# Investigation of sulfur-resistant, highly active unsupported MoS$_2$ catalysts for synthetic natural gas production from CO methanation

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## ABSTRACT

This paper reports on an enhanced activity of sulfur-resistant methanation catalyst by introducing sulfur powder instead of toxic H$_2$S in catalyst preparation. Ammonium heptamolybdate (AHM) was a suitable precursor for this catalyst preparation based on consideration of economy and activity. The effect of S/AHM weight ratio and sulfidation atmosphere on catalyst methanation performance was studied and the optimum S/AHM ratio was 3. Sulfidation atmosphere affected not only methanation activity but also the structure and morphology of the catalysts. The catalyst treated in inert atmosphere exhibited relatively the highest methanation activity with CO conversion as high as 88.2%, which was approaching the thermodynamic equilibrium value. The catalysts characterization results indicated that the as-prepared catalyst at S/AHM ratio as 3 had relatively higher specific surface area and larger pore volume than those with other S/AHM ratio. The MoS$_2$ particles were poorly crystallized with long and straight multi-layered slabs. For the catalyst treated in nitrogen environment, more weakly-bonded sulfur species existed on the surface and more sulfur vacancies resided on the edge planes of MoS$_2$ particles, which are considered to be the active sites for methanation.

## 1. Introduction

As the need for oil and natural gas drastically increases throughout the world, many industrialists and scientists have realized the necessity of producing substitute natural gases in order to meet increasing energy demand. For this purpose, methanation process using syngas as raw material from coal gasification has been the subject of extensive research [1,2]. The research on methanation is important not only because of the increase need for a high Btu fuel, but also because that low concentrations of undesirable carbon monoxide in hydrogen-rich gases can be removed by methanation and the use of methane as a carbon source has increased in the chemical industry [3]. The commonly used methanation catalysts are transition metals like Ni which have high methanation activities [2,4]. However, these metals have certain operating limitations because of their sensitivities to sulfur poisoning. To avoid this problem, molybdenum catalysts supported on alumina [5,6] or other supports and promoted with Co or Ni [6] have received more attention in recent years due to their sulfur-resistant properties [7].

As reported, the catalytic properties of supported and unsupported Mo-based catalysts are nearly the same for hydrotreating process, so unsupported Mo-based catalysts can be regarded as model catalysts for catalytic mechanism study [8], which is very helpful for the design

of supported catalysts. Unsupported Mo-based catalysts can be prepared by various methods including thermal decomposition of thiosalts [9], solution reactions [10,11], hydrothermal and solvothermal processes [12,13]. The thiosalt decomposition is proved to be an effective and reproducible method for obtaining better catalysts [14]. It is reported that unsupported catalysts prepared by thermal decomposition of thiosalts exhibited higher activity than those prepared by other methods [15,16]. The sulfiding process of molybdenum precursors for both supported and unsupported catalysts has also been studied previously [17–19]. The ex-situ or in-situ activation of the precursor has been studied extensively [20–22]. Usually, the activation is achieved by exposing molybdenum precursor in a gaseous mixture containing hydrogen sulfide, resulting in highly active MoS$_2$ catalysts. Lauritsen [23] and his co-workers found the structure–activity relationship of MoS$_2$ obtained under different reducing and sulfiding conditions based on atom-resolved scanning tunneling microscope (STM) analysis combined with DFT calculation. Some studies have indicated that the catalytic activity was not directly related to the surface area but was closely associated with the edge planes of MoS$_2$ layers and the morphology of the catalyst [24], particularly with sulfur vacancies or surface defects formed on the edge sites [25]. It has been recognized that the creation of sulfur vacancies, or unsaturated sites at the edges plays a vital role for absorbing H$_2$ and other reactive gases.

AHM is commonly used in preparing supported Mo-based catalysts for hydrodesulfurization process [26]. However, little attention has been paid on the investigation of the performance of unsupported

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Mo-based catalysts prepared from AHM precursor for methanation reaction. For catalysts prepared from precursors containing oxygen, sulfidation plays a key role for determining the catalytic performance of such catalysts. After sulfidation, whether molybdenum oxysulfide or $MoS_2$ exists on the catalyst needs to be investigated, which is correlated with the activity. Unsupported molybdenum sulfide catalyst had been prepared in laboratory-scale and presented good performance for catalyzing methanation reactions [27]. It is therefore believed that Mo-based sulfides might be promising catalysts for methanation.

In this work, we tried to improve the methanation activity of unsupported Mo-based catalysts by introducing sulfur powder in catalyst preparation and to provide an alternative way to prepare methanation catalysts in an environmentally-friendly way. The catalyst was obtained directly by thermal decomposition method using sulfur powder as sulfiding agent. The effect of molybdenum precursor, S/AHM weight ratio and sulfidation atmosphere on the catalytic methanation performance was studied systematically. In addition, the properties of as-prepared catalysts were further investigated, in aiming to understand the structure–activity relationship.

## 2. Experimental

### 2.1. Catalysts preparation

The unsupported Mo-based catalysts were prepared by the thermal decomposition method. Ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ or other precursors were used and the thermal decomposition was carried out in a quartz tube reactor as follows: (1) Sulfur powder with different S/AHM ratio was added to AHM (or other precursors) solution and then the mixture was stirred and dried in air to remove the excess water and then kept at 80 °C under vacuum for about 5 h. (2) The above mixture was put into a quartz tube and sulfided in 3% $H_2S/H_2$ and/or $N_2$ atmosphere with a gas flowrate of 100 mL/min with a heating rate of 25 °C/min to 450 °C for 5 h. (3) The above sample was passivated by passing a 1% oxygen/nitrogen mixture with a flowrate of 70 mL/min until no appreciable temperature rise was noted. The samples was then pelleted and crushed to particles (20–40 mesh) for methanation activity test. The catalyst identification number and the preparation information were listed in Table 3.

For comparison, the methanation activity of the catalyst prepared from decomposition of ammonium tetrathiomolybdate (ATM) or $MoS_3$ (obtained from acidification of ATM) using the same method was tested. The commercial $MoS_2$ was used for further understanding the catalytic properties of as-prepared $MoS_2$ catalysts.

### 2.2. Catalysts characterization

The $N_2$ adsorption and desorption isotherm of the catalyst were measured using a Micromeritics Tristar-3000 instrument. Pore size distribution of the sample was determined from the isotherms by the BJH method [17,28,29]. The catalyst sample was vacuumed first at 90 °C for 1 h and then at 300 °C for 3 h before the adsorption measurement. The X-ray diffraction (XRD) pattern was obtained using a RigakuD/max-2500 X-ray diffractometer (40 kV, 200 mA) with a Ni-filtered Cu-Kα radiation source ($\lambda = 1.54056$ Å). The scan speed was 8°/min with a scanning angle that ranged from 10° to 90°. The phase identification was determined by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS). The high-resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM-2010F transmission electron microscope instrument. Some amount of sample was grained as small as possible, then suspended in ethanol and sonicated. A drop of the suspension was put on a lacey carbon film supported on a Cu grid for HRTEM measurement. TPR experiment was carried out using a Micromeritics TPR 2910 instrument. The sample

(about 0.056 g) was put in a quartz tube and then flushed with Ar at 120 °C for 60 min. The measurement was carried out under a 30 mL/min flow of 10% $H_2/Ar$ of mixture with a heating rate of 10 °C/min to 700 °C. Laser Raman spectra (LRS) were recorded on a DXR Microscope spectrometer using the 532.0 nm radiation line from a Spectra-Physics-2020 argon laser. The laser beam intensity and the spectrum slit width were 8 mW and 25 μm, respectively. The samples were pressed into pellets for the measurements.

### 2.3. Catalytic activity evaluation

Catalytic performance evaluation was performed in a continuous flow fixed-bed reactor. Prior to the reaction, the catalyst (3 mL) was re-sulfided in situ at 400 °C for about 4 h in a $H_2S/H_2$ flow at atmospheric pressure. The activity was tested at a reaction temperature 550 °C and 3 MPa. The feed gas (GHSV $= 6000$ h$^{-1}$) composition was listed in Table 1. A thermocouple in a 2 mm stainless steel tube was put into the catalyst bed to ensure accurate temperature measurement. The outlet gases were online analyzed using an Agilent 7890A GC system equipped with 2 sets of TCD and 1 FID. External standard method was used to calibrate the GC results getting the composition of each component in the outlet gases. The catalytic activity was represented by conversion of CO and yield of $CH_4$, which were obtained after 20 h reaction.

CO methanation reaction can be described as follows [30]:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \triangle H_{0298} = -206.2 \text{ kJ/mol}. \tag{1}$$
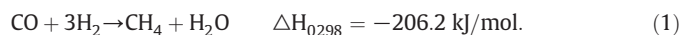
$CO_2$ is produced by water–gas shift (WGS) accompanying with CO methanation process as the following equation:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \triangle H_{0298} = -41.2 \text{ kJ/mol}. \tag{2}$$
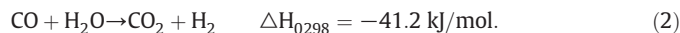
The methanation reaction usually takes place on Mo-based catalyst according to the following equation, which is the sum of reactions (1) and (2):

$$2CO + 2H_2 \rightarrow CH_4 + CO_2 \qquad \triangle H_{0298} = -247.4 \text{ kJ/mol}. \tag{3}$$
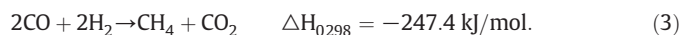
The CO conversion, $CH_4$ selectivity and $CH_4$ yield were calculated based on the following equations:

$$X_{CO} = \frac{F_{CO,in} - F_{CO,out}}{F_{CO,in}} \times 100\%$$

$$X_{H_2} = \frac{F_{H_2,in} - F_{H_2,out}}{F_{H_2,in}} \times 100\%$$

$$S_{CH_4} = \frac{F_{CH_4,out} - F_{CH_4,in}}{F_{CO,in} - F_{CO,out}} \times 100\%$$

$$S_{C_2H_6} = \frac{F_{C_2H_6,out} - F_{C_2H_6,in}}{F_{CO,in} - F_{CO,out}} \times 100\%$$

$$S_{CO_2} = \frac{F_{CO_2,out} - F_{CO_2,in}}{F_{CO,in} - F_{CO,out}} \times 100\%$$

**Table 1**
Feed gas composition.

| Feed gas | CO | $N_2$ | $CH_4$ | 3 vol.% $H_2S/H_2$ |
|---|---|---|---|---|
| Flowrate, mL/min | 69 | 103.5 | 25.5 | 102 |
| Vol. % | 23 | 34.5 | 8.5 | 34 |