Microcalorimetry insight into size effect on standard molar reaction enthalpy of $CdMoO_4$ nanosystem

Yanfen Li[1], Rongli Jiang[1], Zaiyin Huang[2], Hui Lv[1], Lu Zhou[1], Tingyu Liu[1], Xiaoyu Zhang[1]

[1]*School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, People's Republic of China*
[2]*School of Chemistry and Chemical Engineering, Guangxi University for Nationalities, Nanning 530008, People's Republic of China*
E-mail: ronglijcumt@163.com

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Uniform $CdMoO_4$ nanooctahedra with tunable sizes have been synthesised via a facile and mild microemulsion method at room temperature. The reaction between $CdMoO_4$ nanooctahedra and dilute hydrochloric acid was in situ monitored using microcalorimetry at 298.15 K, and microcalorimetric heat flow curves from this reaction process were obtained. Combined with an inductively coupled plasma optical emission spectrometer technique, the size effect of $CdMoO_4$ nanooctahedra on standard molar reaction enthalpy ($\Delta_r H_m^\Theta$) was studied. The results indicate that the value of $\Delta_r H_m^\Theta$ decreased with decreased particle size.

1. Introduction: As important materials, metal molybdates have received great research interest over the past few decades for their potential applications in various fields, such as photoluminescence, optical fibres, catalysis, humidity sensors, scintillators, magnetic properties and so forth [1–4]. To date, numerous properties of metal molybdates nanostructures have been reported [5–12], but very few researches have paid attention to the thermodynamic property, especially reports on the thermodynamic properties of the chemical reaction of molybdate nanomaterial are rarer.

The thermodynamic property is an intrinsic property of nanomaterials. It is well known that the properties of nanomaterials greatly depend on their particle size and morphology [13, 14], thus the thermodynamic properties will be also varied with the change of size and morphology. Early in 1982, Patrilyak [15] concluded that Thompson-Kelvin's law is not applicable to nanoparticles. In 2000, Sanfeld *et al*. [16] obtained the relationship between the equilibrium constant and the conventional equilibrium constant of reactions taking place in spherical microobjects, indicating that there is an influence of the size of objects (droplets, bubbles and solid particles) on equilibrium in living systems. In 2002, Kim *et al*. [17] measured the oxidation enthalpies of both molybdenum (Mo) and tungsten (W) nanoclusters at several cluster sizes, the results show that the oxidation enthalpies went down to corresponding bulk values with increasing cluster size. In 2012, Xue and co-workers [18] found that with the sizes of reactant decreasing, the molar Gibbs free energy $\left(\Delta_r G_m^\Theta\right)$, the molar enthalpy $\left(\Delta_r H_m^\Theta\right)$ and the molar entropy $\left(\Delta_r S_m^\Theta\right)$ decrease, but the equilibrium constant (K) increases. Consequently, there are marked effects of the size and morphology of nanomaterials on thermodynamic properties. However, to the best of our knowledge, the above researches mostly adopted theoretical analysis or quantum chemistry methods. How to innovate the methods to accurately acquire nanothermodynamic functions, explore the effect of the size and morphology of nanoparticles on thermodynamic properties is still a great challenge.

Microcalorimetry is a universal technique widely used for measuring the enthalpies of reaction, dissolution, dilution and excess enthalpies in thermochemistry, which involves physical change, chemical reaction and living biochemical metabolism in the field of industrial and scientific research. It permits one to make an in situ measurement of energy evolution without disrupting the system. Meanwhile, the results give qualitative and quantitative indicators to inform us about the variation of the system. Our group has in situ fabricated a series of metal molybdates [19, 20] and CdS [21] nanomaterials using microcalorimetry. Combined with complementary characterisation techniques, the thermokinetic and growth mechanism of the growth process were studied. Furthermore, standard thermodynamic functions of ZnO nanomaterials with different morphologies were also successfully gained by in situ microcalorimetry [22–24].

Here, uniform $CdMoO_4$ nanooctahedra with three different sizes were achieved by the reverse microemulsion route at room temperature. Microcalorimetry was used to track the energy evolution of the reaction between the as-made $CdMoO_4$ nanooctahedra with different sizes and dilute hydrochloric acid. An inductively coupled plasma (ICP) technique was employed to test the content of Cd^{2+} after the reaction was completed. By combining these two techniques, the size effect of $CdMoO_4$ nanooctahedra on standard molar reaction enthalpy $\left(\Delta_r H_m^\Theta\right)$ was investigated.

2. Experimental

2.1. Materials: Analytical grade $Na_2MoO_4 \cdot 2H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, *n*-octanol, TritonX-100 (OP), cyclohexane and hydrochloric acid were purchased from the Xilong Chemical Reagent Factory and used without further purification. Deionised water was used to prepare all the aqueous solutions.

2.2. Synthesis and characterisation of $CdMoO_4$ nanooctahedra: A typical process is as follows: two 13.20 ml microemulsion solutions were prepared by adding 1.20 ml of 0.10 M $Cd(NO_3)_2$ and 1.20 ml of 0.10 M Na_2MoO_4 aqueous solutions into an OP/*n*-octanol/cyclohexane system (molar ratio of water to OP [or the water content (ω)] = 20), respectively. After 30 min of stirring, the above two different microemulsion solutions with equivalent volume were mixed slowly and stirred for 10 min. The resulting mixture was aged without stirring for 48 h at room temperature. The precipitate was separated by centrifugation, and washed with deionised water and absolute ethanol several times. The final product was dried in a vacuum at room temperature. The nano$CdMoO_4$ structures with ω = 10 and 5 were prepared by the same method.

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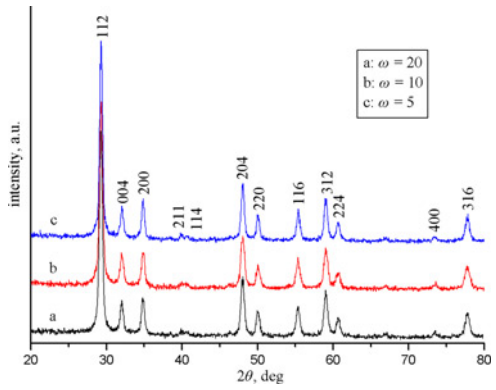

Figure 1 *XRD patterns of the as-formed $CdMoO_4$ nanocrystalline*
Curve *a:* $\omega = 20$
Curve *b:* $\omega = 10$
Curve *c:* $\omega = 5$

The products were characterised by X-ray diffraction (XRD, Philips PW1710 with Cu Kα radiation, $\lambda = 1.5406$ Å), and field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F).

2.3. Calorimetric measurements: Reaction calorimetry was carried out on a microcalorimeter (RD496-CK 2000, MianYang CP Thermal Analysis Instrument Co. Ltd). The microcalorimeter was calibrated first using the Joule effect and its calorimetric constant was $(63.205 \pm 0.031)\ \mu V \cdot mW^{-1}$ at 298.15 K. The dissolution enthalpy of KCl (spectral purity grade) in deionised water was $(17.237 \pm 0.046)\ kJ \cdot mol^{-1}$, which was in good agreement with an earlier measurement of (17.241 ± 0.018) $kJ \cdot mol^{-1}$ [25].

2.4. Calculation of standard molar reaction enthalpy $\left(\Delta_r H_m^{\Theta}\right)$: An inductively coupled plasma optical emission spectrometer (ICP-OES, America Perkin Elmer Co. Ltd) was used to examine the concentration of the cation ion after microcalorimeter reaction was completed. Combining the microcalorimetric results with ICP data, standard molar reaction enthalpy $\left(\Delta_r H_m^{\Theta}\right)$ was investigated.

3. Results and discussion

3.1. Morphology and structure: Fig. 1 shows the representative XRD patterns of the products prepared via reverse-microemulsion at room temperature. From the XRD patterns, we can note strong and sharp diffraction peaks which exhibit well-crystallised samples. All the diffraction peaks can be well indexed to be a tetragonal phase of pure $CdMoO_4$ (JCPDS Card No. 07-0209).

Fig. 2*a* is the FESEM image of $CdMoO_4$ samples for $\omega = 20$, which is composed of high yield homogeneous nanoparticles. These nanostructures can be clearly identified to be an octahedral morphology. The size distribution presents well-developed $CdMoO_4$ octahedra with an edge length of 25 nm (Fig. 2*d*). Decreasing the water content (ω) to ten results in monodisperse $CdMoO_4$ nanooctahedra (Fig. 2*b*) with edge lengths of 30 nm (Fig. 2*e*). When the ω value was further decreased to 5, nanooctahedra (see Fig. 2*c*) with a side length of 200 nm were obtained (Fig. 2*f*). These results indicate that the octahedron size decreases by increasing the ω value when the reaction takes place in reverse microemulsion.

3.2. Theoretical analysis of standard molar reaction enthalpy $\left(\Delta_r H_m^{\Theta}\right)$: In essence, a chemical reaction is a process with old chemical bonds breaking and new chemical bonds forming. The final state of a reaction has nothing to do with the shape and size of the reactants. From the aspect of chemical reaction, nanoCdMoO$_4$ and bulk $CdMoO_4$ can be considered as different substances with the same chemical composition. Therefore the same final state will be achieved if an equivalent amount of nanoCdMoO$_4$ with different particle sizes react with the same substance in identical conditions.

At 298.15 K, the reaction between nanoCdMoO$_4$ octahedra and dilute hydrochloric acid as well as the calculation of standard molar reaction enthalpy $\left(\Delta_r H_m^{\Theta}\right)$ are given below

$$CdMoO_{4(nano)}(s) + 2HCl(l) = CdCl_2(l) + H_2MoO_4(l) \quad (1)$$

$$\Delta_r H_m^{\Theta} = \Delta_f H_m^{\Theta}(CdCl_2,\ l) + \Delta_f H_m^{\Theta}(H_2MoO_4,\ l) - 2\Delta_f H_m^{\Theta}(HCl,\ l) - \Delta_f H_m^{\Theta}\left(CdMoO_{4(nano)},\ s\right) \quad (2)$$

where $\left(\Delta_r H_m^{\Theta}\right)$ is the standard molar enthalpy of reaction; $\left(\Delta_f H_m^{\Theta}\right)(CdCl_2,\ l)$, $\left(\Delta_f H_m^{\Theta}\right)(H_2MoO_4,\ l)$, $\left(\Delta_f H_m^{\Theta}\right)(HCl,\ l)$

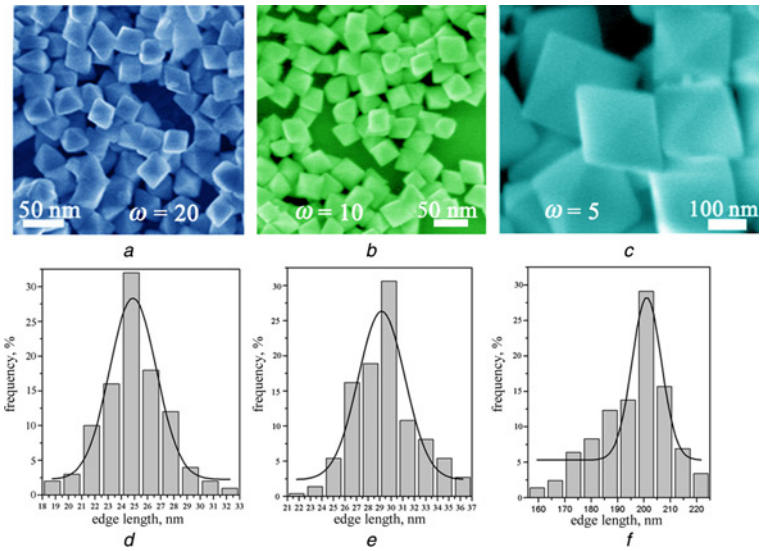

Figure 2 *FE-SEM images and size distributions of the $CdMoO_4$ nanocrystalline prepared at different water content (ω)*
a and *d* $\omega = 20$
b and *e* $\omega = 10$
c and *f* $\omega = 5$

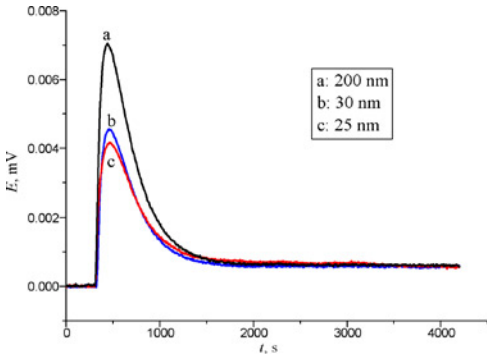

Figure 3 *Microcalorimetric heat flow curves of the reaction between dilute hydrochloric acid and $CdMoO_4$ nanooctahedra with different sizes at 298.15 K*
Curve *a:* 200 nm
Curve *b:* 30 nm
Curve *c:* 25 nm

Table 1 Calculation of standard molar reaction enthalpies of the $CdMoO_4$ nanoreaction systems

Reaction system	$\Delta_r H_m^\Theta/10^7$ kJ · mol^{-1}					
	1	2	3	4	5	Average value
$\omega = 5$ (200 nm)	46.03	46.82	45.96	46.45	45.79	46.21 ± 0.42
$\omega = 10$ (30 nm)	9.90	9.49	9.84	9.98	9.78	9.80 ± 0.19
$\omega = 20$ (25 nm)	9.29	8.75	9.06	8.97	9.23	9.06 ± 0.22

and $\left(\Delta_f H_m^\Theta\right)\left(CdMoO_{4(nano)}, s\right)$ are the standard molar enthalpies of formation, corresponding to $CdCl_2$, H_2MoO_4, HCl and $CdMoO_{4(nano)}$, respectively. According to the literature [26], standard molar enthalpies of the formation of $CdCl_2$, H_2MoO_4 and HCl at 298.15 K are −391.50, −1046.0 and −167.16 kJ · mol^{-1}, respectively.

In addition, so far as we know, standard molar enthalpies of the formation of nanoscale materials will increase with decrease of size [24, 27], that is the value of $\left(\Delta_f H_m^\Theta\right)\left(CdMoO_{4(nano)}, s\right)$ will increase with decrease of size. Thereafter, standard molar enthalpies of reaction $\left(\Delta_r H_m^\Theta\right)$ between nano$CdMoO_4$ octahedra and dilute hydrochloric acid will decrease with decrease of size.

3.3. Experimental calculation of standard molar reaction enthalpy $\left(\Delta_r H_m^\Theta\right)$: To measure the standard molar reaction enthalpies of nano$CdMoO_4$ octahedra reaction systems, some amount of $CdMoO_4$ nanooctahedra with three different sizes reacted with 1.50 ml 0.26 mol·l^{-1} dilute hydrochloric acid in a microcalorimeter, the microcalorimetric heat flow curves are presented in Fig. 3. After reaction was completed, the concentration of Cd^{2+} in each reaction system was determined by ICP. Thereupon, the standard molar enthalpy of reaction of each system could be obtained. The calorimetric experiment of each system was tested five times, and standard molar reaction enthalpies and their average values are displayed in Table 1.

It is notable that standard molar enthalpies of reaction of the $CdMoO_4$ nanosystem are different with diverse sizes, and they are decreased with decrease of size. It agrees very well with our theoretical analysis and the previous report [18].

4. Conclusion: In summary, well-shaped $CdMoO_4$ nanooctahedra have been prepared via a reverse microemulsion route at room temperature. Standard molar enthalpies of the reaction of $CdMoO_4$ nanostructures with $\omega = 5$, 10 and 20 were successfully gained. The results depict that standard molar reaction enthalpies of $CdMoO_4$ nanoreaction systems were different with alteration of sizes, and were decreased with decrease of size. This novel and facile approach to determine the standard molar enthalpies of reaction of other nanosystems can be extensively applied.

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6 References

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