CaMoO₄ 微晶生长过程的原位微量热法研究

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摘要: 在碱性条件下采用原位微量热法对 CaMoO₄ 微晶的构建进行了研究. 首次呈现了 CaMoO₄ 微晶生长过程能量变化的特征热谱曲线; 该特征热谱曲线由一个反映最初反应成核的典型吸热曲线和随后晶体生长的两个相对较弱的不连续放热曲线组成. 在导向机制的基础上, 结合 CaMoO₄ 微晶生长过程的形貌演变, 简要地讨论了 CaMoO₄ 微晶生长过程的热动力学信息. 反应成核过程、晶化过程及微晶的二次生长过程的速率常数分别为 1.54×10^{-4} 、 1.09×10^{-4} 和 $0.71 \times 10^{-4} \text{ s}^{-1}$. 由于晶体的聚集和扩散二者之间强烈的相互作用, 使得反应速率下降, 从而呈现出一个相对较平坦的第二次放热曲线.

关键词: 微量热法; 热动力学; CaMoO₄; 微晶; 特征热谱曲线; 导向机制

中图分类号: O642; O643

In situ Microcalorimetry Insight into the Growth of CaMoO₄ Microcrystallites

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Abstract: *In situ* calorimetric studies of CaMoO₄ microcrystallite fabrication were performed in an alkaline aqueous solution. We first presented an oscillatory microcalorimetric heat flow curve pattern which traced the energy evolution of the CaMoO₄ microcrystallite growth process. A characteristic endothermic peak for the initial reaction and double relatively weak and discontinuous exothermic peaks for the subsequent crystal growth were observed. We briefly discussed the morphology evolution and the thermokinetics information of the growth process of CaMoO₄ microcrystallites on the basis of the oriented attachment mechanism. The rate constants of the reaction and nucleation, crystal crystallization, and microcrystalline secondary growth were found to be 1.54×10^{-4} , 1.09×10^{-4} , and $0.71 \times 10^{-4} \text{ s}^{-1}$, respectively. As the crystals aggregated and repelled each other, the reaction slowed leading to a relatively flatter second exothermic curve.

Key Words: Microcalorimetry; Thermokinetics; CaMoO₄; Microcrystallite; Characteristic heat flow curve; Oriented attachment mechanism

Microscale inorganic materials, such as molybdate and tungstate with well-defined superstructures, have received much attention over the last two decades because of their interesting luminescence and structural properties^[1–3]. How to controllably synthesize the microstructure has been a major challenge, several strategies have been pursued recently^[4–7]. For example, three dime-

nsional (3D) flowerlike MnWO₄ micro/nanocomposite structure has been synthesized in reverse micelles under solvothermal conditions, although the real growth mechanism has been elusive^[8].

In recent years, great efforts have been made to give an insight into the aggregation pathways of crystals^[9–12]. For example, Yang

Received: August 10, 2009; Revised: October 4, 2009; Published on Web: November 3, 2009.

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The project was supported by the National Natural Science Foundation of China (20963001), Natural Science Foundation of Guangxi Province, China (0575030, 0832078), and Innovation Project of Guangxi Graduate Education, China (2009106080817M364).

国家自然科学基金(20963001), 广西自然科学基金(0575030, 0832078)和广西研究生教育创新计划(2009106080817M364)资助项目

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and co-workers^[13] demonstrated the validity of vapor-liquid-solid (VLS) growth mechanism at nanometer scale with a real-time observation of semiconductor nanowire growth in an *in situ* high-temperature transmission electron microscope (TEM). For all that, this method is lack of universality and no energetics involved. The microstructures growth process is mainly interrelated with its thermodynamic and kinetic characters. In theory, we could rationally control the crystal size, structure, and growth directions, if we clearly understand the thermokinetics information of its growth process.

Calorimetry is the most effective measurement of heat effects associated with the crystal growth process^[14,15]. The major advantage of this method is that the system is not disturbed during the measurement and the thermokinetic study gives continuous and accurate recordings of the system's evolution. Navrotsky's group^[16–22] investigated the energy evolution of zeolite and silica synthesis system during the course of crystal growth with the *in situ* calorimetric and delineated the relationship between thermodynamic factors and changes in the solution chemistry and interface properties. The thermodynamics and kinetics information of the CaMoO_4 microcrystallite growth process have not been exploited, although it has been successfully synthesized in several systems.

In the present study, we use an *in situ* microcalorimetric combining with the field-emission scanning electron microscope (FE-SEM) to investigate the energy and morphology evolution of the pure CaMoO_4 microcrystallite growth from an initially clear solution firstly. The CaMoO_4 microcrystallite growth process is discussed on the basis of a crystal growth mechanism of oriented attachment which was proposed by Banfield *et al.*^[23]. The reactants and preparation procedure are the same as those earlier experiments in the literature [6]. This permits us to correlate our new results with the previous studies. Our aims are to investigate the energy evolution of the synthesis system during the course of crystal growth and to delineate the relationship between thermodynamic factors for providing direct experimental evidence of the fundamental forces governing the crystal growth events.

1 Experimental

Calcium chloride (CaCl_2) powder, molybdic acid (H_2MoO_4) powder, and sodium hydroxide (NaOH) were purchased from Tianjin Bodi Chemical Factory Co., Ltd.. These reagents are of analytical grade (AR) and used without further purification. Colorless Na_2MoO_4 and CaCl_2 aqueous solution (pH=12) were prepared according to reference [6]. Potassium chloride (KCl, spectral purity, mass fraction 0.9999) was purchased from Shanghai No.1 Regent Factory, and dried in a vacuum oven at $T=500$ K for 8 h prior to use.

The energy evolution of the synthesis system was measured by an RD496-CK2000 type microcalorimeter. The detailed description about the structure and the technical parameters of this calorimeter has been given elsewhere^[24]. The microcalorimeter was calibrated by Joule effect before experiment, and the sensi-

tivities of the calorimeter were determined to be (64.54 ± 0.02) , (64.56 ± 0.03) , (64.60 ± 0.01) , (64.68 ± 0.02) , and (64.84 ± 0.01) $\mu\text{V} \cdot \text{mW}^{-1}$ at 297.15, 298.15, 301.15, 303.15, and 308.15 K, respectively. The Joule cell, which has 1000 Ω electrical resistance, was given 100 mW electric power for 100 s at $T=298.15$ K. The enthalpy of dissolution of KCl (spectral purity) in deionized water was measured to be (17.237 ± 0.046) $\text{kJ} \cdot \text{mol}^{-1}$, which was in good agreement with the previous value of (17.241 ± 0.018) $\text{kJ} \cdot \text{mol}^{-1}$ ^[25]. The accuracy was 0.02% and the precision was 0.3%, which indicated that the calorimetric system was accurate and reliable. The synthesis reagents of CaCl_2 aqueous solution and Na_2MoO_4 aqueous solution were put into the stainless steel sample cell with the container of 15 mL^[26], separately. The Na_2MoO_4 aqueous solution was placed into the small glass tube and set above the CaCl_2 aqueous solution. After equilibrium, the bottoms of the sample and reference were pushed down simultaneously. As a result, the two liquids were mixed and the thermogram was recorded.

The synthesis of CaMoO_4 crystals was simply achieved by the precipitation reaction between calcium cations and molybdate anions which solubilized in the alkaline aqueous solution, obtained the white precipitates. The samples at various selected time were thoroughly washed with deionized water and ethanol to remove the impurities. The as-prepared products were observed by X-ray diffraction (XRD, the Philips X'Pert Pro MPD with Cu K_α radiation, $\lambda=0.15406$ nm, Holland) and FE-SEM (JEOL JSM-6700F, Japan).

2 Results and discussion

The heat flow curve (ϕ) associated with the *in situ* CaMoO_4 microcrystallite growth process at 298.15 K is presented in Fig.1. After the thermal disturbance caused by loading the stainless steel vessels, a flat segment ($t=0-1$ h) indicates negligible thermal events occurring. Therefore, the heat flow curve during this period is taken as the initial baseline for the following thermal peaks.

It clearly shows that there are one strong endothermic peak and two relatively weak and discontinuous exothermic peaks on

Fig.1 *In situ* heat flow curve of CaMoO_4 microcrystallite growth process at 298.15 K

Φ : the true heat flow curve, ϕ : the recorded heat flow curve

simultaneously. As a result, the two liquids were mixed

Fig.2 XRD pattern of the as-prepared products

and the reaction was initiated. Presented on the heat flow curve is that the energy decreases sharply, the onset of an endothermic peak is discerned. After about 2 min ($t_2=1.05$ h), an endothermic maximum is reached. Thereafter, the endothermic event rapidly changes into a correspondingly more pronounced exothermic event. At $t_3=1.25$ h, the heat flow curve crosses the baseline (taken as the extension of the initial baseline) from endothermic to exothermic. At $t_4=1.45$ h, an exothermic peak is seen. At $t_5=2.08$ h, the microcalorimetric curve flattens and remains flat for about 6 h. At $t_6=7.5$ h, the start of an exothermic peak is observed. For about 0.7 h ($t_7=8.2$ h), the second exothermic peak is reached. At $t_8 \approx 12$ h, the microcalorimetric curve flattens and remains flat for at least 4 more days. Thereafter, the formation event is complete at 12 h and the following flat curve is the final baseline for the preceding thermal peaks. This baseline is slightly shifted to the exothermic direction from the level of the initial baseline. We infer that the small baseline shift reflects that the energy of microcrystallites is higher than that of the bulk materials.

XRD pattern of the as-synthesized products, which can be perfectly indexed to the pure tetragonal phase of CaMoO_4 , with calculated lattice constants $a=0.519$ nm, $c=1.125$ nm (JCPDS Card No.29-0351), is shown in Fig.2. The sequence of FE-SEM

CaCl_2 sample and distilled water reference were pushed the images shown in Fig.3 clearly reveal the crystallite structures of CaMoO_4 obtained from the alkaline aqueous solution ($\text{pH}=12$) for selected time at room temperature. It directly mirrors the morphology evolution process of CaMoO_4 microcrystallites.

At the end of the initial baseline, the initial clear solutions are mixed together. At the same time, large numbers of Ca^{2+} and MoO_4^{2-} ions result in the direct precipitation reaction for CaMoO_4 molecules. The *in situ* heat flow curve is remarkable endothermic. Near the end of the endothermic curve, the compounds start to nucleate. And then, the heat flow curve turns into exothermic. The mixture is still a clear solution at this moment. The reaction and nucleation period is characterized by distinct endothermic. It suggests that there are large numbers of CaMoO_4 nanoparticles formed (Fig.3a). Along with the nucleation, the nanoparticles start to aggregate and the crystals begin to grow. It is significant exothermic. It shows that the crystal growth results in significant reduction of the overall interface between the solid particles and mother liquid. Fig.3b shows that low-magnification FE-SEM image of the CaMoO_4 samples during the end of this stage, which consists of uniform and symmetrical ellipsoidal rods and crossed-ellipsoids with smooth surfaces. Fig.3c is the high-magnification FE-SEM image of crossed-ellipsoids. Subsequently, the *in situ* heat flow curve flattens and keeping flat for about 6 h. The heat effects during this stage are unobvious, because thermodynamic control gradually prevails over kinetic control. This stage is a homeostasis process, the crystals coarsening with some rearrangement of geometry but little change in the number of chemical bonds (Fig.3d). Whereafter, it is a secondary growth process and an oriented self-assemble course. The coarsened products start to oriented self-assemble at each end along the axis, leading to flower- and dumbbell-shaped aggregates (Fig.3(e, f)). The crystals aggregation and dispersion repel each other strongly, so the reaction slows. Which presents on the heat flow curve is that the second exothermic curve is flatter than the first one. At last, well-defined spherules with uniform diameters of 3–4 μm are fabricated (Fig.3g). The *in situ* heat flow curve in the stage shows an exothermic peak.

The time constant (τ) of the microcalorimeter response to thermal perturbation is around 14.016 (0.0242 min), and this is very small relative to the time span of the heat flow peaks (about 12 h).

Fig.3 FE-SEM images of CaMoO_4 products obtained at 298.15 K for different reaction time (t)

condition: $[\text{Ca}^{2+}]=[\text{MoO}_4^{2-}]=0.05 \text{ mol} \cdot \text{L}^{-1}$; t/h : (a) 0.05, (b, c) 0.5, (d) 3, (e, f) 8, (g) 48

Table 1 Thermokinetical data of CaMoO₄ microcrystallites growth process

<i>t</i> /s	Reaction and nucleation process		<i>t</i> /min	Crystallization process		<i>t</i> /min	Secondary growth process	
	<i>H</i> ₁ /mJ	(d <i>H</i> /d <i>t</i>) ₁ /(mJ·s ⁻¹)		<i>H</i> ₂ /mJ	(d <i>H</i> /d <i>t</i>) ₂ /(mJ·s ⁻¹)		<i>H</i> ₃ /mJ	(d <i>H</i> /d <i>t</i>) ₃ /(mJ·s ⁻¹)
3751	1.7525	-0.0580	105	15.1590	0.0141	510	226.9930	0.0150
3753	0.7938	-0.0615	106	15.9477	0.0140	515	231.3071	0.0145
3755	-0.0558	-0.0646	107	16.6063	0.0134	520	235.4484	0.0142
3757	-0.8405	-0.0674	108	17.4613	0.0137	525	239.2742	0.0135
3759	-1.6568	-0.0703	109	18.0151	0.0128	530	243.1017	0.0132
3761	-2.3928	-0.0728	110	18.6362	0.0124	535	246.6867	0.0125
3763	-3.1075	-0.0753	111	19.2955	0.0121	540	250.2445	0.0122
3765	-3.8457	-0.0778	112	19.9255	0.0118	545	253.7348	0.0122
3767	-4.5139	-0.0799	113	20.4373	0.0111	550	256.8258	0.0110
3769	-5.1526	-0.0820	114	21.1406	0.0113	555	260.0262	0.0108
3771	-5.8253	-0.0842	115	21.6114	0.0106	560	263.0552	0.0105
3773	-6.4386	-0.0861	116	22.1633	0.0103	565	265.9884	0.0099
3775	-6.9957	-0.0877	117	22.5375	0.0094	570	269.1440	0.0105
3777	-7.5561	-0.0894	118	23.1443	0.0095	575	272.1055	0.0101
3779	-8.0562	-0.0907	119	23.6640	0.0093	580	275.0912	0.0105

Therefore, the true heat flow curve (Φ) can be accurately recovered from the recorded heat flow curve (ϕ) using the following equation.

$$\Phi(t) = \phi(t) + \tau \frac{d\phi(t)}{dt} \quad (1)$$

Details about how to derive this equation, to determine its applicability, and to correctly measure τ have been reported elsewhere^[27]. The recovered Φ is presented in Fig.1. In order to distinguish the curve, every $\Phi(t)$ was added 0.02 mW.

The energy change of the reaction system depends on the reaction progression. The reaction was triggered when the reagent solutions were mixed. Based on the oriented attachment, the time span from 1.02 to 1.05 h is a reaction and nucleation stage, from 1.05 to 2.08 h is the microcrystallite growth stage, and from 7.5 to 12 h is the secondary growth phase of microcrystallites. (d*H*/d*t*)₁ is the rate of total heat production of reaction and nucleation process at time *t*, (d*H*/d*t*)₂ is the rate of the heat of crystallization of microcrystallites at time *t*, and (d*H*/d*t*)₃ is the rate of the heat of microcrystalline secondary growth at time *t*; and *H*₁ (the enthalpy during a certain time), *H*₂ (the enthalpy of crystallization during a certain time), and *H*₃ (the enthalpy of microcrystalline secondary growth during a certain time) are shown in Table 1.

$$\ln\left(\frac{1}{H_0} \frac{dH_1}{dt}\right) = \ln k + n \ln\left(1 - \frac{H_1}{H_0}\right) \quad (2)$$

where, *n* is reaction order. According to the thermodynamic equation (2)^[28], making use of the data $\ln\left(\frac{1}{H_0} \frac{dH_1}{dt}\right)$ and $\ln\left(1 - \frac{H_1}{H_0}\right)$ to fit a linear equation (*H*₀ is the total enthalpy of CaMoO₄ microcrystallite growth process), one can obtain the rate constant (*k*).

The reaction and nucleation rate constant $k_1 = 1.54 \times 10^{-4} \text{ s}^{-1}$, *R* = 0.993. The crystal crystallization rate constant $k_2 = 1.09 \times 10^{-4} \text{ s}^{-1}$, *R* = 0.988. And the microcrystalline secondary growth rate constant $k_3 = 0.71 \times 10^{-4} \text{ s}^{-1}$, *R* = 0.982.

3 Conclusions

In summary, the *in situ* microcalorimetry is powerful in

tracking the physicochemical events of microcrystallite growth process. Our *in situ* microcalorimetry studying provides a direct evidence for an oscillatory thermokinetics evolution pattern of CaMoO₄ microcrystallite growth process. On the basis of oriented attachment, the process in the foremost period is associated with a strong energetic driving force. It is controlled by chemical reactions. The rest process which is for forming the unique morphology is mainly a kinetically controlled process. Though the details need further researches, in principle, if we could control the thermokinetics evolution, it is to be able to rationally control the crystal size, crystal structures, and growth directions of microstructure inorganic composite materials.

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