_2O} - 2\Delta_f H^{\ominus}_{NaOH} - \Delta_r H_t$$

The standard formation enthalpies of the three samples were presented in Table 3. It can be seen that the amorphous silica with different surface areas are different $\Delta_f H^{\ominus}_m$ values. With the increasing surface area, the values of $\Delta_f H^{\ominus}_m$ increased accordingly. Because the standard formation enthalpy can be regarded as an indication of the stability of a compound, there are differences of stability among the three samples. Besides, the different enthalpy change will be observed in the reaction involved in the amorphous silica with different surface areas. The results also suggest that the silica with larger surface area is more unstable. The relationship between surface area and the formation enthalpy was shown in Fig. 2. As to nano-silicon dioxide, the higher $\Delta_f H^{\ominus}_m$ values will cause the particles to conglobate. In the process of conglobation, on the one hand, the heat released and energy of system lowered because $\Delta_f H^{\ominus}_m$ values of products were less than reactants. On the other hand, the degree of disorder inevitable reduced and the entropy of the system decreased, because the dispersed particles were fixed by covalent bond together with each other. With the changes of enthalpy and entropy in this system having the opposed contribution, the conglobation of silica particles can be regarded as an 'enthalpy-driven' reaction [9, 10].

Because SiO_2 is of high surface free energy, it is easy to be absorbed by water vapor at room temperature. If a surface is fully hydroaxylated, the H_2O molecules were adsorbed and covered all SiOH groups because of multiple hydrogen bonding. The wetting enthalpies were also measured by adding the silica powder into water. On the surface of hydroxylated silica there are two kinds of adsorbed water, the formation of the first type is called 'chemisorption' and the second type is called 'physical adsorption'. The surface of silica changes from silanol groups to siloxane groups after the silica that heated to 600°C and maintained for 4 h. The surface water has been lost completely [11, 12]. The process of wetting is accompanied with the formation of adsorbed water and saturated rehydration of silica surface [13]. The wetting heat of three samples was presented in Table 4. The involved heat derived from

Table 3 The standard enthalpy change for the overall reaction and for the processes in Table 2

Sample	$\Delta_r H_1$/kJ mol^{-1}	$\Delta_r H_2$/kJ mol^{-1}	$\Delta_r H_3$/kJ mol^{-1}	$\Delta_r H_4$/kJ mol^{-1}	$\Delta_r H_t$/kJ mol^{-1}	$\Delta_f H^{\ominus}_{SiO_2}$
1	–208.56±0.65	0.45±0.05	–135.38±0.21	–133.42±0.46	–60.09	–895.52
2			–118.04±0.43		–42.75	–910.86
3			–113.23±0.28		–37.94	–915.67

Table 4 The wetting enthalpy for the three samples

Sample	Wetting heat/J	Wetting enthalpy/J m^{-2}
1	23.77±0.21	0.120
2	3.09±0.05	0.123
3	1.41±0.03	0.118

the formation of silanol, chemisorption and physical adsorption. Theoretically, the larger surface areas of silica lead to the more wetting heat because the more SiOH groups on the surface will interact with H_2O molecules and the more covalent bonds are formed. At the same time, the surface areas and radii of particles have an influence on the surface SiOH groups. Hydroxyl groups on a larger particle are closer together and can form more stable hydrogen- bonded pairs. On the contrary, a smaller particle has the more unstable hydroxyl groups and surface energy. Thus the three samples of silica with different surface areas have the different wetting heat.

The thermodynamic parameters of all substances and materials are very important because they determine whether a reaction can take place and how far toward completion the reaction proceed. For example, the changes of enthalpy, ΔH, can be considered as an indicator of the increase of intermolecular bond energies in binding process, while the entropy changes, ΔS, reflect the change of disorder of the system during the reaction [14]. In the past, the thermodynamics for most of the inorganic substances has been reported. Nowadays, more and more nanomaterials were synthesized and the reactions involved were studied widely. Therefore, there is a need for providing the thermodynamics of these substances [15]. Most of substances and materials are inreactive and difficult to react with other substances. So a thermo-chemical cycle may be designed to solve the problem and calculate their thermodynamic parameters. Of course, these substances must be characterized with the state parameters, such as particle radii, surface area, groups of surface and so on when their thermodynamic properties are reported.

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