

**Catalytic activity and chemical structure of Nano MoS<sub>2</sub>  
synthesized in a controlled environment**

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# Reaction Chemistry & Engineering

## ARTICLE

### Catalytic activity and chemical structure of Nano MoS<sub>2</sub> synthesized in a controlled environment

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A novel hydrothermal method for preparation of nano MoS<sub>2</sub> for hydrodesulfurization (HDS) with MoO<sub>3</sub> as precursors is presented. The redox reaction mechanism is, for the first time, revealed. It is shown to involve the oxidation of S<sup>2-</sup> to SO<sub>4</sub><sup>2-</sup> while hexavalent Mo is reduced to quadrivalent Mo to form MoS<sub>2</sub>. HS<sup>-</sup> group is identified to play a key role in reduction of MoO<sub>3</sub>. The acid-base behaviour of Na<sub>2</sub>S to HS<sup>-</sup> group and the yield of the resulting MoS<sub>2</sub> are controlled via the pH of the synthesis solution. Various characterization methods, e.g. XRD, TEM, SEM, BET, TPR, XPS, XANES, EXAFS, etc. are employed for the characterization of the synthesized MoS<sub>2</sub>. The results show that high purity MoS<sub>2</sub> is obtained. The ratio of precursors, MoO<sub>3</sub> and Na<sub>2</sub>S, influences the crystal structure and catalytic activity. Slight less sulfur than stoichiometric ratio of S/Mo produces defect sites, which promotes catalyst activities in the hydrodesulfurization of real light cycle oil (LCO).

#### Introduction

Nano-scaled molybdenum disulfide (MoS<sub>2</sub>) has a layered structure with individual sheets strongly covalently bonded within but held together through weak van der Waals interactions. This results in two distinct surfaces of MoS<sub>2</sub>: basal and edge planes. Within a layer, each Mo (IV) center is bonded to six sulfurs forming a trigon prismatic coordination while every sulfur atom is connected with three Mo forming pyramidal interstices<sup>1,2</sup>. The unique structure and chemistry properties make MoS<sub>2</sub> widely applied as a functional material in diverse fields of lubrication, electronic transistors, batteries, photovoltaics, catalysis, and sensing<sup>3</sup>. MoS<sub>2</sub> also shows high activity in hydrodesulfurization reaction<sup>4</sup>.

There are different methods for synthesis of nano MoS<sub>2</sub> including solid-gas sulfidation, thermal decomposition, and solution reactions<sup>5</sup>. Hydrothermal method is an alternative route to preparing nano MoS<sub>2</sub> with MoO<sub>3</sub> as precursor<sup>6</sup>. Compared to thiomolybdate, MoO<sub>3</sub> is an attractive precursor as it is cost-effective. MoO<sub>3</sub> has been used as precursor to synthesize nano MoS<sub>2</sub> of different morphologies, e.g. nano-sheet<sup>4</sup>, nanowires<sup>7</sup>, nanotubes and nanorods<sup>8</sup>. Our previous study discussed the effect of temperature on the nucleation and growth process<sup>6</sup>. A relationship has been established between the crystallization process and MoS<sub>2</sub> structure. Successful production of nano MoS<sub>2</sub> through hydrothermal route is associated with a number of synthesis parameters such as pH of solvent, precursor

concentration, and temperature. However the reaction mechanisms for formation of MoS<sub>2</sub> are poorly understood.

This work tends to address this deficiency. In particular, the role of reducing agent in transformation of hexavalent Mo to quadrivalent Mo to form MoS<sub>2</sub> will be studied. The reaction mechanism of the nano MoS<sub>2</sub> formation is discussed. Appropriate synthesis condition results in high yield of highly dispersed nano MoS<sub>2</sub> crystalline that has high hydrodesulfurization activity. The textural and chemical structure of synthesized catalysts were extensively characterized by various techniques, e.g. TEM, BET, XRD, XPS, TPR and XAFS, etc. The hydrodesulfurization (HDS), hydrodenitrogenation (HDN) activities were evaluated using a real diesel fraction - light cycle oil (LCO).

#### Experimental Section

**Preparation of MoS<sub>2</sub> catalysts.** A series of molybdenum sulfide catalysts were synthesized using MoO<sub>3</sub> (STEM Scientific) and Na<sub>2</sub>S·9H<sub>2</sub>O (Fisher Scientific) as precursors<sup>6</sup>. 14.4 grams of MoO<sub>3</sub> was used in the synthesis. Different molar ratios of Na<sub>2</sub>S to MoO<sub>3</sub> were employed and listed in Table 1. Na<sub>2</sub>S·9H<sub>2</sub>O and MoO<sub>3</sub> were gradually dissolved in deionized water and 4M HCl was added dropwisely to adjust the pH of the solution. The mixture was then transferred into autoclave and reacted for 2 h at 320 °C at 500 rpm in nitrogen or hydrogen atmospheres. The resultant black solid was filtered, washed using deionized water and ethanol, and then dried under nitrogen protection at 150 °C for 4 h. The catalyst recovery rate was calculated based on theoretical MoS<sub>2</sub> yield (Equation 1). The prepared MoS<sub>2</sub> catalysts at various Na<sub>2</sub>S to MoO<sub>3</sub> molar ratios were denoted as CAT-x (where x stands for the molar ratio of Na<sub>2</sub>S to MoO<sub>3</sub>). pH values of the initial synthesis solution and the final filtrate were determined using a pH meter (AB 15, Fisher Scientific). The concentrations of sulfur anions S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> in the filtrate

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were determined by an ion chromatography (DIONEX, DX-120). The reference MoS<sub>2</sub> was purchased from SPI supplies.

$$\text{Recovery} = \frac{\text{Actual } W_{\text{MoS}_2}}{\text{Theoretical } W_{\text{MoS}_2}} \times 100\% \quad \text{Equation 1}$$

**Catalyst characterization.** The transmission electron microscopic (TEM) images were recorded on a JEOL 2011 STEM (JEOL Ltd., Tokyo, Japan) operated under high-resolution mode and 200 keV electronical energy. The average length and thickness of MoS<sub>2</sub> crystals calculated using Equations 2 and 3 were expected values. At least 200 images of different MoS<sub>2</sub> particles (particle' refers to one MoS<sub>2</sub> crystalline) were used. The morphology of catalysts was also observed by Scanning electron microscopy (JEOL JSM6400 SEM).

$$\text{Average thickness } \bar{T} = \frac{\sum_{i=1,2,\dots} N_i T_i}{\sum_{i=1,2,\dots} N_i} = \frac{\sum_{i=1,2,\dots} N_i T_i}{N} \quad \text{Equation 2}$$

$$\text{Average length } \bar{L} = \frac{\sum_{i=1,2,\dots} N_i L_i}{\sum_{i=1,2,\dots} N_i} = \frac{\sum_{i=1,2,\dots} N_i L_i}{N} \quad \text{Equation 3}$$

where  $T$ ,  $L$ , and  $i$  stand for thickness, length, and number of layers, respectively.  $\bar{T}$  is the expected value of particle thickness and  $\bar{L}$  is the expected value of particle length. It is assumed that all  $i$ -th layered particles have the same thickness ( $T_i$ ). The length of  $i$ -th layered particles,  $L_i$ , is an average length of the particles that have the same numbers of layers ( $i$ ).  $N_i$  denotes the number of  $i$ -th layered particles and  $N$  represents the total number of particles.

The measurement of nitrogen adsorption-desorption isotherm was conducted on Autosorb-1 (Quantachrome Instruments). The specific surface area of catalyst was determined using the Brunauer-Emmett-Teller (BET) method. The total pore volume was calculated from the volume of nitrogen adsorbed at the relative pressure  $p/p_0$  0.995. Pore size distribution was analyzed from the isotherms by the Barrett-Joyner-Halenda (BJH) method.

The synthesized products were identified by the X-ray diffraction (XRD) pattern, which were recorded on a diffractometer (Bruker AXS D8 XRD) using CuK $\alpha$  radiation with the  $2\theta$  range of 5-85° and the scan speed of 1°/min.

The elemental analysis for molybdenum and sulfur was conducted on a JEOL-733 Superprobe, operating at 15 keV and 100 nA.

Temperature programmed reduction (TPR) was conducted on Autosorb-1 (Quantachrome Instruments). 100 mg catalyst was added in a quartz tube and heated to 700°C at a rate of 10°C/min, under a 50 ml/min flow of 2% H<sub>2</sub> in Ar. The consumption of H<sub>2</sub> and production of H<sub>2</sub>S was monitored by a mass spectrometer (RGA 200 Stanford Research Systems, Inc.).

The XPS measurements were performed on an AXIS 165 spectrometer (Kratos Analytical, University of Alberta). The base pressure in the analytical chamber was lower than  $3 \times 10^{-8}$  Pa. Monochromatic Al K $\alpha$  source ( $h\nu = 1486.6$  eV) was used at a power of 210 W. The analysis spot was 400  $\times$  700  $\mu\text{m}$ . The resolution of the

instrument is 0.55 eV for Ag 3d and 0.70 eV for Au 4f peaks. The survey scans were collected for binding energy extending from 1100 eV to 0 with pass energy of 160 eV and a step of 0.4 eV. 20 eV with a step of 0.1 eV was used for the pass-energy for high-resolution spectra. The number of scans varied from 3 to 30 to ensure a good signal to noise ratio.

The X-ray absorption near edge structure (XANES) spectra were obtained at a Soft X-ray Microanalysis Beamline (SXRMB) of the Canadian Light Source (CLS; Saskatoon, SK, Canada) equipped with a Si (1 1 1) double crystal monochromator. CLS, a 2.9 GeV, third generation storage ring, presently operates with an injection current of 250 mA. Samples were sulfided at 280°C in H<sub>2</sub> with dimethyl disulfide (DMDS) for 2h prior to measurement. Catalyst powders were uniformly dispersed on double-sided conducting carbon tapes under a dry nitrogen atmosphere. The measurements of S K-edge and Mo L<sub>3</sub>-edge were made in total electron yield by recording the sample drain current. Data analysis of the XANES spectra was performed using Athena software. Mo K-edge EXAFS spectra were recorded in the transmission mode at room temperature. Fourier transformation of the  $k/f$  ( $k$ ) weighted EXAFS data for  $\Delta k = 14 \text{ \AA}^{-1}$  ( $3 < k < 17$ ) was performed to obtain the radial distribution function around Mo. Detailed procedure was described elsewhere<sup>8</sup>.

**Hydrodesulfurization evaluation.** A batch reactor (Parker Autoclave Engineers) was employed in this experiment. A light cycle oil (LCO) with 1.46% S and 156 ppm N provided by a local refinery was used as feedstock. When the reactor was heated to 375 °C, LCO was introduced into the reactor. The weight ratio of catalyst to oil is 1:200. The hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) took place at 375 °C under H<sub>2</sub> gas pressure of 1400-1500 psi and 1000 rpm.

The total sulfur and nitrogen concentrations of the feedstock and the hydrotreated products were measured by a Sulfur/Nitrogen analyzer (9000 series, Antek Instruments Inc). The sulfur species were analyzed by a gas chromatography (GC) equipped with a non-polar VF-1ms capillary column (15 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ , max temperature: 325°C) and a PFPD detector (Varian 450). The following temperature profile was used: 2 min at 120°C, followed by a linear increase at 6°C /min to 170°C and a further increase at 20°C /min to 290°C, kept for 2 min. Density of the liquid oil was measured by a portable density meter (DMA 35N, Anton Paar GmbH, Graz, Austria) following ASTM 4052. The HDS/HDN conversion was calculated by subtracting the sulfur/nitrogen in the feed from product and divided by the sulfur/nitrogen in the feed. The calculation of rate constant  $k$  was based on pseudo-first order reaction.

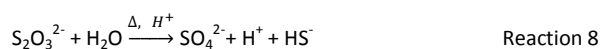
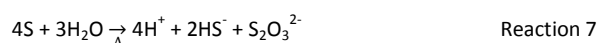
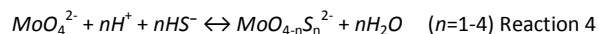
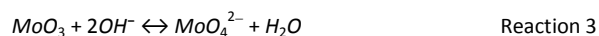
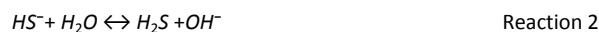
## Results and discussion

**Synthesis of MoS<sub>2</sub> in controlled medium.** A series of MoS<sub>2</sub> were synthesized in a medium of controlled pH values. The experimental parameters are shown in Table 1. MoO<sub>3</sub> and Na<sub>2</sub>S serve as molybdenum and sulfur sources, respectively. Without addition of HCl, precursor Na<sub>2</sub>S is first mixed in deionized water. Then MoO<sub>3</sub> powders were slowly stirred in and completely dissolved in the

basic solution. A clear yellow liquid with pH=12.59 was resulted, which liquid was then transferred to an autoclave for 2 hour hydrothermal reaction at 320°C. No solid catalyst was produced (entry 1). HCl was used to adjust the pH of resulted liquid mixture for all other entries. The clear yellow liquid turns to be dark red or brown once HCl was dropped in. Slightly reducing initial pH of the Na<sub>2</sub>S-MoO<sub>3</sub> solution from 12.59 to 10.61, a small amount of dark solid product was detected after the 2-hour synthesis (entry 2). The single 002 diffraction peak shown in the XRD pattern (Figure 1) confirmed that the solid product was amorphous MoS<sub>x</sub>. Continuous adjustment of the Na<sub>2</sub>S-MoO<sub>3</sub> solution to pH=5.70 (entry 3) leads to a satisfactory result. The yield of MoS<sub>2</sub> reached as high as 96% of its theoretical value. The obtained MoS<sub>2</sub> also shows satisfactory crystallinity as indicated by the XRD pattern (Figure 1). Further acidification of the Na<sub>2</sub>S-MoO<sub>3</sub> solution to pH=0.95 lead to an unsuccessful synthesis (entry 4) with significant amount of MoO<sub>2</sub> identified. This finding suggests that the initial pH of synthesis solution plays a key role in formation of nano crystalline MoS<sub>2</sub>.

Gaseous environment is also a factor that influences the conversion from MoO<sub>3</sub> to MoS<sub>2</sub>. With inert gas (nitrogen) filled in the reaction chamber, Na<sub>2</sub>S (S<sup>2-</sup>) acted as reduction agent and crystallized MoS<sub>2</sub> was successfully synthesized (entry 3, 5 and 6). However, reductive gas, e.g. hydrogen gas, can replace Na<sub>2</sub>S, function as a reduction agent during the synthesis, reducing MoO<sub>3</sub> to MoO<sub>2</sub> instead of formation of MoS<sub>2</sub> (Figure 1). Compared to entries 5 & 6, entry 7 has a very high pH of filtrate suggests little consumption of Na<sub>2</sub>S during the synthesis (Table 1). Reductive gas atmosphere has negative impact on the formation of crystallized MoS<sub>2</sub>.

**Synthesis reactions: identification of the key role of H<sup>+</sup> and HS<sup>-</sup>.** In the hydrothermal synthesis, crystalline MoS<sub>2</sub> is formed from the redox reaction of MoO<sub>3</sub> and Na<sub>2</sub>S, where Mo is reduced from Mo<sup>6+</sup> to Mo<sup>4+</sup>. Sodium sulfide is hydrolyzed in water to give strong alkaline solutions, as shown in Reaction 1 and Reaction 2. Due to acid nature, MoO<sub>3</sub> is easily dissolved in the basic solution to give MoO<sub>4</sub><sup>2-</sup> (Reaction 3), forming a clear yellow solution, as seen in entry 1 of Table 1. Unfortunately, MoO<sub>4</sub><sup>2-</sup> group is not directly responsible for the precipitation of solid MoS<sub>2</sub>.



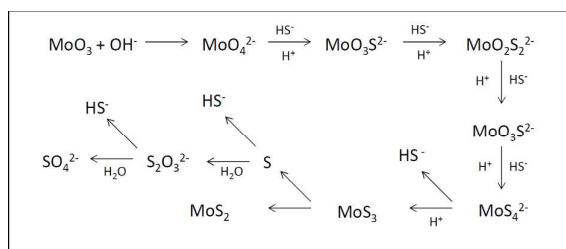
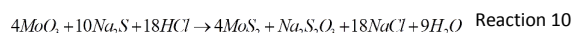
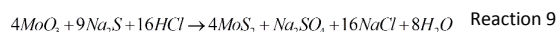
Addition of a few drops of HCl darkens the solution. Continuous titration of acids leads to precipitation of solids (entry 2), which is confirmed to be molybdenum sulfides (amorphous). H<sup>+</sup> appears to be a likely mechanistic requirement for the solid precipitation. It is known that MoO<sub>4</sub><sup>2-</sup> could react with H<sup>+</sup> and HS<sup>-</sup> to form tetrahedral sulfido-molybdenum complexes such as MoOS<sub>3</sub><sup>2-</sup>, MoO<sub>2</sub>S<sub>2</sub><sup>2-</sup>, MoO<sub>3</sub>S<sup>2-</sup> and MoS<sub>4</sub><sup>2-</sup><sup>10</sup>. This is a [H<sup>+</sup>]-dependent process and high [H<sup>+</sup>] is beneficial to O removal. The HS<sup>-</sup> was confirmed to be an effective incoming nucleophile to interact with O<sup>2-</sup> on Mo (VI)<sup>10</sup>. Sufficient [H<sup>+</sup>] and [HS<sup>-</sup>] is then led to initial precipitation of MoS<sub>x</sub> at room temperature<sup>5</sup>, which is the seed for production of crystal MoS<sub>2</sub><sup>7</sup>. Reaction 4 and Reaction 5 are proposed to describe the process.

HS<sup>-</sup> group plays a key role in the redox reaction. The hydrolysis of sulfide ion gives three species: S<sup>2-</sup>, HS<sup>-</sup> and H<sub>2</sub>S. Given the ΔH and ΔG<sup>16</sup>, rate constants can be calculated and then the molar concentrations of the three species at different pH can be determined. The theoretical acid-base behaviour of the S<sup>2-</sup>, HS<sup>-</sup> and H<sub>2</sub>S as a function of pH are shown in Figure 2. In strong alkaline solutions, sulfide ion presents in the deprotonated form as the sulfide dianion, S<sup>2-</sup> while in strong acid environment, it exists in the form of H<sub>2</sub>S. HS<sup>-</sup> becomes inadequate in both strong acid and strong alkaline synthesis solution. Without sufficient HS<sup>-</sup> Reaction 4 most likely stops and thus formation of intermediate complexes MoO<sub>4-n</sub>S<sub>n</sub><sup>2-</sup> becomes limited. The presence of S<sup>2-</sup> in strong alkaline solution cannot facilitate Reaction 4 to proceed (entry 2). This suggests that S<sup>2-</sup> plays no role in formation of MoS<sub>2</sub>. With strong acid solution, large amount of H<sub>2</sub>S produced and remains in gaseous phase due to its poor solubility in acidic solution. A certain amount of MoO<sub>2</sub> is formed (entry 4). On the other hand, HS<sup>-</sup> is produced in mild acid solution (entry 3, 5 and 6) and good yields of MoS<sub>2</sub> are obtained. Therefore, the formation and the production yield of crystalline MoS<sub>2</sub> is highly associated with [H<sup>+</sup>] and [HS<sup>-</sup>]. Both insufficient [H<sup>+</sup>] and overdose [H<sup>+</sup>] generate inappropriate pH of the synthesis solution, which results in unsatisfactory concentration of HS<sup>-</sup> and then little MoS<sub>2</sub> can be produced. Species HS<sup>-</sup> presents in neutral and basic solutions at room temperature. The pH for HS<sup>-</sup> group shifts to lower values at the hydrothermal synthesis temperature, 320°C, with an optimal range falling between 6 and 8. It is fair to comment that formation of MoS<sub>2</sub> is a [H<sup>+</sup>] and [HS<sup>-</sup>] dependent process. Up to this point, it seems that both weak acid and basic initial solutions are suitable for MoS<sub>2</sub> synthesis. A further discussion presents below to interpret whether mild acid or mild basic solution is optimal for the production of MoS<sub>2</sub>.

At synthesis temperature, 320°C, the precipitated solid MoS<sub>3</sub> from Reaction 5 is reduced to MoS<sub>2</sub> accompanying by production of sulfur element in Reaction 6 (Sulfur element was observed in the synthesis). Sulfur element reacts with water to S<sub>2</sub>O<sub>3</sub><sup>2-</sup> which may be further oxidized to SO<sub>4</sub><sup>2-</sup>. Reaction 7 and 8 are proposed. It is worth mentioning that H<sup>+</sup> and HS<sup>-</sup> are released in both redox Reactions. Generation of HS<sup>-</sup> directly enhances the precipitation of MoS<sub>3</sub> that is further reduced to MoS<sub>2</sub>. Produced H<sup>+</sup> lowers the pH value of final filtrate than its initial solution. Apparently, complete oxidation of sulfur to SO<sub>4</sub><sup>2-</sup> favors high yield of MoS<sub>2</sub>. S<sub>2</sub>O<sub>3</sub><sup>2-</sup> is more stable in basic aqueous solution than acid solution. S<sub>2</sub>O<sub>3</sub><sup>2-</sup> tends to be

oxidized to  $\text{SO}_4^{2-}$  in acidic solution. Two catalysts, named CAT-2.5 and CAT-3.0 (Table 2) were synthesized at weak acid and weak basic initial solutions. 96.2% and 55.1% of the theoretical yield were obtained respectively. Concentration of  $\text{SO}_4^{2-}$  in the filtrates directly corresponds to the  $\text{MoS}_2$  yield. This demonstrates that initial synthesis solution must be weak acid to achieve optimal yield of  $\text{MoS}_2$ . A reaction scheme for hydrothermal synthesis of  $\text{MoS}_2$  using  $\text{MoO}_3$  and  $\text{Na}_2\text{S}$  as precursors is summarized and shown in Scheme 1. The overall reactions are shown in Reaction 9 and Reaction 10 with  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SO}_4^{2-}$  as main oxidized product, respectively.

**Adjustment of S/Mo ratio.** Six atomic ratios of sulfur to molybdenum of the precursors, ranging from 2 to 5, are prepared and the results are shown in Table 2. The stoichiometric S/Mo molar ratio in  $\text{MoS}_2$  is 2. Since a portion of  $\text{Na}_2\text{S}$  acts as redox mediator during the synthesis, the S/Mo ratios of the obtained  $\text{MoS}_2$  are inevitably lower than its corresponding S/Mo ratios of precursors. Under-dosed  $\text{Na}_2\text{S}$  inevitably leads to excessive  $\text{MoO}_3$  in the synthesis, e.g. CAT-2.0. Molybdenum-dominant solid particles are generated and embedded between the layered  $\text{MoS}_2$ , resulting in poor uniformity of  $\text{MoS}_2$  (Figure 3). On the other hand, excessive  $\text{Na}_2\text{S}$  results in strong alkaline synthesis solution and thus scarce solid catalyst is formed, e.g. CAT-5.0. The XRD patterns and electron diffraction rings of the four catalysts, as shown (Figures 4 and 5), confirm the successful synthesis of  $\text{MoS}_2$ .



Scheme 1. Proposed reaction scheme for synthesis of  $\text{MoS}_2$

**Determination of  $\text{MoS}_2$  chemical structure.** Their S/Mo ratios of three catalysts, CAT-2.5, CAT-3.0, and CAT-3.75 determined by microprobe analysis are 1.85, 2.05 and 2.10, respectively (Table 3). The bulk and surface chemical states of the catalysts are identified by XANES and XPS spectra. The S K-edge (a) and Mo  $L_3$ -edge (b) XANES spectra are displayed in Figure 6. The spectra acquired simultaneously in total electron yield (TEY) with an estimated 100 nm in probing depth are more bulk sensitive. The peak (whiteline) at 2471eV (peak A) is due to the S 1s to 3p dominated transitions of S in -2 oxidation state<sup>11</sup>. According to the typical periodic slab model<sup>12</sup>, two types of S coordination are noticed on the  $\text{MoS}_2$  surface. Thus, two broad peaks (B and C) located at 2478-2484eV and 2489-2495eV may be attributed to S pyramidal coordination on basal planes and S hexogen structure, respectively. The Mo  $L_3$ -edge (whiteline) observed at 2524eV with the shoulder peak (2532eV) is associated with the electron transition from Mo  $2p_{3/2}$  to vacant 4d

<sup>13, 14</sup> and the trigonal prismatic coordination of Mo atoms, respectively<sup>13, 15</sup>. Apparently, all spectra exhibit identical vacancy state as the reference, indicating a high purity of  $\text{MoS}_2$ .

Typical XPS spectra of S 2p core level region of as-prepared  $\text{MoS}_2$  catalysts are shown in Figure 7. All the spectra exhibit typical profiles of pure  $\text{MoS}_2$  with strong S and Mo peaks. The S 2p spectra contain the S  $2p_{3/2}$  (161.8 eV) and the S  $2p_{1/2}$  (163.0 eV) spin-orbit doublet with intensity ratio of around 2:1, which are indexed to a typical spectrum of sulfide  $\text{S}^{2-}$  ion<sup>17</sup>. Small but unmistakable differences in chemical shift are also observed among the catalysts. S  $2p_{3/2}$  peak of CAT-2.5 slightly shifts to lower energy, whereas the peak of CAT-3.0 shifts to higher energy (circled), giving the electron binding energy order of CAT-2.5 < CAT-3.75 < CAT-3.0.

The TPR traces of sulfide catalysts are shown in Figure 8, illustrating the consumption of  $\text{H}_2$  and the production of  $\text{H}_2\text{S}$  in the temperature range of 100-500°C. For  $\text{H}_2$  consumption, typical peaks for weakly bonded sulfur are observed in the low temperature range of 200-370°C. It is commonly accepted that the consumption of  $\text{H}_2$  can reflect the number of weakly bonded sulfur on the surface of catalysts<sup>12, 18</sup>.  $\text{H}_2$  is firstly dissociative adsorbed on two sulfur dimers which are bonded on adjacent Mo sites, creating two S-Mo-SH groups. Then one hydrogen atom transfers from one group to another to form a SH-Mo-SH group. Finally,  $\text{H}_2\text{S}$  is released from an active site of \*-Mo-S, where \* refers to the sulfur vacancy<sup>12</sup>. However, one assumption is made that the two sulfur dimers bonded on the same Mo atom. Otherwise, the SH-Mo-SH group cannot be formed properly, in which case, the system needs to be stabilized by a state of two \*-Mo-SH groups, thus, no  $\text{H}_2\text{S}$  can be released. Therefore, the difference between  $\text{H}_2$  consumption and  $\text{H}_2\text{S}$  production in the TPR spectrum may differentiate the existing active sites from those that can be potentially formed. For catalyst CAT-2.5, the TPR spectrum shows a large  $\text{H}_2$  consumption but no  $\text{H}_2\text{S}$  production. The absence of a  $\text{H}_2\text{S}$  peak suggests a high deficiency of S on the surface. The wide peak also suggests inhomogeneous defect sites. For the CAT-3.0 and CAT-3.75, the  $\text{H}_2\text{S}$  content is highly associated with the  $\text{H}_2$  consumption, indicating the high coverage of S on the surface. It is noted from the TPR spectra that the initiation temperature for releasing  $\text{H}_2\text{S}$  is lower on CAT-3.75 than CAT-3.0 and the  $\text{H}_2\text{S}$  curve is wider. This may be due to the different type of sulfur on the catalyst surface. CAT-3.75 contains over-stoichiometric sulfur that may be weakly bonded to catalyst thus easy to eliminate. In contrast,  $\text{H}_2\text{S}$  curve over CAT-3.0 barely has none-stoichiometric sulfur. Sulfur species are uniformly bonded within CAT-3.0 so that  $\text{H}_2\text{S}$  peak is sharp.

Figure 9 shows the Fourier transform of the Mo K absorption edge for all the three catalysts. The spectra show two notable peaks corresponding to Mo-S (peak A) and Mo-Mo (peak B)<sup>15</sup>. The first largest peak at 1.90Å (phase shift uncorrected) arises from sulfur atoms in the first coordination sphere around Mo atoms, while the second peak at 2.86Å (phase shift uncorrected) is due to the nearest neighbor Mo atoms. The EXAFS results exhibit a similar  $\text{MoS}_2$  structure. The only difference noticed is that the Mo-Mo bond for CAT-2.5 is lower than the other two catalysts. The calculated coordination number (CN) from the Fourier transform is shown in

Table 4. It is noticed that all the three catalysts exhibit lower CN than the MoS<sub>2</sub> in bulk. Similar to the spectra, the smallest CN of Mo-Mo is observed with CAT-2.5, indicating more disordered matrix on the surface.

**Characterization of textural structure.** The morphologies of the three catalysts with different S/Mo molar ratios are revealed by TEM (Error! Reference source not found.10). The dark thread-like lines shown in the fringes are the reflection of (0 0 2) lattice plane of the crystalline MoS<sub>2</sub>, representing the stacked slabs. All the catalysts show dendritic morphologies and layered nanocrystallines. A large number of curved slabs are observed on the catalysts (circled in Figure 10), which may result in more defects created on the basal plane<sup>20</sup>. The three catalysts have similar size distributions. Table 3 shows narrow size ranges of 15.8-17.9 nm and 2.3-2.6nm, for the average slab length and thickness, respectively. The average lengths obtained in the present work are similar to the catalysts using (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> (ATM) as precursors<sup>20, 10</sup> while are significantly shorter than the crystallized MoS<sub>2</sub> synthesized by Li et al. who reported 50 nm in length<sup>8</sup>. Figure 11 shows FE-SEM images of MoS<sub>2</sub>. For both catalysts, thread-like MoS<sub>2</sub> crystals are associated in bundles and twisted together forming a flower-like morphology. The images exhibit nanosized particles with an average size of 100-200 nm. Mesopores over 10 nm are formed in between the crystals, as shown in the grey part surrounded by white MoS<sub>2</sub> layers. A slight difference observed is that CAT-2.5 looks more dendritic, while CAT-3.75 crystal favors growth on the boundary of particles.

The three catalysts have large surface area ranging from 200 to 262 m<sup>2</sup>/g (Table 3). A high pore volume of 0.9 to 2.3 m<sup>3</sup>/g is also observed, which is much higher than that of other catalysts previously reported<sup>20</sup>.

**Catalytic activities.** Catalysts synthesized under hydrothermal method with Na<sub>2</sub>S and MoO<sub>3</sub> precursors are subjected to undergo a performance test on HDS, HDN, and hydrocracking activities, using LCO (Figures 12, 13 and 14). The initial HDS rate constants in the first hour for all catalysts are higher than 2×10<sup>-4</sup> s<sup>-1</sup> g cata<sup>-1</sup>. The rates drop by half in the second hour and a further 50% off was observed in the rest of the reaction. The decrease of reaction rates for each catalyst along with reaction time is due to the fact that LCO contains both easy (benzothiophen and its derivatives) and hard sulfur (dibenzothiophen and its derivatives) compounds (Table 5). Nevertheless, it is still observable that CAT-2.5 presents the highest HDS activity and CAT-3.0 has the lowest activity. CAT-3.75 positions in between. CAT-2.5 also exhibits the highest HDN (Figure 12) and hydrocracking (seen from the product density in Figure14) ability.

The relationship between the properties and activities is plotted in Figure 15. The ratio of Mo atoms on edge to the total Mo atoms is calculated based on the slabs length, the method reported by Vrinat et. al.<sup>22</sup>. Apparently, if only Mo on the edges were active sites, the activity order would be totally opposite. It is indicated that the imperfect basal plane is important for the activities, and defects should be also largely located on the curved or twisted basal plane. This can be verified with TEM images; all the catalysts show highly curved morphologies. In particular, CAT-2.5 exhibits

more blurred slabs, indicating more imperfect crystalline structure than the other two, which explains the highest activity of the three. There are also no clear relationship between activity and surface area (Figure 15 b). This statement has been mentioned by several researchers<sup>21</sup>. Certain surface area is essential to provide more accessible active sites, however, effect gets infinitesimal when sufficient exposed area are provided. Most of the calculated area is inert to the reaction.

As discussed in TPR, the hydrogen adsorbed is highly related to the active sites on the catalyst. From Figure 15 c, it's easy to see that there is a good linear relationship between the H<sub>2</sub> adsorption sites (Table 6) and HDS rate constant. The amount of active sites (as in H<sub>2</sub> reacted sites) reflects the catalyst activities. Similar phenomenon also can be seen from S/Mo atomic ratio macroscopically. The lack or excess of sulfur might be related to the deformation of the crystal structure and defects on the catalysts. When S/Mo ratio is lower than the stoichiometric atom ratio of MoS<sub>2</sub> (2), defect sites might be already generated due to the deficiency of S. On the other hand, over-stoichiometric sulfur may exist in the form of S<sub>2</sub><sup>2-</sup> species, which can react with H<sub>2</sub> to form -HS species and enhance hydrotreating reaction. As more defects are created during the synthesis, the MoS<sub>2</sub> would deviate further from the perfect crystal, in other words, S/Mo ratio would further deviate from the stoichiometric number 2. This is consistent with our results that MoS<sub>2</sub> has the highest difference with largest hydrogen adsorption sites. It is also showing excellent relationship between the difference and the activities, as in Figure 15 d.

Relationship also can be seen from binding energy, coordination, disorder and activities. Although the difference is not obvious, it's also found the binding energy and MoS<sub>2</sub> cluster size (reflected by Mo-Mo coordination number) show the similar trend of HDS activity.

## Conclusions

Novel nanocrystalline MoS<sub>2</sub> were successfully synthesized via hydrothermal method using commercially available MoO<sub>3</sub> and Na<sub>2</sub>S. The synthesis mechanism of hydrothermal approach was investigated and the reaction pathways were proposed for the formation of crystalline MoS<sub>2</sub>. [HS<sup>-</sup>] in the synthesis solution is identified as a key factor. Insufficient [HS<sup>-</sup>] can lead to a failure synthesis. Mild acidic medium is essential for a successful synthesis. The ratio of reactants, MoO<sub>3</sub> and Na<sub>2</sub>S, is important to the nanocrystal structure and the yield. Excessive MoO<sub>3</sub>/Na<sub>2</sub>S ratio may result in poor uniformity of MoS<sub>2</sub>. Various characterization techniques are employed to assess the structure of synthesized catalysts. The three catalysts synthesized at the proper range of Na<sub>2</sub>S/MoO<sub>3</sub> (from 2.5 to 3.75 in the work) have nanosized structure, large surface area, and high pore volume (mesopores). More defects at the rims are found on the CAT-2.5 than the other two catalysts. HDS activity of hydrotreating LCO also exhibits a decreasing order of CAT-2.5>CAT-3.75>CAT-3.0.

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## References

1. R. Tenne, *Angew. Chem. Int. Ed.*, 2003, **42**, 5124-5132.
2. R. Tenne, *Nat Nano*, 2006, **1**, 103-111.
3. X. Hu, W. Zhang, X. Liu, Y. Mei, Y. Huang, *Chem. Soc. Rev.*, 2015, **44**, 2376-2404.
4. X. H. Zhang, H. Tang, M. Q. Xue, C. S. Li, *Mater. Lett.*, 2014, **130**, 83-86.
5. Y. Araki, Y. Iwata, Y. Miki, K. Honna, N. Matsubayashi, H. Shimada, in: *Hydrotreatment and Hydrocracking of Oil Fractions* by B. Delmon, G.F. Froment, P. Grange (Eds.), Elsevier Science B.V., The Netherlands, 1999, pp. 69-76.
6. H. Zhang, H. Lin;Y. Zheng;Y. Hu;A. MacLennan *Appl. Catal., B*, 2015, **165**, 537-546.
7. W.J. Li, E.W. Shi, J. M.Ko, Z.Z. Chen, H. Ogino, T. Fukuda, *J. Cryst. Growth*, 2003, **250**, 418-422.
8. Y. Tian, Y. He, J. Shang, Y.F. Zhu, *Acta Chim Sinica*, 2004, **62**, 1807-1810.
9. C. Calais, N. Matsubayashi, C. Geantet, Y. Yoshimura, H. Shimada, A. Nishijima, M. Lacroix, M. Breyse, *J. Catal.*, 1998, **174**, 130-141.
10. B. Yoosuk, J.H. Kim, C. Song, C. Ngamcharussrivichai, P. Prasassarakich, *CATAL TODAY*, 2008, **130**, 14-23.
11. V. R. Surisetty, Y. F. Hu, A.K. Dalai, J. Kozinski, *Appl. Catal., A*, 2011, **392**, 166-172.
12. N. Dinter, M. Rusanen, P. Raybaud, S. Kasztelan, P. da Silva, H. Toulhoat, *J. Catal.*, 2009, **267**, 67-77.
13. H. Aritani, T. Tanaka, T. Funabiki, S. Yoshida, K. Eda, N. Sotani, M. Kudo, S. Hasegawa, *J. Phys. Chem.*, 1996, **100**, 19495-19501.
14. H. Aritani, O. Fukud, A. Miyaji, S. Hasegawa, *Appl. Surf. Sci.*, 2001, **180**, 261-269.
15. Y.V. Zubavichus, A.S. Golub, Y.N. Novikov, Y.L. Slovokhotov, A.N. Nesmeyanov, P.J. Schilling, R.C. Tittsworth, *J. Phys. IV*, 1997, **7**, 1057-1059.
16. Robert G Mortimer, *Physical chemistry*, San Diego: Harcourt/Academic Press, ©2000, 2<sup>nd</sup> ed.
17. R.S. Smart, W.M. Skinner, A.R. Gerson, *Surf. Interface Anal.*, 1999, **28**, 101-105.
18. X.S. Li, Q. Xin, X.X. Guo, P. Grange, B. Delmon, *J. Catal.*, 1992, **137**, 385-393.
19. A.K. Datye, S. Srinivasan, L.F. Allard, C.H.F. Peden, J.R. Brenner, L.T. Thompson, *J. Catal.*, 1996, **158**, 205-216.
20. E. Devers, P. Afanasiev, B. Jouguet, M. Vrinat, *Catal. Lett.*, 2002, **82**, 13-17.
21. G. Alonso, G. Berhault, A. Aguilar, V. Collins, C. Ornelas, S. Fuentes, R.R. Chianelli, *J. Catal.*, 2002, **208**, 359-369.
22. M. Vrinat, M. Breyse, C. Geantet, J. Ramirez, F. Massoth, *Catal. Lett.*, 1994, **26**, 25-35.

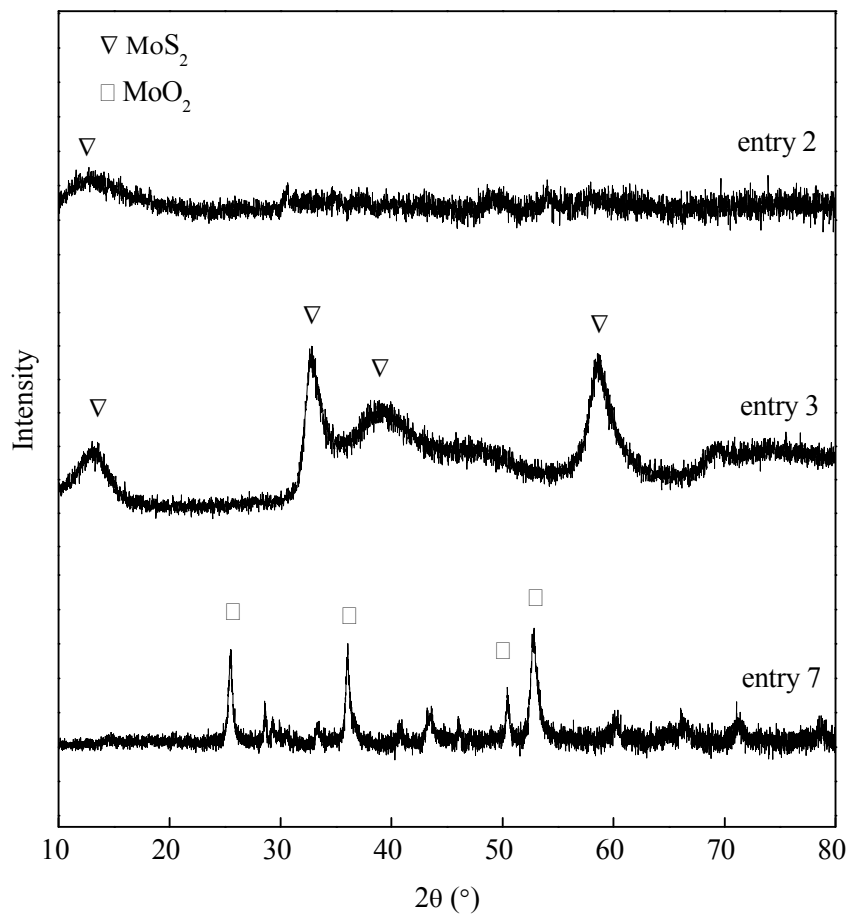


Figure 1 XRD spectra of product in different gas environment



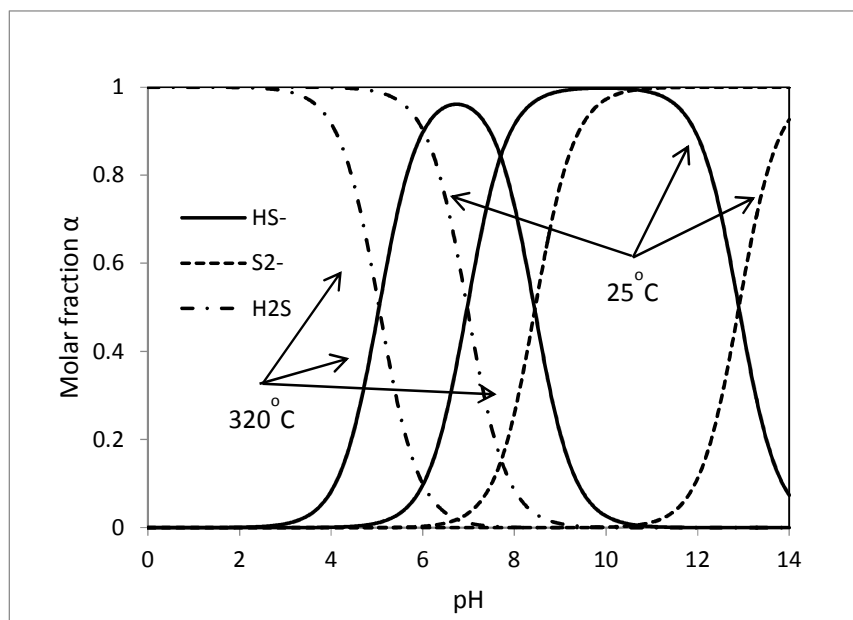


Figure 2 Influence of pH on the acid-base behaviour of the dissolved  $\text{Na}_2\text{S}$  at  $25^\circ\text{C}$  and  $320^\circ\text{C}$ .

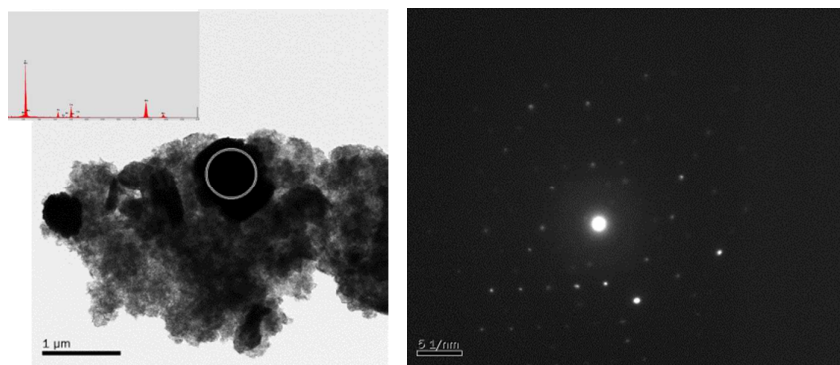


Figure 3 TEM image and diffraction pattern

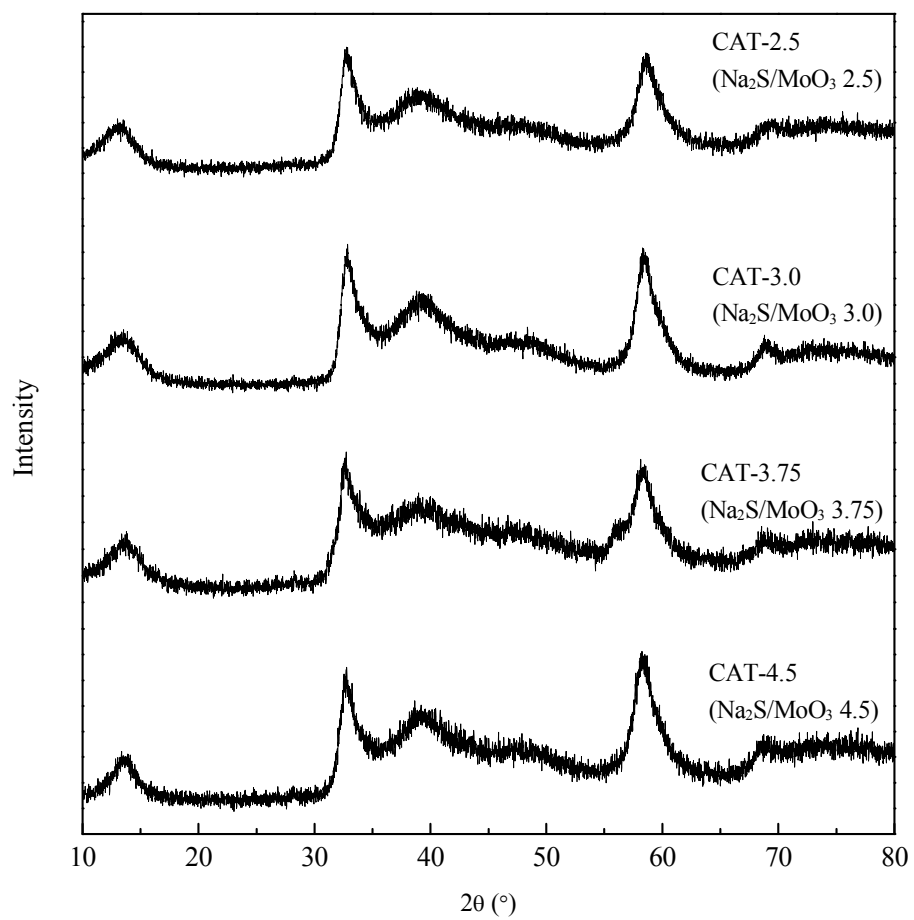


Figure 4 XRD spectra of MoS<sub>2</sub> synthesized at different Na<sub>2</sub>S addition

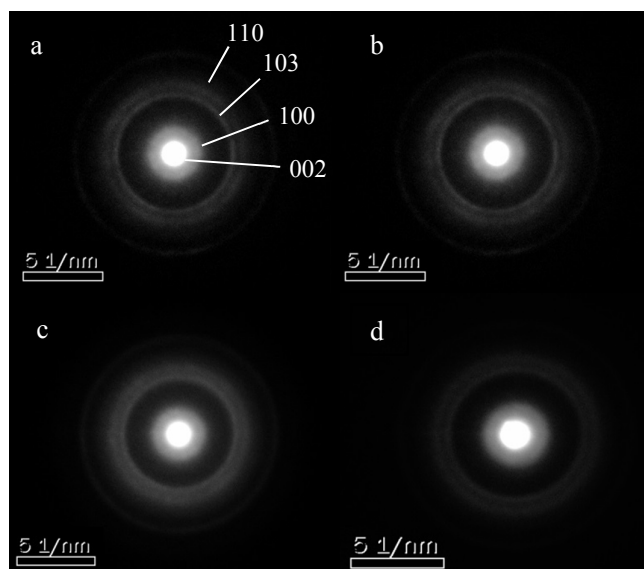


Figure 5 Diffraction rings of MoS<sub>2</sub> at different Na<sub>2</sub>S /MoO<sub>3</sub> ratios

a: CAT-2.5; b: CAT-3.0; c: CAT-3.75; d: CAT-4.5

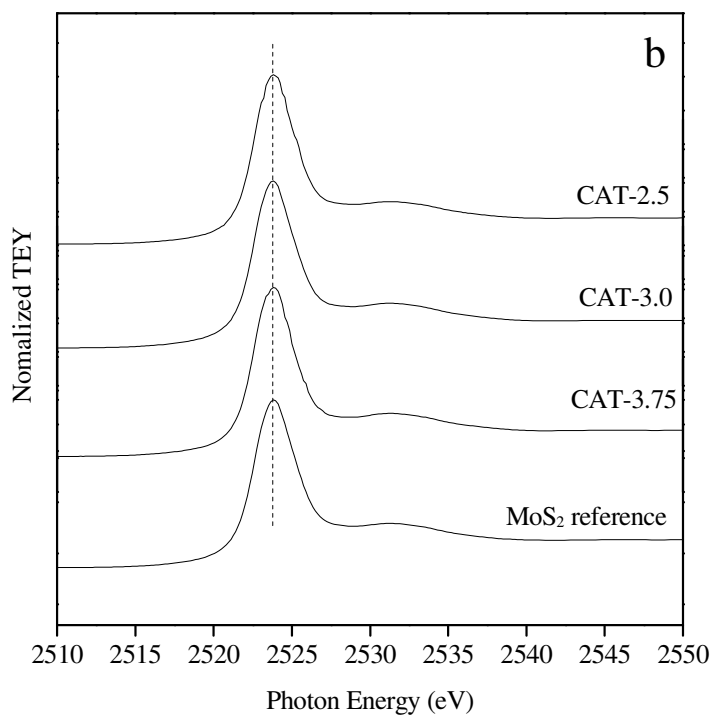
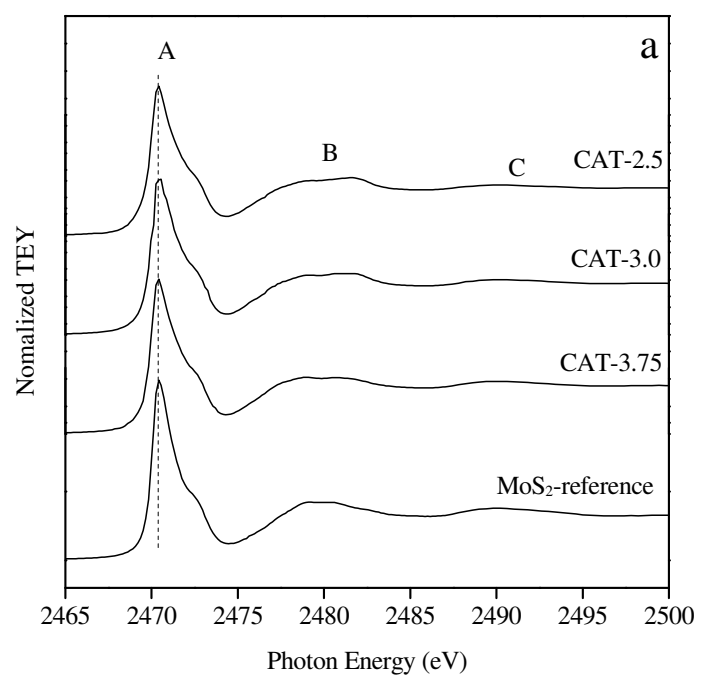


Figure 6 S K-edge (a) and Mo L<sub>3</sub>-edge (b) XANES spectra of unsupported MoS<sub>2</sub>

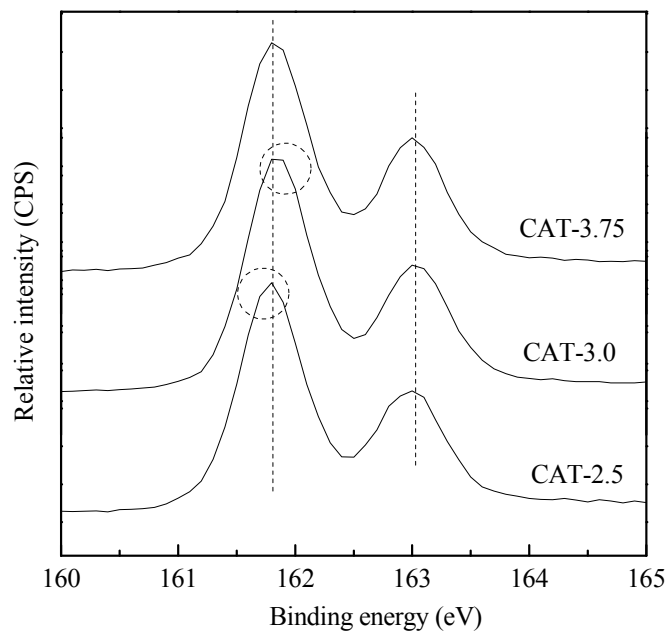


Figure 7 S 2p XPS spectra of unsupported MoS<sub>2</sub>

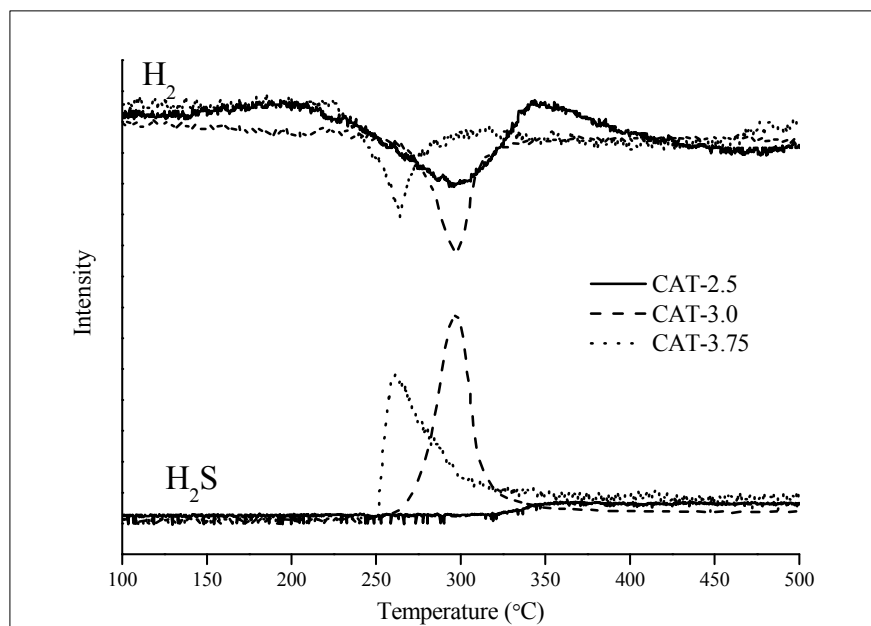


Figure 8 H<sub>2</sub> consumption and H<sub>2</sub>S production during TPR treatment

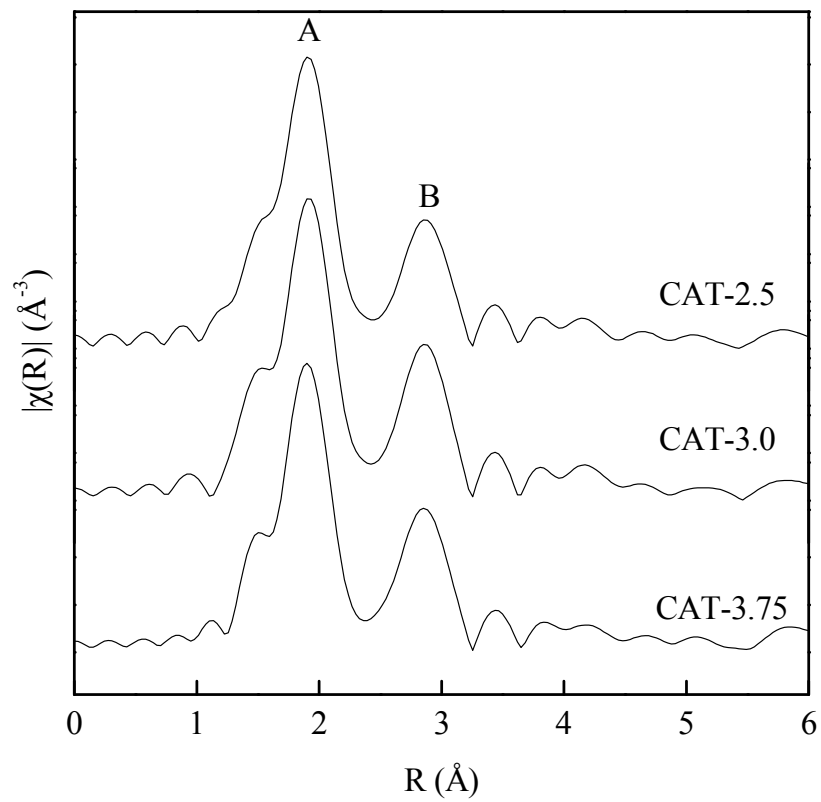


Figure 9 Fourier transformed EXAFS spectra of unsupported MoS<sub>2</sub>



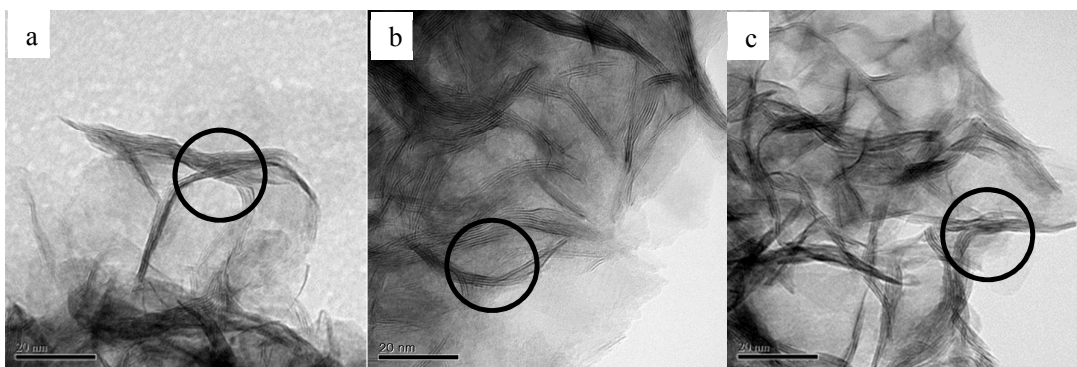


Figure 10 TEM images of MoS<sub>2</sub> at different Na<sub>2</sub>S /MoO<sub>3</sub> ratios

a: CAT-2.5; b: CAT-3.0; c: CAT-3.75.

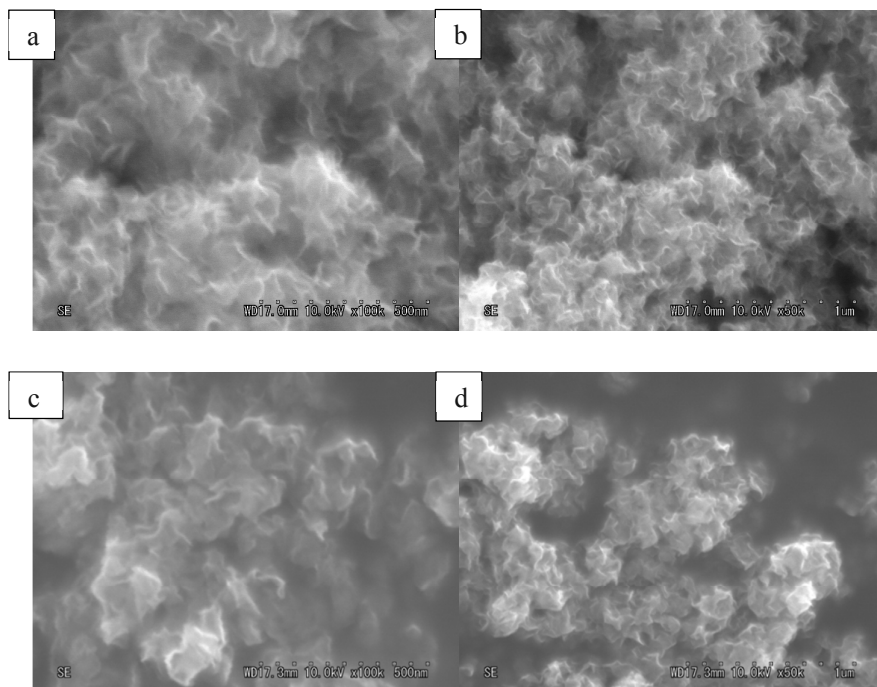


Figure 11 SEM images of unsupported MoS<sub>2</sub>

a,b: CAT-2.5; c,d: CAT-3.75

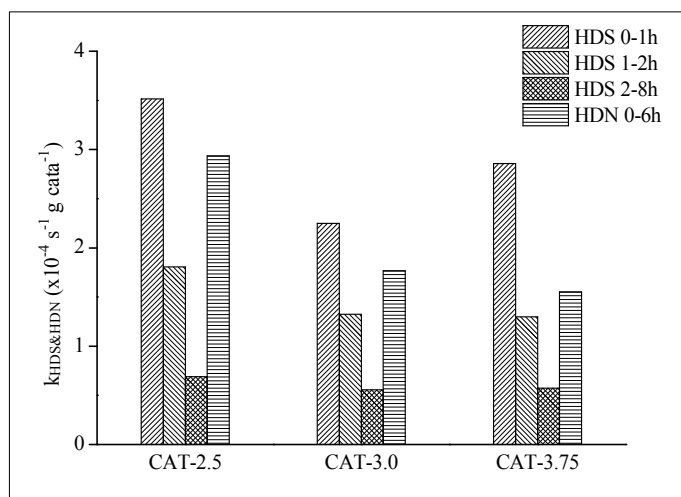


Figure 12 HDS and HDN activities of unsupported MoS<sub>2</sub> catalysts

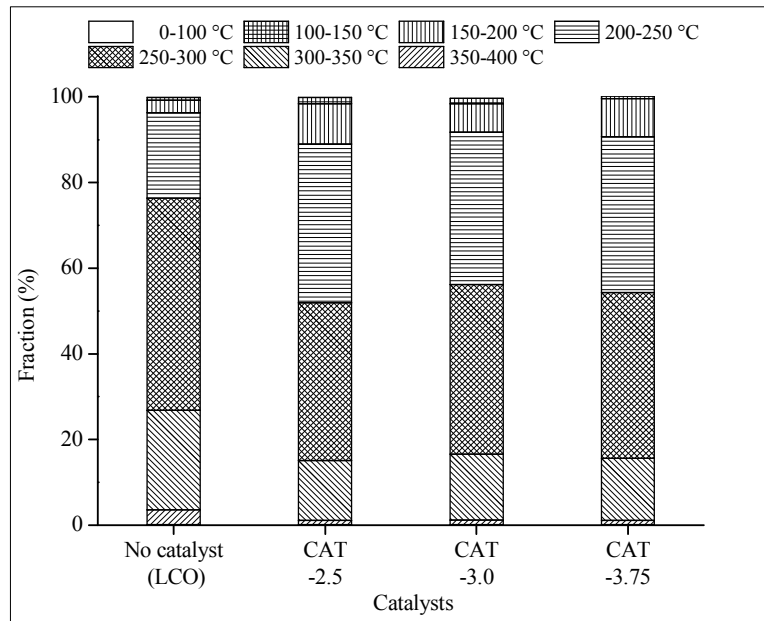


Figure 13 Boiling point distribution of LCO and hydrotreated product

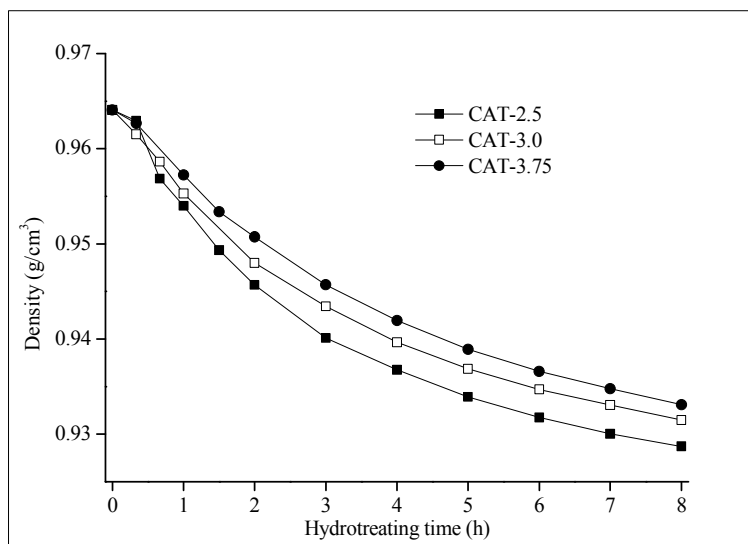


Figure 14 Density of hydrotreated LCO by unsupported MoS<sub>2</sub> catalysts (hydrocracking)

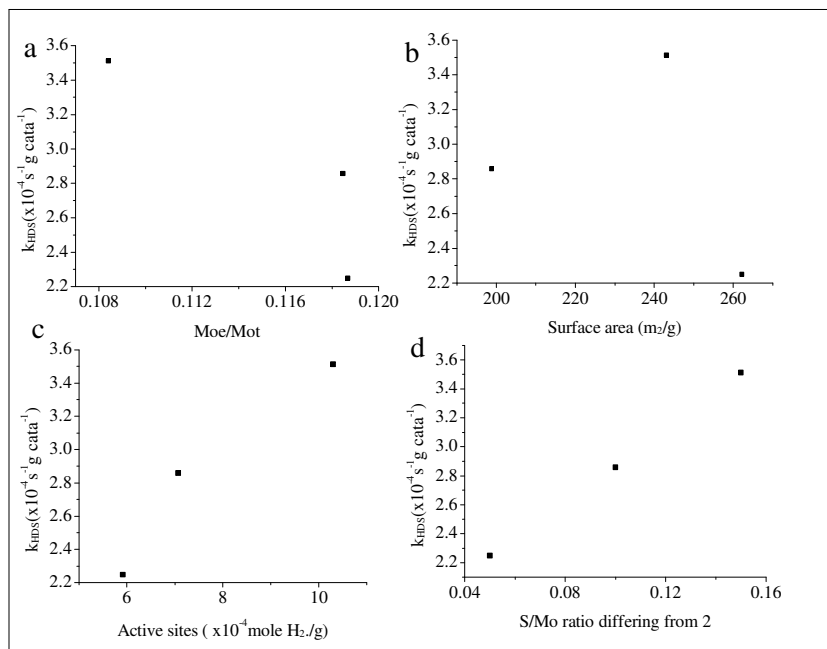


Figure 15 Relationship between catalyst properties and activities

In a, Moe: Number of Mo atoms on the edge; Mot: Number of total Mo atoms (both calculated on the TEM images)

Table 1 Reaction conditions and products

Entry	Reaction Conditions				Products		
	Na <sub>2</sub> S/ MoO <sub>3</sub> Molar Ratio	HCl/MoO <sub>3</sub> Ratio	Gas Atmosphere (psi)	Initial pH	Filtrate pH	Solid Product	Solid Recovery (%)
1	2.50	0	N <sub>2</sub> (15)	12.59	13.29	Little solid	---
2	2.50	2.25	N <sub>2</sub> (15)	10.61	12.92	Amorphous MoS <sub>x</sub> (x>2)	<1
3	2.50	4.50	N <sub>2</sub> (15)	5.70	2.61	Nanocrystalline MoS <sub>2</sub>	96
4	2.00	4.50	N <sub>2</sub> (15)	0.95	---	MoO <sub>2</sub> , MoS <sub>2</sub> MoS <sub>x</sub> (x<<2)	---
5	3.75	7.00	N <sub>2</sub> (15)	4.07	3.02	Nanocrystalline MoS <sub>2</sub>	95
6	2.50	4.50	N <sub>2</sub> (200)	5.70	2.53	Nanocrystalline MoS <sub>2</sub>	~100
7	2.50	4.50	H <sub>2</sub> (200)	5.70	9.85	MoO <sub>2</sub>	---

Table 2 Effect of Na<sub>2</sub>S/MoO<sub>3</sub> molar ratio on MoS<sub>2</sub> recovery and composition

Catalysts name	Initial S/Mo	S/Mo in final MoS <sub>2</sub>	Filtrate color	MoS <sub>2</sub> Yield (%)	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> Conc. (g/L)	SO <sub>4</sub> <sup>2-</sup> Conc. (g/L)
CAT-2.0	2.00	-	Colourless	little		
CAT-2.5	2.50	1.85	Colourless	96.2	0.13	3.1
CAT-3.0	3.00	2.05	Yellow	55.1	1.74	1.28
CAT-3.75	3.75	2.10	Orange	25.6	1.53	0.31
CAT-4.5	4.50	1.95	Red	11.8	1.23	0.05
CAT-5.0	5.00	-	Grey	<1.0	0.18	0



Table 3 Texture properties and elemental composition of unsupported MoS<sub>2</sub>

Catalysts	S/Mo ratio	Average Slab length (nm)	Average Slab thickness (nm)	BET surface area (m <sup>2</sup> /g)	Total pore volume (m <sup>3</sup> /g)
CAT-2.5	1.85	17.4	2.3	231.1	2.3
CAT-3.0	2.05	15.8	2.6	262.2	1.6
CAT-3.75	2.1	17.9	2.5	198.9	0.9

Table 4 Structural parameters resulting from the Mo K-edge Fourier-filtered  $k^3$ -weighted EXAFS functions of catalysts

Sample	Path	CN	R (Å)	$E_0$ (eV)	$R_f$
MoS <sub>2</sub>	Mo-S	6	2.413	-	-
	Mo-Mo	6	3.166		
CAT-2.5	Mo-S	5.0±0.1	2.408±0.003	2.2±0.6	0.0047
	Mo-Mo	4.0±0.3	3.164±0.004		
CAT-3.0	Mo-S	5.0±0.2	2.415±0.004	2.7±0.7	0.0053
	Mo-Mo	4.7±0.3	3.173±0.004		
CAT-3.75	Mo-S	4.8±0.2	2.406±0.005	1.7±0.9	0.0071
	Mo-Mo	4.6±0.4	3.171±0.006		

Estimated error:  $\sigma^2_{\text{Mo-S}} \pm 0.002 \text{ \AA}^2$ ,  $\sigma^2_{\text{Mo-Mo}} \pm 0.004 \text{ \AA}^2$ .

Table 5 Major sulfur compounds composition of LCO

	S in BT-MBT <sup>*</sup> (ppm)	S in DBT-MDBT <sup>#</sup> (ppm)	Total S (ppm)
LCO	9193.3	5371.5	14564.7

<sup>\*</sup> Benzothiophen-methyl benzothiophen, <sup>#</sup> Dibenzothiophen-methyl dibenzothiophen

Table 6 The calculated the H<sub>2</sub> consumption and H<sub>2</sub>S production

Catalysts	H <sub>2</sub>		H <sub>2</sub> S	
	Amount (x10 <sup>-4</sup> mol/g cata)	Peak temperature (°C)	Amount (x10 <sup>-4</sup> mol/g cata)	Peak temperature (°C)
CAT-2.5	10.3	296.2	---	---
CAT-3.0	5.9	291.9	3.6	294.3
CAT-3.75	7.1	264.1	4.3	269.5