



Understanding of the effect of synthesis temperature on the crystallization and activity of nano-MoS₂ catalyst



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ABSTRACT

Temperature is a key factor in the hydrothermal synthesis of MoS₂ with high catalytic activity. In this paper, the effect of synthesis temperature (sTemp) and initial temperature (iTemp) was carefully investigated against catalyst crystal structure and hydrotreating activities. The synthesized nano-MoS₂ was extensively characterized and evaluated using light cycle oil. There is a minimum sTemp for the formation of crystalline MoS₂. Temperatures lower than the minimal sTemp result in amorphous structures. Surpassing this temperature leads to crystallization which goes through different growth routes. Higher iTemp promotes fast nucleation and thus nuclei combination growth. This leads to shorter slabs with a larger degree of defects, and a higher hydrotreating activity. At lower iTemp, crystal tends to grow in a continuous way, resulting in fewer defects. In this way, with the increased sTemp, crystallinity is enhanced and slabs are curved and shortened. Both effects lead to improved hydrotreating performances.

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1. Introduction

Recent environmental regulations that are becoming more heavily stringent on the sulfur content in the transportation fuels are signaling for new hydrodesulfurization (HDS) catalysts with higher deep desulfurization activity [1,2]. Unsupported MoS₂-based catalysts with a high density of active sites have a great potential for the improvement of HDS performance [3,4]. It is reported that the unsupported catalysts, e.g., commercialized NEBULA catalysts, are more active in deep HDS than the conventional supported catalysts [4–7]. Thus, study on the preparation of dispersed MoS₂ is a promising research direction.

Nanocrystalline MoS₂ can be synthesized by a variety of techniques, and hydrothermal method is one of the desirable approaches [8–10]. In this technique, temperature is a key factor in controlling nucleation and crystal growth. External energy (heating) is needed to overcome the activation energy barriers for the nucleation and consequent growth. Meanwhile, activation energy of different crystal facets is also affected by temperature through the effect on interfacial energy [11]. In addition, variation of crystallization temperature changes the equilibrium solubility of the subjected material, i.e., the supersaturation state. An elevated

supersaturation would significantly enhance the growth on a preferred surface [12]. Through the control of crystallization, temperature can further influence the crystallinity, crystalline size, and morphology [13–16]. It is reported that crystalline MoS₂ cannot be generated at too low or high temperatures [9,10]. In a low temperature range of 120–150 °C, only amorphous MoS₂ nanospheres were observed without any layered crystalline structure present [17]. When MoS₂ was successfully produced, the morphology and crystalline size can also be largely affected by temperature. The trend that increasing temperature led to larger particle sizes was found between 230 and 260 °C by Li et al. with different morphologies observed [10]. At high temperature range 300–375 °C, on the other hand, the sizes of promoted MoS₂ crystalline decrease with increasing temperature. The morphology also changed with temperature as given by an increased curvature of MoS₂ slabs [18].

However, although several investigations have been performed on the hydrothermal conditions of MoS₂ synthesis, there is lack of systematic study on temperature effect. From a catalysis view, a comprehensive study of the effect of temperature is yet not conducted. In our previous work, a novel one-step hydrothermal technique was established for preparation of dispersed MoS₂ using commercially available MoO₃ and Na₂S as precursors [19]. The present work focuses on the effect of temperature on MoS₂ properties and activities. Both synthesis temperature and initial temperature were investigated. The properties of MoS₂ catalysts synthesized at different temperatures were extensively

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Table 1
Synthesis conditions and textural structure of synthesized catalysts.

Catalysts	Synthesis conditions		Average slab length, L (nm)	Average slab thickness, T (nm)	L/T ratio ^c	BET surface area (m ² /g)
	iTemp ^a (°C)	sTemp ^b (°C)				
CAT-20-200	20	200	10.2/12.6 ^d	5.1/4.8 ^d	2.0	84.5
CAT-20-270	20	270	13.4/13.6 ^d	1.9/1.9 ^d	7.1	218.4
CAT-20-320	20	320	17.9/18.2 ^d	2.5/2.5 ^d	7.2	198.9
CAT-20-350	20	350	11.3	2.0	5.7	155.9
CAT-270-320	270	320	12.3	1.7	7.3	236.3
CAT-270-320*	270	320	7.9	1.1	7.2	261.9

^a iTemp: Initial temperature at which the heating starts.

^b sTemp: Synthesis temperature at which synthesis maintains.

^c L/T ratio: Ratio of average slab length to slab thickness.

^d The crystalline size of spent catalysts after 8 h hydrotreatment.

characterized by TEM, BET, XRD, XPS, TPR, and XAFS, etc.; the hydrotreatment activities were evaluated using light cycle oil (LCO). A relationship is also attempted to build between the syntheses conditions to catalysts structure and activity.

2. Experimental

2.1. Catalyst synthesis

A series of molybdenum sulfide catalysts were synthesized via a hydrothermal method in a 1000 ml stainless steel autoclave (Parker Autoclave Engineers). 5.436 g of MoO₃ (STEM Scientific) and 33.989 g of Na₂S·9H₂O (Fisher Scientific) were first dissolved in 300 ml deionized water after which, 42.5 ml of 4 M HCl solution (Fisher Scientific) was slowly added. The molar ratio of precursors was 1: 3.75: 4.5. The synthesis reaction occurred at different temperatures in the range of 200–350 °C. For the synthesis temperature of 320 °C, two initial temperatures of 20 °C and 270 °C were investigated. A special heating protocol was applied for the higher initial temperature (270 °C). The reactor, containing 300 ml water, was first preheated to 270–280 °C. Sixty milliliter of concentrated precursor solution was then instantaneously injected into the reactor by nitrogen drive to achieve the high-temperature start-up. For a special run, an immediate shutdown was applied once the reactor hits the setting temperature 320 °C. All the other synthesis runs lasted for 2 h under the stirring of 500 rpm unless indicated. After each run, the reactor was immediately cooled down with cooling water.

Black solid residue, which resulted from synthesis, was filtered and carefully washed with distilled water and ethanol. Catalysts prepared at different temperatures were denoted as CAT-initial temperature-synthesis temperature, e.g., CAT-20-200 stands for catalysts prepared at 200 °C with an initial temperature of 20 °C (room temperature). A suffix “*” was used to indicate immediately suspended run at time zero, e.g., CAT-270-320*. The conditions are listed in Table 1.

2.2. Catalyst characterization

Nitrogen adsorption–desorption isotherms were measured at 77 K using an Autosorb-1 (Quantachrome Instruments, Florida, US). The specific surface area of the catalyst powder was calculated using the Brunauer–Emmett–Teller (BET) method with linear region in the P/P_0 range of 0.10–0.30. Pore size distribution of the catalyst powder was determined from the isotherms via the Barrett–Joyner–Halenda (BJH) method. X-ray diffractograms were recorded on a diffractometer (Bruker AXS D8 XRD) using CuK α radiation. For all the samples, the 2θ range was 5–85° and the scan speed was 1°/min. The morphology of catalysts was measured with TEM (JEOL 2011 STEM, JEOL Ltd., Tokyo, Japan). The length and

thickness of crystals were determined using image analysis software and the averages were calculated based on at least 200 MoS₂ crystals measured from different particles according to Eqs. (1) and (2). The morphology of catalyst particles was observed using scanning electron microscopy (JEOL JSM6400 SEM). The atomic ratio of the catalyst was estimated by energy dispersive X-ray emission (EDX) coupled with TEM.

$$\text{Average slab thickness } \bar{T} = \frac{\sum_{i=1,2,\dots,n} T_i}{n} \quad (1)$$

$$\text{Average slab thickness } \bar{L} = \frac{\sum_{i=1,2,\dots,n} L_i N_i}{\sum_{i=1,2,\dots,n} N_i} \quad (2)$$

where L , T , and N stand for slab length, slab thickness, and number of layers in each crystal, respectively.

Temperature-programmed reduction (TPR) was conducted on Autosorb-1 (Quantachrome Instruments, Florida, US). Approximately, 100 mg catalyst was placed in a quartz U-tube and reduced by heating from room temperature to 700 °C at a rate of 10 °C/min under a 50 ml/min flow of 2% H₂/Ar. The consumption of H₂ was recorded using a mass spectrometer (RGA 200 Stanford Research Systems, Inc.).

XPS spectra of Mo3d and S2p were recorded using an AXIS 165 spectrometer (Kratos Analytical) equipped with a 210 W Al K α monochromatic source ($h\nu = 1486.6$ eV). The resolution of the instrument is 0.55 eV for Ag 3d and 0.70 eV for Au 4f peaks. Sample preparation was carried out under an Ar atmosphere to avoid oxidation. The survey scans were collected for binding energy extending from 1100 eV to 0 with analyzer pass energy of 160 eV and a step of 0.4 eV and the high-resolution spectra were collected at a pass energy of 20 eV with a step of 0.1 eV.

The X-ray absorption near-edge structure (XANES) of S K-edge and Mo L3-edge was measured at the Soft X-ray Microanalysis Beamline (SXRMB) of the Canadian Light Source (CLS; Saskatoon, SK, Canada). The spectra were recorded in a total electron yield mode at room temperature using a Si (111) double crystal monochromator. Data analysis of the XANES spectra was performed using Athena software. The extended X-ray absorption fine structure (EXAFS) spectra of Mo K-edge were recorded in the transmission mode at room temperature. The structure parameters around Mo were obtained by Fourier transformation using FEFF 6 software. Detailed procedure was described elsewhere [20,21].

2.3. Evaluation of unsupported catalysts

A batch reactor from Parker Autoclave Engineers was employed in this experiment. Light cycle oil with 1.5 wt% S and 159 ppm N was selected as the feedstock. 0.6 g catalyst filtered through 200 meshes was added into autoclave. After heating the reactor to 375 °C, 120 g LCO was introduced into the reactor, making the weight

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