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Synthesis and Surface Thermodynamic Functions of CaMoO₄ Nanocakes

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Abstract: CaMoO₄ nanocakes with uniform size and morphology were prepared on a large scale via a room temperature reverse-microemulsion method. The products were characterized in detail by X-ray powder diffraction, field-emission scanning electron microscopy, transmission electron microscopy, and high-resolution transmission electron microscopy. By establishing the relations between the thermodynamic functions of nano-CaMoO₄ and bulk-CaMoO₄ reaction systems, the equations for calculating the surface thermodynamic functions of nano-CaMoO₄ were derived. Then, combined with *in-situ* microcalorimetry, the molar surface enthalpy, molar surface Gibbs free energy, and molar surface entropy of the prepared CaMoO₄ nanocakes at 298.15 K were successfully obtained as (19.674 ± 0.017) kJ·mol⁻¹, (619.704 ± 0.016) J·mol⁻¹, and (63.908 ± 0.057) J·mol⁻¹·K⁻¹, respectively.

Keywords: nanothermodynamics; CaMoO₄; nanocake; molar surface enthalpy; molar surface Gibbs free energy; molar surface entropy

1. Introduction

The thermodynamic properties are some of the most important attributes of nanomaterials. In 2001, Hill [1–3] started to work on the nanothermodynamics area, and his research has opened up the door for the development of the discipline of nanothermodynamics. Surface effect is a basic effect of

nanomaterials and many unique properties of nanomaterials are derived from it [4]. Surface thermodynamic properties, including surface Gibbs free energy, surface enthalpy and surface entropy, are an important expression of surface effects, and they have a direct relationship with the chemical thermodynamics [5], chemical kinetics [6], catalysis [7,8], sense [9], adsorption [10], phase transition [11], electrochemistry [12] of nanomaterials. The study of the surface thermodynamic properties of nanomaterials and their structure-function relationships with particle size, morphology and structure is valuable to understand the nature of chemical reactions, but, till now, the development of the surface thermodynamics of nanomaterials is quite poor [13]. How to acquire surface thermodynamic functions of nanomaterials such as molar surface Gibbs free energy, molar surface enthalpy and molar surface entropy is still a great challenge.

Calcium molybdate (CaMoO₄) with scheelite type structure has attracted broad interest due to its interesting potential applications in various realms such as photoluminescence [14,15], scintillation detectors [16], optical fibers [17], catalysts [18], microwave applications [19], energy storage [20], *etc*. As we know, nanostructured materials possess many unique and interesting properties which differ from their bulk versions. These properties depend closely on their uniform shape and narrow size distribution. So far, various properties of CaMoO₄ nanostructures have been well studied, but, to the best of our knowledge, very few reports on their surface thermodynamic properties are available. Studying the surface thermodynamic properties of CaMoO₄ nanostructures is of great significance to understand their reaction mechanism. Besides, the obtained values will also play an important role in their theoretical study and industrial production.

In this paper, we report a simple and facile route for the large scale synthesis of uniform, singlecrystalline and well-defined CaMoO₄ nanocakes, and presented an effective and general route for acquiring the surface thermodynamic functions of nanomaterials by *in-situ* microcalorimetry.

2. Results and Discussion

A typical X-ray powder diffraction (XRD) pattern of the prepared products is shown in Figure 1a. All of the diffraction peaks of the products can be indexed to the pure tetragonal phase of CaMoO₄ with the cell parameters a = 5.19 Å and c = 11.25 Å (JCPDS Card No. 029-0351). No impurity peaks were detected, indicating the formation of pure products. The sharp and narrow diffraction peaks suggest that the products are highly crystalline. Figure 1b presents a field-emission scanning electron microscopy (FE-SEM) image of the prepared products. The FE-SEM image reveals that a large number of cake-like structures with uniform size and morphology have been achieved. Figure 1c is the transmission electron microscopy (TEM) image of the products. It further proves that the obtained products are cake-like structures, and each cake is about 300 nm in diameter and 60 nm in thickness. To obtain further information about the prepared CaMoO₄ nanocakes, high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) analysis of a randomly chosen single CaMoO₄ nanocake were performed. Figure 1d is the TEM image of a single CaMoO₄ nanocake of about 300 nm in diameter. Figure 1e is the SAED pattern of the single CaMoO₄ nanocake shown in Figure 1d. The presence of sharp diffraction spots rather than an amorphous ring is suggestive of the predicted formation of a single-crystal form of CaMoO₄. The SAED pattern can be indexed to pure CaMoO₄ crystals with a tetragonal scheelite structure. It also demonstrates that the

nanocake is a single crystal with the (001) plane as the 2D exposed surface. The HRTEM image shown in Figure 1f further indicates that the observed CaMoO₄ nanocakes are single crystals with no defects or dislocations. The lattice fringes reveal that the single crystal CaMoO₄ nanocakes possess interplanar spacing of about 0.263 nm, corresponding to the (200) and (020) planes of tetragonal CaMoO₄.



Figure 1. (a, b, c) XRD pattern, SEM image and TEM image of the prepared CaMoO₄ nanocakes, (d) TEM image of a single prepared CaMoO₄ nanocake, (e, f) SAED pattern and HRTEM image corresponding to the single prepared CaMoO₄ nanocake in (d).

The RD496-III type microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., Ltd., Mianyang, China), based on thermokinetic theory, can simultaneously output both *in-situ* thermodynamic and kinetic information [21]. Briefly, equivalent amounts of the prepared nano-CaMoO₄ and bulk-CaMoO₄, respectively, were reacted with 1.0 mL of 0.1 M HCl in the microcalorimeter at 298.15 K and standard pressure. The microcalorimetric experiment of each reaction system was repeated five times, and the molar enthalpy of reaction and rate constants obtained are listed in Table 1.

Applying Equations (6), (11) and (12), the molar surface enthalpy, molar surface Gibbs free energy and molar surface entropy of the prepared $CaMoO_4$ nanocakes were respectively calculated as below:

$$\begin{aligned} H_{\rm m}{}^{\rm s} &= \Delta_{\rm r} H_{\rm m}{}^{\rm b} - \Delta_{\rm r} H_{\rm m}{}^{\rm n} = (-29.622 \pm 0.008) - (-49.296 \pm 0.015) \\ &= (19.674 \pm 0.017) \text{ kJ} \cdot \text{mol}{}^{-1} \\ G_{\rm m}{}^{\rm s} &= RT (\ln k_{\rm nano} - \ln k_{\rm bulk}) = 8.314 \times 298.15 \times [(-6.653 \pm 0.010) - (-6.903 \pm 0.013)] \\ &= (619.704 \pm 0.016) \text{ J} \cdot \text{mol}{}^{-1} \\ S_{\rm m}{}^{\rm s} &= (H_{\rm m}{}^{\rm s} - G_{\rm m}{}^{\rm s}) / T = [(19.674 \pm 0.017) \times 10^{3} - (619.704 \pm 0.016)] / 298.15 \\ &= (63.908 \pm 0.057) \text{ J} \cdot \text{mol}{}^{-1} \text{ K}{}^{-1} \end{aligned}$$

Reaction system	No.	<i>m</i> /mg	Q/mJ	$\Delta_{\rm r} H_{\rm m}^{\theta} / \text{kJ} \cdot \text{mol}^{-1}$	ln <i>k</i>
Bulk CaMoO4	1	5.109	-756.75	-29.627	-6.913
	2	5.114	-757.61	-29.632	-6.919
	3	5.089	-753.38	-29.611	-6.887
	4	5.094	-754.27	-29.617	-6.895
	5	5.099	-755.43	-29.621	-6.901
Average value				-29.622 ± 0.008	-6.903±0.013
Nano CaMoO4	1	5.167	-1273.75	-49.308	-6.659
	2	5.157	-1270.66	-49.284	-6.647
	3	5.171	-1274.91	-49.315	-6.665
	4	5.163	-1272.42	-49.295	-6.654
	5	5.156	-1270.34	-49.280	-6.641
Average value				-49.296±0.015	-6.653±0.010

Table 1. Molar enthalpies of reaction and rate constants for the bulk CaMoO₄ and nano CaMoO₄ reaction systems.

3. Experimental Section

The typical synthesis process for CaMoO₄ nanocakes is as follows: two microemulsion solutions were respectively prepared by adding at room temperature 1.76 mL of 0.64 M Na₂MoO₄ and 1.76 mL of 0.08 M CaCl₂ aqueous solution into a 13 mL TritonX-100/*n*-octanol/cyclohexane system (according to the mass ratio 3:2:8). After 10 min of stirring, the two microemulsion solutions were slowly mixed and stirred for another 20 min. The resulting mixture was aged without stirring for 48 h at room temperature. The white precipitates formed were separated by centrifugation, washed successively with acetone, deionized water and absolute ethanol, and then dried under vacuum at room temperature. Finally, the products were harvested. The products were characterized by X-ray powder diffraction (XRD, Philips PW 1710, The Netherlands, with Cu Ka radiation, $\lambda = 1.5406$ Å), field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Japan), transmission electron microscopy (TEM, JEOL JEM-200CX, 200 KV, Japan), and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010, 200 KV, Japan).

4. Methodology

When the dimension of a material reaches nanometer level, the proportion of surface activated atoms is significantly increased, so the surface thermodynamic properties can no longer be ignored. Accordingly, the thermodynamic functions of nanomaterials should consist of two parts: bulk phase and surface phase. The molar Gibbs free energy for a chemical reaction in nanosystem can be expressed as [22]:

$$\Delta_{\rm r} G_{\rm m}{}^{\rm n} = \Delta_{\rm r} G_{\rm m}{}^{\rm b} + \Delta_{\rm r} G_{\rm m}{}^{\rm s} \tag{1}$$

where superscript n denotes nanosystem, b denotes bulk phase, and s denotes surface phase.

In the same way, the standard molar enthalpy for a chemical reaction in nanosystem can be written as:

$$\Delta_{\rm r} H_{\rm m}^{\ n} = \Delta_{\rm r} H_{\rm m}^{\ b} + \Delta_{\rm r} H_{\rm m}^{\ s} \tag{2}$$

In order to clarify the specific meaning of $\Delta_r G_m^s$, the chemical reaction equations for $\Delta_r G_m^n$ and $\Delta_r G_m^b$ should be expresses first. In this work, we used CaMoO₄ (nano or bulk) and HCl as a reaction system. Thus the chemical reaction equations for $\Delta_r G_m^n$ and $\Delta_r G_m^b$ are as follows:

$$CaMoO_4 (nano) + 2HCl (aq) \rightarrow H_2MoO_4 (aq) + CaCl_2 (aq) \qquad (A) \qquad \Delta_r G_m^{\ n}$$

$$CaMoO_4 (bulk) + 2HCl (aq) \rightarrow H_2MoO_4 (aq) + CaCl_2 (aq) \qquad (B) \qquad \Delta_r G_m^{\ b}$$

According to Equation (1), $\Delta_r G_m^s$ can be expressed as:

$$\Delta_{\rm r} G_{\rm m}^{\ \rm s} = \Delta_{\rm r} G_{\rm m}^{\ \rm n} - \Delta_{\rm r} G_{\rm m}^{\ \rm b} \tag{3}$$

Thus, based on the state function characteristics, the chemical equations for $\Delta_r G_m^s$ should be written as: reaction (A) – reaction (B). Namely, the chemical equation for $\Delta_r G_m^s$ is as below:

$$CaMoO_4 (nano) \rightarrow CaMoO_4 (bulk)$$
 (C) $\Delta_r G_m^{s}$

According to the definition of surface Gibbs free energy of a material [23], the chemical equation for molar surface Gibbs free energy of nano CaMoO₄ is as follows:

$$CaMoO_4 (bulk) \rightarrow CaMoO_4 (na$$
 (D) G_m^{s}

Combining reaction (C) with reaction (D), the molar surface Gibbs free energy of nano $CaMoO_4$ can be expressed as:

$$G_{\rm m}{}^{\rm s} = -\Delta_{\rm r} G_{\rm m}{}^{\rm s} \tag{4}$$

Coupling Equation (3) with Equation (4), the molar surface Gibbs free energy of nano $CaMoO_4$ can also be written as:

$$G_{\rm m}^{\ \rm s} = \Delta_{\rm r} G_{\rm m}^{\ \rm b} - \Delta_{\rm r} G_{\rm m}^{\ \rm n} \tag{5}$$

In the same way, the molar surface enthalpy of nano CaMoO₄ can be expressed as:

$$H_{\rm m}^{\rm s} = \Delta_{\rm r} H_{\rm m}^{\rm b} - \Delta_{\rm r} H_{\rm m}^{\rm n} \tag{6}$$

Since the standard molar enthalpy for a chemical reaction can be measured directly by *in-situ* microcalorimetry (namely, $\Delta_r H_m^{b}$ and $\Delta_r H_m^{n}$ can be measured directly), the molar surface enthalpy of nano-CaMoO₄ can be calculated by employing Equation (6).

As we know, a chemical reaction occurs on the molecular or atom level and has nothing to do with the size of a material. Thus, the nano-CaMoO₄ reaction system and its corresponding bulk-CaMoO₄ reaction system possess the same transition states and final states, and the only difference is their initial states [24,25]. The Gibbs free energies for both the nano and its corresponding bulk reaction system are depicted in Figure 2.

From Figure 2, the following equations can be obtained on the basis of characteristics of state function.

$$\Delta_{\rm r} G_{\rm m}^{\ b} = \Delta_{\rm r}^{\neq} G_{\rm m}^{\ b} + \Delta_{\rm r} G_{\rm m} \tag{7}$$

$$\Delta_{\rm r} G_{\rm m}^{\ n} = \Delta_{\rm r}^{\neq} G_{\rm m}^{\ n} + \Delta_{\rm r} G_{\rm m} \tag{8}$$

Combining Equations (5), (7) and (8), the molar surface Gibbs free energy of nano CaMoO₄ can be expressed as:

$$G_{\rm m}^{\ \rm s} = \Delta_{\rm r}^{\neq} G_{\rm m}^{\ \rm b} - \Delta_{\rm r}^{\neq} G_{\rm m}^{\ \rm n} \tag{9}$$

According to the transition state theory proposed by Eyring *et al.*, the relation between rate constant and Gibbs free energy of activation can be expressed as:

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta_{\rm r}^{\neq} G_{\rm m}}{RT}\right) \tag{10}$$

where $k_{\rm B}$ represents Boltzmann constant, and h represents Planck constant.



Figure 2. Schematic diagram for the Gibbs free energies of nano-CaMoO₄ and its corresponding bulk-CaMoO₄ reaction systems.

Combining with Equations (9) and (10), the expression of $G_{\rm m}^{\rm s}$ can be transformed as:

$$G_{\rm m}^{\rm s} = RT \left(\ln k_{\rm nano} - \ln k_{\rm bulk} \right) \tag{11}$$

Since the rate constant can be acquired through regression analysis of the thermokinetic data recorded by *in-situ* microcalorimetry [26], the molar surface Gibbs free energy of nano-CaMoO₄ can be acquired by using Equation (11).

In accordance with the formula G = H - TS, the molar surface entropy S_m^s of nano-CaMoO₄ can be obtained as:

$$S_{\rm m}^{\ \rm s} = (H_{\rm m}^{\ \rm s} - G_{\rm m}^{\ \rm s}) / T \tag{12}$$

Thus, the molar surface enthalpy, molar surface Gibbs free energy, and molar surface entropy of nano CaMoO₄ can be acquired from Equations (6), (11) and (12), respectively.

5. Conclusions

In summary, large-scale uniform CaMoO₄ nanocakes were obtained by a simple and facile room temperature reverse-microemulsion method. XRD, FESEM, TEM and HRTEM were employed to demonstrate the high purity and good crystallinity of the CaMoO₄ nanocakes. The equations for calculating the surface thermodynamic functions of nano-CaMoO₄ were derived by building the relationships between the thermodynamic functions of the nano-CaMoO₄ and bulk-CaMoO₄ reaction systems. Then, coupled with *in-situ* microcalorimetry, the molar surface enthalpy, molar surface Gibbs

free energy and molar surface entropy of the prepared CaMoO₄ nanocakes were successfully acquired. Moreover, this is an effective and general route for acquiring the surface thermodynamic functions of other nanomaterials.

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Author Contributions

Gaochao Fan and Zaiyin Huang conceived the idea; Xingxing Li did the experiment and wrote the paper. All authors have read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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