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Article

Surfactant-assisted hydrothermally synthesized MoS₂ samples with controllable morphologies and structures for anthracene hydrogenation

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ARTICLE INFO

Article history:

Received 30 November 2016

Accepted 30 December 2016

Published 5 March 2017

Keywords:

Molybdenum sulfide

Surfactant-assisted

Controllable morphology

Mono-dispersed

Active edges

Anthracene hydrogenation

ABSTRACT

MoS₂ samples with controllable morphologies and structures were synthesized using surfactant-assisted hydrothermal processes. The effects of surfactants (PEG, PVP, P123, SDS, AOT, and CTAB) on the morphologies and structures of MoS₂ samples were investigated. The results revealed that spherical, bulk-like, and flower-like MoS₂ particles assembled by NH₄⁺-intercalated MoS₂ nano-sheets were synthesized. The morphologies of the MoS₂ samples and their structures (including the slab length and the number of stacked layers) of MoS₂ nano-sheets in these samples could be controlled by adjusting the surfactants. Mono-dispersed spherical MoS₂ particles could be synthesized with PEG via the creation of MoS₂ nano-sheets with slab lengths shorter than 15 nm and fewer than six stacked layers. Possible formation mechanisms of these MoS₂ samples created via surfactant-assisted hydrothermal processes are proposed. Further, the catalytic activities of MoS₂ samples for anthracene hydrogenation were evaluated in a slurry-bed reactor. The catalyst synthesized with the surfactant PEG exhibited the highest catalytic hydrogenation activity. Compared with the other catalysts, it had a smaller particle size, mono-dispersed spherical morphology, shorter slab length, and fewer stacked layers; these were all beneficial to exposing its active edges. This work provides an efficient approach to synthesize transition metal sulfides with controllable morphologies and structures.

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1. Introduction

Molybdenum sulfide (MoS₂), a typical lamellar transition metal sulfide, has been widely used in catalysis, electrochemistry, lubrication, and intercalation chemistry [1–4]. MoS₂ has a S-Mo-S layered structure, where a Mo atom is sandwiched be-

tween two trigonal atomic layers of S atoms [5]. The Mo and S atoms are linked by strong covalent bonds, while the S-Mo-S layers interact with each other via van der Waals forces [2,6]. In MoS₂ crystals, there are two types of exposed surfaces: the (001) planes along the S-Mo-S edges (*c* axis), which are referred to as the basal planes, and the (100) planes along the edges of

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This work was supported by the National Natural Science Foundation of China (21303186) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA07020300).

DOI: 10.1016/S1872-2067(17)62779-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 3, March 2017

S-Mo, which are referred to as edges. Density functional theory calculations and atom-resolved scanning tunneling microscopy (STM) have revealed that the edges of MoS₂ nano-sheets are active sites for the hydro-treating processes of crude petroleum products and for electrochemical hydrogen evolution reaction (HER) [3,7,8]. It has been reported that the number of active sites is closely related to the morphological and structural characteristics of the MoS₂ catalysts [1,9,10].

Recently, various approaches have been used to prepare MoS₂ nano-sheets with controllable morphologies and structures. Guo et al. [11] synthesized graphene-like MoS₂ nano-sheets with tunable stacking layers via the thermal decomposition of a single source (Mo(Et₂NCS₂)₄) under an Ar atmosphere. Gao et al. [12] synthesized interlayer-expanded MoS₂ nano-sheets with edge-terminated structures using a microwave-assisted strategy and investigated their catalytic activities for HER. The results revealed that the excellent HER performances of these MoS₂ nano-sheets could be ascribed to the exposure of the active edges, which was promoted by having edge-terminated structures and an expanded interlayer distance. Varrla et al. [13] synthesized MoS₂ nano-sheets with different slab lengths and different numbers of stacked layers using shear exfoliation. They found that the slab length and the number of stacked layers of the MoS₂ nano-sheets could be changed by adjusting the surfactant solutions, and that MoS₂ nano-sheets with short slab lengths and reduced numbers of stacked layers promoted the exposure of the active edges. Uz-canga et al. [14] synthesized hollow spherical MoS₂ aggregates assembled from MoS₂ nano-sheets using an aqueous sono-chemical route. They found that the high catalytic activities of hollow spherical MoS₂ catalysts for thiophene hydrodesulfurization could be ascribed to the material having a high content of exposed active edge sites and that the spherical skeletons facilitate the exposure of the active edges of the MoS₂ nano-sheets. Wang et al. [10] synthesized three-dimensional (3D) hierarchical MoS₂ nano-spheres and large aggregated MoS₂ nano-particles via a hydrothermal method using surfactants as soft templates. Surfactant-assisted hydrothermal preparation has been widely used to control the morphology and structure of metal oxides and sulfides such as SnS and CeO₂ [15–18]. However, there are still very few studies on surfactant-assisted hydrothermal preparation of MoS₂ samples with controllable morphologies and structures.

As crude oil becomes heavier and more inferior, the conversion of heavy oils into liquid fuels has increased greatly in significance. Hydrogenation of heavy oils can increase their H/C ratio and decrease their viscosity, which aids the realization of clean and efficient upgrading of heavy oils. Slurry bed technology is an advanced technique for hydrotreating heavy oils into liquid fuels. However, the challenge for heavy oil hydrogenation lies in developing MoS₂ catalysts with high catalytic activities. Therefore, to develop high activity catalysts, it is essential to synthesize MoS₂ catalysts with controllable morphologies and structures.

In this work, surfactant-assisted hydrothermal processes were applied to synthesize MoS₂ samples with controllable morphologies and structures. Here, we employed six surfac-

tants, namely polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), polyoxyethylene-polypropylene oxygen-polyoxyethylene (P123), sodium dodecyl sulfonate (SDS), sodium di-2-ethylhexylsulfosuccinate (AOT), and cetyl trimethyl ammonium bromide (CTAB). The effects of these surfactants on the morphologies and structures of MoS₂ samples were systematically investigated, and the growth mechanisms of the MoS₂ samples with their various morphologies and structures are proposed in this paper. Further, the catalytic activities of these samples were investigated in a slurry-bed reactor via the hydrogenation of anthracene. Anthracene (AN) was used as a model compound for polyaromatic hydrocarbons in heavy oil fractions such as bitumen, which are the most difficult constituents in heavy oils to hydrogenate. Of these samples, one was a mono-dispersed spherical MoS₂ sample synthesized with the PEG surfactant; the sample was assembled from MoS₂ nano-sheets with short slabs and which contained only a few stacked layers; it exhibited the highest catalytic activity for anthracene hydrogenation of all the samples tested here.

2. Experimental

2.1. Synthesis of MoS₂ samples

A certain amount of surfactant (PEG, PVP, P123, SDS, AOT, or CTAB) was dissolved into 60 mL of distilled water under constant stirring at room temperature for 0.5 h. 1.4 mmol ammonium molybdate and 22.9 mmol thioacetamide were dissolved into the above mentioned solution under stirring to form a homogenous solution. Then, 2 mL hydrazine hydrate was added into the resulting solution. After stirring for 0.5 h, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 200 °C for 24 h. The precipitate was centrifuged and washed with water and then ethanol three times, and then dried at 60 °C for 12 h in a vacuum drying oven. The samples prepared with PEG, P123, SDS, PVP, AOT, and CTAB are referred to as MoS₂-PEG, MoS₂-P123, MoS₂-SDS, MoS₂-PVP, MoS₂-AOT, and MoS₂-CTAB, respectively. MoS₂-PEG was annealed at 400 °C for 4 h in H₂ and is referred to as MoS₂-PEG-C.

2.2. Characterization of the MoS₂ samples

X-ray diffraction (XRD) measurements were performed on a PANalytical X'Pert Pro diffractometer with Cu radiation ($\lambda = 0.15418$ nm). Fourier transform infrared spectroscopy (FTIR) measurements were conducted using a Nicolet iS50 instrument. The thermogravimetry-differential scanning calorimetry (TG-DSC) measurements were performed with a Netzsch STA449F3 TG-DSC analyzer under a protective nitrogen atmosphere. The Brunauer-Emmett-Teller (BET) surface area was measured using a Micromeritics ASAP 2040 apparatus via N₂ physisorption at -196 °C. Static contact angle measurements of the MoS₂ samples under ambient conditions using deionized water were performed with a DSA100 optical contact angle measuring device. Scanning electron microscopy (SEM) images were taken on a Quanta 200 FEG at a voltage of 20 kV. Trans-

mission electron microscopy (TEM) measurements were carried out with a JEM 2100 EX field emission electron microscope at a voltage of 200 kV.

2.3. Catalytic activities of the MoS₂ samples

The catalytic activities of the MoS₂ samples synthesized with the different surfactants for AN hydrogenation were evaluated in a slurry-bed reactor (a Parr batch micro-reactor). The micro-reactor was loaded with 30 g of tridecane as the solvent, 3.0 g of anthracene as the model compound, and 0.15 g of MoS₂ sample as the catalyst. The system was purged three times and pressurized with H₂ to 80 bar. Then the reactor was heated to 400 °C and maintained for 4 h. The stirring speed was 300 r/min. Liquid products were filtered with microporous membranes to remove the catalysts and analyzed using an Agilent 7890A gas chromatograph (GC) fitted with a flame ionization detector (FID). The GC used nitrogen as the carrier gas and was equipped with a HP-5 column (60 m × 320 μm × 0.25 μm). The liquid products were identified using an Agilent 7890B-5977A GC-mass spectrometer (GC-MS). The GC-MS was equipped with a HP-5 column (30 m × 250 μm × 0.25 μm).

The selectivity of the hydrogenated products (anthracene derivatives) is defined as the molar ratio of one single AN derivative to the total amount of hydrogenated products obtained. Hydrogenated products including anthracene perhydro (14HN), octahydroanthracene (8HN), tetrahydroanthracene (4HN), and dihydroanthracene (2HN) were detected. No cracking products were detected. Conversion of AN (Conv.) is defined as: $\text{Conv.} = ([\text{AN}]_0 - [\text{AN}]) / [\text{AN}]_0 \times 100\%$, where $[\text{AN}]_0$ is the concentration of AN before the hydrogenation reaction, and $[\text{AN}]$ is the AN concentration after the hydrogenation reaction.

To visualize the activities of the MoS₂ catalysts in anthracene hydrogenation, it was proposed to study the hydrogenation ratio (HR). The hydrogenation ratio is defined as the ratio of moles of hydrogen incorporated into the hydrogenated products per mol of AN divided by 7. The hydrogenation ratio of 14HN is 100%, and that of unreacted AN is 0%. The overall hydrogenation ratio is calculated according to: $\text{HR}\% = ([2\text{HN}] \times 1 + [4\text{HN}] \times 2 + [8\text{HN}] \times 4 + [14\text{HN}] \times 7) / 7 \times \text{Conv.}$

3. Results and discussion

3.1. Structures and compositions of the MoS₂ samples synthesized with different surfactants

The XRD patterns of the MoS₂ samples synthesized with different surfactants are shown in Fig. 1. In the high angle range (30°–75°), each sample exhibits diffraction peaks at 33.8° and 57.7°, corresponding to the (100) and (110) peaks of standard 2H-MoS₂ (JCPDS Card No. 37-1492). However, the (100) peak is obviously asymmetric, which is similar to results reported by Gao et al. [12] for edge-terminated MoS₂. They ascribed the asymmetric (100) peak to the existence of stacking faults in the MoS₂ layers resulting from a-b plane gliding. In the low angle range (5°–20°), each sample exhibits two broad, but weak

Fig. 1. XRD patterns of MoS₂ samples synthesized with different surfactants.

peaks, referred to as peak I and II. The locations of the two peaks in each sample and their corresponding interlayer spacings are listed in Table 1. For each sample, a near diploid relation of the two interlayer spacings indicate that the expanded interlayer spacing of MoS₂ may result from the intercalation of hetero molecules. Similar results have also been reported in the case of oxygen-incorporated, alkali metal ions-intercalated, and NH₄⁺-intercalated MoS₂ samples [19–24]. Compared with standard 2H-MoS₂, the interlayer spacings of our samples were 0.33–0.40 nm larger, which is comparable to the increase in interlayer spacing observed in MoS₂ nano-sheets in our previous report, in ammoniated layered molybdenum, and in other transition metal chalcogenides [22–24]. In those studies, the enlarged interlayer spacings in the 0.31–0.37 nm range were ascribed to the intercalation of NH₄⁺ ions whose diameter is ~0.35 nm. Thus, it can be deduced that the enlarged interlayer spacing of 0.33–0.40 nm may be caused by the intercalation of NH₄⁺ ions [22]. The slight differences in the enlarged interlayer spacings may be caused by different amounts of intercalated NH₄⁺. Hence, MoS₂ samples synthesized with different surfactants all have intercalated NH₄⁺ in their structures.

The compositions of the MoS₂ samples synthesized with different surfactants were characterized using CHNS and TG-DSC measurements. The results of the CHNS analysis are listed in Table 2. Each sample contained S and a small amount of N, H, and C. This suggests that the samples contained MoS₂, NH₄⁺, surfactant molecules, and H₂O. The presence of the element C should originate from the surfactant molecules, and the

Table 1

The locations of peak I and peak II for each sample and the corresponding interlayer distances.

Sample	2θ _I (°)	d _I (nm)	2θ _{II} (°)	d _{II} (nm)
MoS ₂ -PEG	9.29	0.95	16.40	0.54
MoS ₂ -P123	9.01	0.98	17.02	0.52
MoS ₂ -SDS	8.69	1.02	17.02	0.52
MoS ₂ -PVP	8.74	1.01	15.52	0.57
MoS ₂ -AOT	9.40	0.94	16.40	0.54
MoS ₂ -CTAB	9.01	0.98	17.72	0.49

Table 2CNHS analysis of MoS₂ samples synthesized with different surfactants.

Sample	Composition (wt%)				Hetero species		
	C	N	H	S	(surfactant) _x	(NH ₄) _y	(H ₂ O) _z
MoS ₂ -PEG	1.87	1.34	4.34	25.72	(C ₂ H ₄ O) _{0.19}	0.24	3.27
MoS ₂ -PVP	2.87	1.81	8.93	27.50	(C ₆ H ₉ NO) _{0.08}	0.30	8.17
MoS ₂ -AOT	1.61	1.04	6.94	30.41	(C ₈ H ₁₅ O) _{0.03}	0.16	6.17
MoS ₂ -P123	3.57	1.67	4.95	27.69	(C ₁₈ H ₃₆ O ₅) _{0.03}	0.28	3.18
MoS ₂ -SDS	1.67	1.03	6.85	32.05	(C ₁₂ H ₂₅ SO ₄) _{0.02}	0.15	5.75
MoS ₂ -CTAB	1.13	1.47	7.15	29.78	(C ₁₉ H ₄₂ N) _{0.01}	0.23	6.26

presence of N may mainly arise from NH₄⁺ ions, which may originate from ammonium hepta-molybdate and the hydrolysis of hydrazine hydrate. The approximate chemical formulae of these samples were calculated and are listed in Table 2. The results show that there are 0.19 mol of PEG monomers and 0.24 mol of NH₄⁺ ions per mole of MoS₂ in MoS₂-PEG. For other samples, there are only 0.01–0.08 mol of surfactant monomers for one mole of MoS₂.

TG-DSC measurements of these samples were performed in N₂, as shown in Fig. 2. The MoS₂ samples synthesized with different surfactants exhibited similar thermal degradation processes. The weight loss in the 40–180 °C range can be ascribed to the removal of adsorbed H₂O. The weight losses at this stage for different samples were in the range of 0.77%–2.31%. The weight loss in the 180–800 °C range was ascribed to the removal of NH₄⁺ ions and surfactant molecules. In that stage, the weight losses were 33.59%, 17.42%, 14.64%, 13.87%, 8.27%, and 7.11% for MoS₂-PEG, MoS₂-PVP, MoS₂-P123, MoS₂-AOT, MoS₂-SDS, and MoS₂-CTAB, respectively. In the DSC curves, only a broad exothermal peak in the 180–800 °C range was observed for each sample, which may be ascribed to the removal of NH₄⁺ ions and surfactant molecules. The broad peaks centered at 280–350 °C may result from peak overlapping owing to the removal of NH₄⁺ ions and surfactant molecules. It has been reported that for nano-MoS₂ materials with different embedded guest species, the differences in the interactions between the MoS₂ and guest species resulted in a shift of the endothermal peak corresponding to the oxidation of MoS₂ [20]. Thus, the different shifts of the endothermal peak corresponding to the removal of NH₄⁺ ions and surfactant molecules was

ascribed to the differences in the interactions between the NH₄⁺ ions, the surfactants, and the MoS₂.

Fig. 3 shows the FTIR spectra of adsorbed surfactant molecules. It can be observed that the spectrum of each sample weakly shows the broad bonds of C–O–S (940 cm^{−1} and 901 cm^{−1}) and C–S (604 cm^{−1}) [20,25]. In the spectra of MoS₂-AOT, MoS₂-PVP, and MoS₂-CATB the C–N (1120 cm^{−1}) bonds and –NH groups (1620 cm^{−1}) may origin from the hydrophilic groups of AOT, PVP, and CTAB [26,27]. In these samples, the surfactants bridge the MoS₂ mainly through C–O–S and C–S bonds. Hence, MoS₂ samples synthesized with different surfactants mainly contain MoS₂, NH₄⁺, surfactant molecules, and H₂O.

Fig. 3. FTIR spectra of MoS₂ samples synthesized with different surfactants. **Fig. 2.** TG (a) and DSC (b) curves of MoS₂ samples synthesized with different surfactants.

3.2. The morphologies of MoS₂ samples synthesized with different surfactants

The morphologies of the MoS₂ samples synthesized with different surfactants were characterized by SEM and high resolution TEM (HRTEM). From Fig. 4 it can be deduced that both MoS₂-PEG and MoS₂-PVP are spherical particles. The mono-dispersed spherical particles in MoS₂-PEG have a diameter of about 250 nm (Fig. 4(a)). However, the aggregated spherical particles in MoS₂-PVP have a diameter of 200–450 nm (Fig. 4(b)). Both MoS₂-P123 and MoS₂-AOT are composed of bulk-like particles that show obvious signs of aggregation. These particles are 1–3 μm in size in MoS₂-P123 (Fig. 4(d)) and 1–2.2 μm in size in MoS₂-AOT (Fig. 4(c)). Highly aggregated MoS₂-SDS and MoS₂-CTAB display flower-like particles with diameters of 0.8–1.5 μm (Fig. 4(c)) and 1–3 μm (Fig. 4(f)), respectively. Therefore, MoS₂-PEG has a good morphology consisting of mono-dispersed spheres and relatively small-sized particles.

The morphologies and structures of the MoS₂ samples were further characterized by HRTEM, as shown in Fig. 5. In Fig. 5(a)–(c) the loosely arranged and disordered MoS₂ nano-sheets with slab lengths shorter than 15 nm and 4–6 stacked layers can be observed in MoS₂-PEG, MoS₂-PVP, and MoS₂-AOT. In Fig. 5(d)–(f) it can be observed that the compacted and ordered MoS₂ nano-sheets in MoS₂-P123, MoS₂-AOT, and MoS₂-P123 exhibit slabs longer than 20 nm with more than 8 stacked layers. From the HRTEM images of all the MoS₂ samples, the detected interlayer distances of the MoS₂ nano-sheets are in the range of 0.94–1.02 nm or 0.49–0.57 nm; these distances coincide with the calculated values from the XRD patterns. The MoS₂ samples synthesized with the different surfactants show obvious differences in their morphologies and structures including the interlayer distances, slab lengths, and the number of stacked layer. Among these samples, MoS₂-PEG, which has

Fig. 5. HRTEM images of MoS₂ samples synthesized with different surfactants. (a) MoS₂-PEG; (b) MoS₂-PVP; (c) MoS₂-AOT; (d) MoS₂-P123; (e) MoS₂-SDS; (f) MoS₂-CTAB.

the smallest diameter of 250 nm, exhibits a mono-dispersed spherical morphology, and the MoS₂ nano-sheets in MoS₂-PEG exhibit enlarged interlayer distances, shorter slabs, and fewer stacked layers.

3.3. The formation of MoS₂ samples in hydrothermal processes

Spherical, bulk-like and flower-like MoS₂ samples assembled from MoS₂ nano-sheets were synthesized using surfactant-assisted hydrothermal processes. The possible growth mechanisms of MoS₂ samples in surfactant-assisted hydro-

Fig. 4. SEM images of MoS₂ samples synthesized with different surfactants. (a) MoS₂-PEG; (b) MoS₂-PVP; (c) MoS₂-AOT; (d) MoS₂-P123; (e) MoS₂-SDS; (f) MoS₂-CTAB.

Fig. 6. The formation mechanisms of MoS₂ samples in surfactant-assisted hydrothermal synthesis.

thermal processes follow a soft-template mechanism, as shown in Fig. 6. First, surfactant molecules self-assemble into micelles from which the hydrophilic groups are projected outward and in which the hydrophobic alkyl backbones face toward the interior; these micelles act as soft templates, as shown in step (I). It has been reported that the self-assembly behaviors of surfactant micelles depend on balancing the hydrophobic attraction between their hydrophobic tails and the electrostatic repulsion or steric repulsions between their hydrophilic head groups; these issues play a key role in the formation of thermodynamically stable morphologies (shapes and sizes) for surfactant micelles [28]. In this work, the surfactants PEG, PVP, SDS, and CTAB all self-assemble into spherical micelles because of the strong hydrophobic attraction between the straight alkyl tails. In addition, the diameter of the SDS and CTAB micelles are larger than those of PEG and PVP micelles owing to the greater steric repulsion between their hydrophilic groups. However, P123 and AOT surfactants give rise to lamellar micelles. P123, as a common triblock copolymer, has a central hydrophobic chain and two hydrophilic chains and is facile to assemble into “lamellar” micelles because it is weakly hydrophobic [29]. It is easy for AOT to form lamellar micelles owing to the steric hindrance of its wedge-like structures [30]. Second, molybdate ions ($\text{Mo}_7\text{O}_{24}^{6-}$) are easily adsorbed on the outer surfaces of these micelles via electrostatic interactions, as shown in step (II). For PEG, PVP, and P123 micelles are easily protonated because PEG, PVP, and P123 are non-ionic surfactants. The adsorption of $\text{Mo}_7\text{O}_{24}^{6-}$ on protonated PEG, PVP, and P123 micelles is facile owing to electrostatic interactions. With regard to AOT and SDS micelles, AOT and SDS are ionic surfactants and so their micelles carry negative charges: the negatively charged micelles thus attract the NH_4^+ ions in the precursor solution. With the assistance of the NH_4^+ ions, the adsorption of $\text{Mo}_7\text{O}_{24}^{6-}$ groups on AOT and SDS micelles can overcome the charge incompatibility between $\text{Mo}_7\text{O}_{24}^{6-}$ and the negatively charged AOT and SDS molecules. As CTAB is a cationic surfactant, CTAB micelles carry positive charges. Hence, the adsorption of $\text{Mo}_7\text{O}_{24}^{6-}$ on CTAB micelles is easy because of favorable electrostatic interactions. Then, $\text{Mo}_7\text{O}_{24}^{6-}$ is sulfurized in situ into MoS_4^{2-} by H_2S , which is produced by the hydrolysis of $(\text{NH}_2)_2\text{CS}$ according to Eqs. (1) and (2).

Third, MoS_4^{2-} is reduced by N_2H_4 into MoS_2 as shown in Eq. (3). MoS_2 nano-sheets are generally obtained because of the material's inherent 2D crystalline structure, as shown in step (III). Then, as the hydrothermal crystallization proceeds, the growth and assembly of the MoS_2 nano-sheets takes place, as shown in step (IV). The growth of the MoS_2 nano-sheets is inhibited by the surfactant molecules. The slab length and the number of stacked layers are closely correlated with the steric hindrance of the surfactant molecules, which is determined by the interactions and the electrostatic interaction distance between the MoS_2 nano-sheets and the surfactant molecules. This is in agreement with research reported by Wang et al. [31], which details the formation of MoS_2 /graphene composites with the assistance of cationic surfactants. According to their report, MoS_2 nano-sheets with short slab lengths and few stacked layers were obtained when using CTAB because of the strong interactions and short interaction distances between MoS_2 and CTAB. Here, when it comes to MoS_2 -PEG and MoS_2 -PVP, MoS_2 nano-sheets with short slabs (15 nm) and few stacked layers (4–6 layers) were obtained owing to the strong interactions and short electrostatic interaction distances between the MoS_2 nano-sheets and PEG or PVP. For MoS_2 -SDS and MoS_2 -CATB, MoS_2 nano-sheets with long slabs (> 20 nm) and many more stacking layers (> 8 layers) were obtained because of the weak interactions and long electrostatic interaction distances between the MoS_2 nano-sheets and SDS or CTAB. Meanwhile, the assembly of these MoS_2 nano-sheets was templated on these micelles, thus resulting in the formation of MoS_2 samples with different morphologies. In addition, the nano-sheets of the samples exhibited a structure with NH_4^+ intercalated in MoS_2 . The intercalation of NH_4^+ ions from the precursors into the structures of the MoS_2 nano-sheets was promoted by the relatively high temperature and pressure used during the hydrothermal process, leading to the formation of MoS_2 nano-sheets with obvious lattice expansions, which agrees with the results reported by Xie et al. [19]. Hence, MoS_2 samples with different morphologies and structures can be achieved by adjusting the surfactants.

To further confirm the growth mechanism, a calcination at 400 °C in H₂ for 4 h was performed to remove the templates from the obtained MoS₂ samples. MoS₂-PEG was used as a representative example. MoS₂-PEG after the calcination is referred to as MoS₂-PEG-C. The four peaks in the XRD patterns of MoS₂-PEG-C (Fig. 7(a)) at around 14.0°, 33.4°, 39.7°, and 59.2° can be ascribed to the (002), (100), (103), and (110) peaks of hexagonal 2H-MoS₂, respectively. The TG curve of MoS₂-PEG-C shows hardly any weight loss in the 20–800 °C range, revealing the absence of NH₄⁺ and surfactant molecules. In the material's DSC curve, a broad exothermic peak centered around 400 °C is visible, which corresponds to the crystallization of 2H-MoS₂ [32]. We propose that during the calcination process the structural transformation from NH₄⁺ intercalated MoS₂ into crystallized 2H-MoS₂ took place, with the removal of NH₄⁺ and surfactant molecules. The SEM image (Fig. 7(c)) of MoS₂-PEG-C shows that the particles have a good spherical morphology with a diameter of 100–200 nm and that they show no obvious signs of aggregation. The HRTEM image (Fig. 7(d)) of MoS₂-PEG-C shows MoS₂ nano-sheets with slab lengths much longer than 20 nm and up to 10 stacked layers. An interlayer spacing of 0.62 nm was detected in MoS₂-PEG-C, which is in agreement with the value calculated from its XRD pattern. The comparison between MoS₂-PEG and MoS₂-PEG-C with regard to the morphology revealed that after calcination, the good spherical shape of the MoS₂ particles was retained; however, the diameter of the MoS₂-PEG-C spheres decreased. The removal of the NH₄⁺ and the surfactant molecules did not influence the spherical shape of the MoS₂ particles, but resulted in them shrinking. Meanwhile, the slab length and number of stacked layers of the MoS₂ nano-sheets increased; however, the interlayer spacing of the MoS₂ nano-sheets decreased, which may also result from the

Scheme 1. The pathway for anthracene hydrogenation using the MoS₂ samples as catalysts.

removal of NH₄⁺. The results confirm the role of the surfactant molecules as a template during the growth process of MoS₂ samples with different morphologies and structures.

3.4. The catalytic performances of MoS₂ samples in anthracene hydrogenation

The catalytic performance of MoS₂ samples with different morphologies and structures was evaluated, using the anthracene hydrogenation in a slurry-bed batch micro-reactor. In accordance with the GC-MS results, the pathway for the anthracene hydrogenation using the MoS₂ samples as catalysts is shown in Scheme 1. The stepwise reaction pathway of the anthracene hydrogenation is the same as in our previous research using MoS₂ nano-sheets as catalysts and the same as that reported by Pinilla et al. [22,33,34]. The hydrogenation of AN to the primary product 2HN is fast, and proceeds to a nearly complete conversion. The hydrogenation of 2HN proceeds via the intermediate product 4HN, and subsequently produces 8HN (*cis* and *trans*, symmetric). Then, 8HN was hydrogenated into 14HN. The high catalytic activity may result from the high selectivity of the highly hydrogenated products (8HN and 14HN).

The selectivity of the hydrogenation products is shown in Fig. 8(a). It can be observed that the highly hydrogenated product 14HN could only be detected when MoS₂-PEG was used as a catalyst. The selectivity of the highly hydrogenated product 8HN for MoS₂ catalysts decreased in the following order: MoS₂-PEG > MoS₂-PVP > MoS₂-P123 > MoS₂-AOT > MoS₂-SDS > MoS₂-CATB. The highest 8HN selectivity achieved was with MoS₂-PEG (52.8%), and the lowest 8HN selectivity was achieved with the MoS₂-CATB catalyst and was 19.5%. However, the selectivity to 4HN and 2HN decreased in reverse order. MoS₂-PEG exhibited the lowest selectivity toward 4HN and 2HN, while the MoS₂-CATB catalyst exhibited the highest selectivity to 4HN and 2HN. The AN conversion and hydrogenation ratio of AN have been used to evaluate the catalytic activities of MoS₂ catalysts [33,34]. The AN conversions and hydrogenation ratios of AN for our samples are shown in Fig. 8(b). The AN conversions for different MoS₂ catalysts were all above 92.0%. Further, the hydrogenation ratio decreased in the following order: MoS₂-PEG > MoS₂-PVP > MoS₂-P123 > MoS₂-AOT > MoS₂-SDS > MoS₂-CATB. The highest hydrogenation ratio of 44.04% was achieved with MoS₂-PEG, and the lowest hydrogenation ratio of 29.55% was achieved with MoS₂-CATB. MoS₂-PEG had a higher selectivity to the highly hydrogenated products 8HN and 14HN and a lower selectivity

Fig. 7. XRD pattern (a), TG/DSC profiles (b), SEM (c) and HRTEM images (d) of MoS₂-PEG-C.

Fig. 8. (a) The selectivity of AN derivatives; (b) the conversion of AN and hydrogenation ratio of anthracene for the MoS₂ catalysts prepared with different surfactants. Reaction conditions: anthracene 3.0 g, tridecane 30.0 g, catalyst 0.15 g, 400 °C, 4 h, an initial pressure 80 bar.

to 2HN and 4HN, and exhibited the highest catalytic activity. The increase in the hydrogenation ratio of our samples resulted in a concurrent increase of the 8HN selectivity and decreases of the selectivity to 4HN and 2HN. It can be deduced that the high selectivity to the highly hydrogenated products 8HN and 14HN is at the expense of the selectivity to 4HN and 2HN, which results in the pathway of anthracene hydrogenation that is presented in Scheme 1.

Summarizing the above results, it was found that the highest activity for AN hydrogenation was obtained with the MoS₂-PEG catalyst, which was composed of mono-dispersed spherical particles with smaller particle sizes. Furthermore, the MoS₂ nano-sheets in the MoS₂-PEG catalyst had shorter slab lengths and fewer stacked layers (Table 3). Conversely, the lowest catalytic activity was obtained with the MoS₂-CTAB catalyst, which was composed of aggregated micro-scaled flower-like particles with MoS₂ nano-sheets with longer slab lengths and more stacked layers (Table 3). With the increase of the particle size, aggregation, slab length, and number of stacked layers in the MoS₂ catalysts, the catalytic activity decreased. In addition, the physical properties of the MoS₂ catalysts, such as their surface areas (A_{BET}) and water contact angles were determined and are listed in Table 3. The results reveal that A_{BET} and the contact angles had no direct relationship with the catalytic hydrogenation activities of these catalysts. It is noteworthy, however, that MoS₂-SDS possesses the largest surface area. For MoS₂ materials, the surface area may depend on the basal plane (001), which may be much larger than the edge plane (100). The basal plane possesses excellent lubricating properties and photo-

catalytic activities [35]. Thus, the surface areas may not dictate the catalytic hydrogenation activity. Moreover, MoS₂-SDS, which has longer slab lengths and more stacked layers, exposed few active sites. Increased aggregation of these particles was observed (Fig. 5(e)). Aggregation inhibits the exposure of active MoS₂ edges and decreases the dispersion of the catalyst. Therefore, MoS₂-SDS, which has a large surface area but only a few exposed active MoS₂ edges, exhibited a low catalytic hydrogenation activity. It can be deduced that the catalytic activities of these MoS₂ catalysts are mainly correlated with their morphological and structural features.

Both the experimental results and theoretical calculations reveal that MoS₂ nano-sheets with short slab lengths and few stacked layers exhibit a large number of exposed active edges [12,36,37]. As the slab lengths and number of stacked layers in the MoS₂ nano-sheets increases in the MoS₂ catalysts, the number of exposed active edges decreases. In addition, mono-dispersed spherical MoS₂ particles with smaller particle sizes could be highly dispersed in a slurry-bed reactor, which facilitated the exposure of the active edges. However, aggregated particles showed poor dispersion, which impeded the exposure of partially active edges. Furthermore, a mono-dispersed spherical morphology of the MoS₂ catalysts is helpful to further expose the active edges and improve the dispersion of the catalyst in the slurry-bed reactor. The excellent hydrogenation activity of MoS₂-PEG may be ascribed to its highly exposed active edges. Therefore, it can be concluded that the catalytic activities of MoS₂ catalysts for anthracene hydrogenation mainly depend on the number of exposed active edges.

Table 3

Surface areas, water contact angles, and the shape and diameter of the MoS₂ samples synthesized with different surfactants along with the number of stacked layers and slab lengths of the MoS₂ nano-sheets, as well as the hydrogenation ratio of AN when the MoS₂ samples were used as catalysts.

Sample	Shape	Diameter (μm)	Stacking layers	Slab length (nm)	A_{BET} (m ² /g)	Contact angle (°)	Hydrogenation ratio (%)
MoS ₂ -PEG	mono-dispersed spherical	0.25	4–6	<15	17.13	77.46	44.04
MoS ₂ -PVP	spherical	0.20–0.45	4–6	<15	39.29	60.40	41.51
MoS ₂ -P123	bulk-like	1.0–3.0	4–6	<15	27.36	43.75	40.19
MoS ₂ -AOT	bulk-like	1.0–2.2	>8	>20	18.51	33.82	39.37
MoS ₂ -SDS	flower-like	0.8–1.5	>8	>20	126.98	57.20	32.13
MoS ₂ -CTAB	flower-like	1.0–3.0	>8	>20	11.71	59.14	29.55

4. Conclusions

We have successfully and controllably synthesized spherical, bulk-like, and flower-like MoS₂ samples assembled from MoS₂ nano-sheets with different structures (such as with different slab lengths and different number of stacked layers) using a facile surfactant-assisted hydrothermal approach. We found that the morphologies and structures of the MoS₂ samples could be controlled by adjusting the surfactants. Further, we proposed a possible formation mechanism. The catalytic activities of MoS₂ catalysts for anthracene hydrogenation revealed that MoS₂-PEG exhibited the highest catalytic activity, which was ascribed to the high exposure of its active edges, which was the result of MoS₂-PEG's the smaller particle size, mono-dispersed spherical morphology, short slab lengths, and low number of stacked layers. This study thus provides a rational direction for designing other metal oxides and sulfides with controllable morphologies and structures.

References

- [1] A. S. Walton, J. V. Lauritsen, H. Topsøe, F. Besenbacher, *J. Catal.*, **2013**, 308, 306–318.
- [2] Y. X. Huang, J. H. Guo, Y. J. Kang, Y. Ai, C. M. Li, *Nanoscale*, **2015**, 7, 19358–19376.
- [3] C. F. Zhang, X. Wang, M. R. Li, Z. X. Zhang, Y. H. Wang, R. Si, F. Wang, *Chin. J. Catal.*, **2016**, 37, 1569–1578.
- [4] C. L. Ma, X. Jin, L. Ding, Q. M. Zhang, J. S. Qiu, C. H. Liang, *Chin. J. Catal.*, **2009**, 30, 78–82.
- [5] J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuvsen, D. W. McComb, P. D. Nellist, V. Nicolosi, *Science*, **2011**, 331, 568–571.
- [6] T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Horch, and I. Chorkendorff, *Science*, **2007**, 317, 100–102.
- [7] K. Vignarooban, J. Lin, A. Arvay, S. Kolli, I. Kruusenberg, K. Tammeveski, L. Munukutla, A. M. Kannan, *Chin. J. Catal.*, **2015**, 36, 458–472.
- [8] A. K. Tuxen, H. G. Fächtbauer, B. Temel, B. Hinnemann, H. Topsøe, K. G. Knudsen, F. Besenbacher, J. V. Lauritsen, *J. Catal.*, **2012**, 295, 146–154.
- [9] K. H. Hu, X. G. Hu, X. J. Sun, *Appl. Surf. Sci.*, **2010**, 256, 2517–2523.
- [10] X. W. Wang, Z. A. Zhang, Y. Q. Chen, Y. H. Qu, Y. Q. Lai, J. Li, *J. Alloys Compd.*, **2014**, 600, 84–90.
- [11] J. Guo, X. Chen, Y. J. Yi, W. Z. Li, C. H. Liang, *RSC Adv.*, **2014**, 4, 16716–16720.
- [12] M. R. Gao, M. K. Y. Chan, Y. G. Sun, *Nat. Commun.*, **2015**, 6, 7493.
- [13] E. Varrla, C. Backes, K. R. Paton, A. Harvey, Z. Gholamvand, J. McCauley, J. N. Coleman, *Chem. Mater.*, **2015**, 27, 1129–1139.
- [14] I. Uzcanga, I. Bezverkhyy, P. Afanasiev, C. Scott, M. Vrinat, *Chem. Mater.*, **2005**, 17, 3575–3577.
- [15] W. J. Dan, L. Chang, H. J. Guo, L. H. Yang, X. N. Wang, Z. C. Feng, *Chin. J. Catal.*, **2011**, 32, 4, 1336–1341.
- [16] S. K. Panda, A. Datta, A. Dev, S. Gorai, S. Chaudhuri, *Cryst. Growth Des.*, **2006**, 6, 2177–2181.
- [17] Y. X. Zhou, Q. Zhang, J. Y. Gong, S. H. Yu, *J. Phys. Chem. C*, **2008**, 112, 35, 13383–13389.
- [18] W. D. Shi, S. Y. Song, H. J. Zhang, *Chem. Sov. Rev.*, **2013**, 42, 5714–5743.
- [19] J. F. Xie, J. J. Zhang, S. Li, F. Grote, X. D. Zhang, H. Zhang, R. X. Wang, Y. Lei, B. C. Pan, Y. Xie, *J. Am. Chem. Soc.*, **2013**, 135, 17881–17888.
- [20] X. F. Wang, Z. R. X. Guan, Y. J. Li, Z. X. Wang, L. Q. Chen, *Nanoscale*, **2015**, 7, 637–641.
- [21] J. Shao, Q. T. Qu, Z. M. Wan, T. Gao, Z. C. Zuo, H. H. Zheng, *ACS Appl. Mater. Interfaces*, **2015**, 7, 22927–22934.
- [22] M. Li, D. E. Wang, J. H. Li, Z. D. Pan, H. J. Ma, Y. X. Jiang, Z. J. Tian, *RSC Adv.*, **2016**, 6, 71534–71542.
- [23] Z. Z. Wu, C. Y. Tang, P. Zhou, Z. H. Liu, Y. S. Xu, D. Z. Wang, B. Z. Fang, *J. Mater. Chem. A*, **2015**, 3, 13050–13056.
- [24] A. A. Jeffery, C. Nethravathi, M. Rajamathi, *J. Phys. Chem. C*, **2014**, 118, 1386–1396.
- [25] K. Q. Zhou, S. H. Jiang, C. L. Bao, L. Song, B. B. Wang, G. Tang, Y. Hu, Z. Gu, *RSC Adv.*, **2012**, 2, 11695–11703.
- [26] Z. Y. Guo, Q. X. Ma, Z. W. Xuan, F. L. Du, Y. Zhong, *RSC Adv.*, **2016**, 6, 16730–16735.
- [27] M. W. Xu, F. L. Yi, Y. B. Niu, J. L. Xie, J. K. Hou, S. G. Liu, W. H. Hu, Y. T. Li, C. M. Li, *J. Mater. Chem. A*, **2015**, 3, 9932–9937.
- [28] M. S. Bakshi, *Cryst. Growth Des.*, **2016**, 16, 1104–1133.
- [29] G. Wanka, H. Hoffmann, W. Ulbricht, *Macromolecules*, **1994**, 27,

Graphical Abstract

Chin. J. Catal., 2017, 38: 597–606 doi: 10.1016/S1872-2067(17)62779-7

Surfactant-assisted hydrothermally synthesized MoS₂ samples with controllable morphologies and structures for anthracene hydrogenation

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MoS₂ particles with controllable morphologies and structures were synthesized with various surfactants. Mono-dispersed spherical MoS₂ catalysts exhibited higher catalytic activities for anthracene hydrogenation, which can be ascribed to its highly exposed active edges.

- 4145–4159.
- [30] D. De, A. Datta, *Langmuir*, **2013**, 29, 7709–7714.
- [31] Z. Wang, L. Ma, W. X. Chen, G. C. Huang, D. Y. Chen, L. B. Wang, J. Y. Lee, *RSC Adv.*, **2013**, 3, 21675–21684.
- [32] J. L. Brito, M. Ilija, P. Hernandez, *Thermochim. Acta*, **1995**, 256, 325–338.
- [33] J. L. Pinilla, A. B. García, K. Philippot, P. Lara, E. J. García-Suárez, M. Millan, *Fuel*, **2014**, 116, 729–735.
- [34] J. L. Pinilla, H. Purón, D. Torres, I. Suelves, M. Millan, *Carbon*, **2015**, 81, 574–586.
- [35] P. Afanasiev, *C. R. Chim.*, **2008**, 11, 159–182.
- [36] M. Brorson, A. Carlsson, H. Topsøe, *Catal. Today*, **2007**, 123, 31–36.
- [37] C. Kisiowski, Q. M. Ramasse, L. P. Hansen, M. Brorson, A. Carlsson, A. M. Molenbroek, H. Topsøe, S. Helveg, *Angew. Chem. Int. Ed.*, **2010**, 49, 2708–2710.

表面活性剂辅助水热制备形貌结构可控的MoS₂及其蒽加氢性能

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摘要: 随着原油资源重质化和劣质化的加剧以及对清洁燃料油品需求的不断增加, 将重质油加工成清洁燃料成为现代炼厂面临的挑战。悬浮床加氢是重质油转化为清洁液体燃料的先进技术, 其核心难题是高效加氢催化剂的开发。MoS₂在石油化工领域油品加氢提质研究中表现出非常好的催化加氢性能。MoS₂晶体结构中有两种面: 沿S-Mo-S层间的剥离面, 又称基面, 化学性质稳定; 沿Mo-S的断裂面, 又称棱面, 具有大量的不饱和键, 化学性质不稳定, 可做催化活性中心。由于MoS₂结构和形貌对其物理化学性能有重要影响, 所以通过合理设计和调控MoS₂的结构和形貌可增加暴露的催化活性位, 进而改善其催化性能。

本文以七钼酸铵和硫代乙酰胺为原料, 水合肼做还原剂, 采用不同表面活性剂(包括PEG, PVP, P123, SDS, AOT和CTAB)辅助的水热合成法制备了结构及形貌可控的MoS₂, 并提出不同表面活性剂条件下MoS₂催化剂的生长机理, 进一步研究了重油模型化合物稠环芳烃蒽的催化加氢性能。结果表明, 在不同表面活性剂辅助的条件下分别制得了由MoS₂纳米片组装而成的球形、块状和花状的MoS₂产物; 通过改变表面活性剂种类可调节MoS₂纳米片的长度、堆积层数、层间距以及最终产物的形貌。在PEG或PVP辅助下得到了球形MoS₂产物, 其中MoS₂纳米片长<15 nm, 堆积层数<6。在PEG辅助下制备的球形MoS₂粒径约为250 nm, 尺寸均一且分散性好。在PVP辅助下MoS₂粒径在200–450 nm, 粒径分布范围宽且有明显团聚。在P123或SDS辅助下得到了团聚较明显的块状微米级MoS₂产物。在P123辅助下得到的MoS₂纳米片长<15 nm, 层数<6。在SDS辅助下制备的MoS₂纳米片长>20 nm, 堆积层数>8。在AOT或CTAB辅助下得到团聚比较严重的花状微米级MoS₂产物, 其中MoS₂纳米片长>20 nm, 堆积层数>8。另外, 水热反应过程中, 高温高压的环境促进了反应体系中游离的NH₄⁺插入到MoS₂层状结构中, 导致MoS₂纳米片层间距增大。基于此, 本文提出了不同表面活性剂辅助的水热过程中不同结构和形貌MoS₂产物的形成机理。

对不同结构和形貌的MoS₂样品进行了悬浮床蒽加氢催化性能评价。结果表明, PEG辅助制备的MoS₂催化剂具有最高催化加氢活性。该MoS₂催化剂中纳米片层短, 堆积层数少, 暴露了更多的加氢活性位。单分散的球形MoS₂颗粒粒径小, 分散性好, 有利于加氢活性位的充分暴露, 进而表现出较好的催化性能。本文所采用的表面活性剂辅助的水热法为可控合成不同结构和形貌的过渡金属硫化物提供了有效指导和借鉴。

关键词: 二硫化钼; 表面活性剂辅助; 形貌可控; 单分散; 活性位; 蒽加氢

收稿日期: 2016-11-30. 接受日期: 2016-12-30. 出版日期: 2017-03-05.

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基金来源: 国家自然科学基金(21303186); 中国科学院重点战略研究项目(XDA07020300).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).