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Investigation of the Active Phase in K-Promoted MoS₂ Catalysts for Methanethiol Synthesis

Miao Yu, Nikolay Kosinov, Lennart van Haandel, Patricia J. Kooyman, and Emiel J. M. Hensen*

ABSTRACT: K-promoted MoS₂ is an active catalyst for the synthesis of CH₃SH, a valuable chemical intermediate, from synthesis gas (CO/H₂) and H₂S. The promotion of MoS₂ by K increases the CO conversion rate and the CH₃SH selectivity and is usually linked to the stabilization of the 1T-MoS₂ polymorph as compared to the 2H-MoS₂ in K-free samples. Sulfided catalysts were characterized using TEM, XPS, and EXAFS. TEM showed that MoS₂ particles became larger and more stacked when the K/Mo ratio increased above unity. XPS and EXAFS evidenced the formation of the 1T-MoS₂ phase at higher K/Mo ratio in addition to 2H-MoS₂. The addition of K to MoS₂ led to increased CH₃SH productivity due to both increased CO conversion and CH₃SH selectivity (T = 300–400 °C, P = 10 bar). The performance of the most active catalyst with a K/Mo ratio of 2 was found to be stable, despite the observation that the initially present 1T-MoS₂ phase slowly converted to the 2H-MoS₂ phase during the reaction at high pressure. There is no correlation between the CH₃SH productivity and the amount of 1T-MoS₂ in K-promoted MoS₂ catalysts.

KEYWORDS: methanethiol, synthesis gas, MoS₂, K promotion, characterization

1. INTRODUCTION

Methanethiol (CH₃SH) is an important raw material, widely used in the synthesis of valuable organosulfur compounds such as pharmaceuticals and pesticides. CH₃SH is currently manufactured through thiolation of methanol (CH₃OH) on sulfided tungsten catalysts, and supported alkali catalysts have been also recently reported to be active in this reaction. This multistep process, involving the synthesis of CH₃OH from syngas, is costly, which is the main reason why a more efficient direct process is desired.

Olin et al. reported the first attempt to produce CH₃SH directly from H₂S-containing synthesis gas (a mixture of CO and H₂). The preferred catalyst for this reaction is supported molybdenum sulfide (MoS₂) promoted by alkali metals, because it shows a high CH₃SH selectivity. Yang et al. synthesized CH₃SH from H₂S and synthesis gas using K₂MoS₃/SiO₂. XRD and XPS results suggested that a Mo–S–K phase was the active species for CH₃SH synthesis and that bridged (S–S)₂⁻ species inhibit the generation of this phase. The same group further investigated the promotional effect of transition metal oxides (Fe, Co, Ni, and Mn) and rare-earth oxides (La and Ce) on K₂MoS₃/SiO₂. Based on XPS characterization, Mo⁶⁺ and S²⁻ species on the surface of the catalysts were suggested to be responsible for the high yield of CH₃SH.

Detailed kinetic studies proposed carbonyl sulfide (COS) to be the first intermediate formed from CO and H₂S in CH₃SH synthesis from synthesis gas and H₂S. COS is subsequently hydrogenated to CH₃SH in the rate-determining step. Based on this, Gutiérrez et al. investigated CH₃SH synthesis from COS over K-promoted Mo sulfide catalysts at 30 bar from 423 to 673 K. They found that, compared to the direct COS hydrogenation to CH₃SH, a two-step pathway including COS disproportionation to CO₂ and carbon disulfide (CS₂) followed by consecutive CS₂ hydrogenation to CH₃SH was preferred. XRD, Raman spectroscopy, and FTIR analysis of NO adsorption suggested that two types of surface species, namely MoS₂ and K’-decorated MoS₂, are present in this type of catalysts. K’-decorated MoS₂ was proposed to be the active phase for CH₃SH synthesis by promoting COS disproportionation and CS₂ hydrogenation.

Recently, Córdova et al. evaluated a set of sulfided Mo-, K-, and Mo–K-based catalysts supported on γ-Al₂O₃. Based on XPS, the authors proposed 1T-MoS₂ to be the active phase in Mo–K-based catalysts, which were sulfided with H₂S and H₂/
H₂S under atmospheric pressure. When a large quantity of K⁺ was present, K⁺ tended to intercalate between the MoS₂ layers to form a 1T-MoS₂ phase. This phase could be reduced under hydrogen, as confirmed by XPS. Reduction facilitates the insertion of K⁺ to compensate for the lower than +4 oxidation state of Mo, leading to the formation of more 1T-MoS₂.

Generally, MoS₂ is one of the most studied layered transition metal dichalcogenides and it exists in three polymorphs: distorted tetragonal (1T), hexagonal (2H), and rhombohedral (3R) phases. 16,17 The most stable 2H-MoS₂ can be transformed to 1T-MoS₂ by chemical exfoliation and intercalation of various ions such as Li⁺, Na⁺, and K⁺. 18–21 1T-MoS₂ exhibits metallic properties with much higher conductivity than the semiconducting 2H-MoS₂ 22,23 and, therefore, shows better performance in applications such as the hydrogen evolution reaction and as a material for supercapacitors. While most previous 1T-MoS₂ samples were synthesized/prepared in the form of thin films, the study of Cordova et al. is the first observation of 1T-MoS₂ in sulfided Mo–K–based supported nanoparticles. 15 Furthermore, the relative amount of 1T-MoS₂ as quantified by XPS, correlated with both CO conversion and CH₃SH productivity during the conversion of synthesis gas with H₂S at 10 bar. Later on, a similar 1T-WS₂ phase was observed in sulfided W–K–based catalysts, and its concentration was correlated to the catalytic performance in CH₃SH synthesis as well. 24

The observation of the 1T-MoS₂ phase in Mo–K–based catalysts for CH₃SH synthesis is remarkable. Sulfided Mo–K catalysts have been thoroughly studied for the conversion of synthesis gas to higher alcohols, but the presence of 1T-MoS₂ or similar structures in these catalysts has never been reported. 22–25 Notably, the pressure used to obtain higher alcohols is much higher (70–90 bar) than the pressure applied for CH₃SH synthesis. The XPS analysis in the work of Cordova et al. was performed after sulfidation at atmospheric pressure, 15 while the CH₃SH synthesis reaction was carried out at 10 bar.

As the stability of 1T-MoS₂ in supported catalysts remains unclear, we assumed that this phase might be unstable under high pressure. Thus, the correlation between XPS results and catalytic performance might also be questionable. It is, therefore, important to systematically investigate the stability of 1T-MoS₂ under the actual reaction conditions to identify the truly active phase of Mo–K–S CH₃SH synthesis catalysts. For the current study, we prepared a series of K-promoted Mo catalysts with different K/Mo ratios on γ-Al₂O₃. We used these catalysts for CH₃SH synthesis from syngas and H₂S and characterized them by XPS and EXAFS to analyze the phase composition of MoS₂ during different stages of reaction. The combination of characterization results and catalytic performance showed that the 1T-MoS₂ phase is not stable under reactions conditions and is, therefore, not the active component of the CH₃SH synthesis catalysts.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. K-promoted MoS₂ catalysts were prepared by incipient wetness impregnation of a 75–125 μm sieve fraction of crushed γ-Al₂O₃ extrudates with an aqueous solution of suitable metal salts, ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄.4H₂O, Sigma-Aldrich), and potassium nitrate (KNO₃, Sigma-Aldrich). After impregnation, the catalyst precursors were dried at 110 °C for 24 h and subsequently calcined at 450 °C in flowing air for 2 h. The molybdenum loading was about 7–8 wt %, while the loading of potassium was varied to achieve atomic K/Mo ratios of 0, 0.5, 1, and 2. The metal loadings were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The catalysts are denoted in the following as KₓMo, in which x is the atomic K/Mo ratio.

2H-MoS₂ (Sigma-Aldrich) and 1T-MoS₂ materials were used as references during the EXAFS measurement. 1T-MoS₂ powder was prepared through lithium intercalation according to ref 30.

2.2. Characterization. X-ray diffraction (XRD) patterns were recorded on a Bruker D2 Phaser diffractometer using Cu Kα radiation with a time per step of 0.25 s and a step size of 0.01° in the 2θ range of 5–70°.

Quasi in situ X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra spectrometer, equipped with a monochromatic X-ray source (Al Kα = 1486.6 eV) and a delay line detector. Samples were sulfided as described in section 2.3 and dispersed on carbon tape coated aluminum sample holders in a nitrogen-filled glovebox (H₂O < 1 ppm, O₂ < 1 ppm). The samples were transferred to the XPS apparatus using a protective atmosphere transport vessel. The background pressure prior to analysis was 2 × 10⁻⁹ mbar. Survey scans were collected at a constant pass energy of 160 eV, region scans at 40 eV. The spectra were fitted using the CasaXPS software. The C 1s signal served as a reference and was set at 284.8 eV. A Shirley background subtraction was applied and spectra were fitted with Gaussian–Lorentzian curves.

Extended X-ray absorption fine structure (EXAFS) spectroscopy was carried out at the DUBBLE beamline (BM26A) of the ESRF (6 GeV storage ring, 200 mA ring current). Ex situ samples were prepared in the glovebox as self-supporting wafers and sealed with Kapton tape. Spectra were collected at room temperature in transmission mode at the Mo K-edge. In situ experiments were performed in a custom-built stainless-steel (SS316) reactor equipped with glassy carbon windows as described in ref 31. The reactor was loaded with 100 mg of catalyst and connected to a mobile high-pressure setup installed at the beamline. The setup was equipped with a set of mass flow controllers to supply the required gases (H₂, CO, and H₂S/H₂ (10/90 vol %)). The reactor was pressurized to 10 bar and tested for potential leaks with He at the start of each experiment. Then, the pressure was released to 1 bar and the gas feed was switched to 30 mL/min H₂S/H₂ (10/90 vol %) for sulfidation. The sulfidation was started by heating the reactor (6 °C/min) to 350 °C with a 2 h dwell time. Subsequently, 3 mL/min CO was added. The CO:H₂:S ratio was kept at 1:9:1 at a total flow rate of 33 mL/min. The reactor was then pressurized to 10 bar to simulate the reaction conditions, for 3 h. Afterward, the reactor was cooled to room temperature, depressurized to atmospheric pressure, and flushed with He before the final EXAFS spectra of the used sample were collected. EXAFS spectra were background-subtracted with Athena and fitted with Artemis, which are interfaces of the IFEFFIT software package. 32 Scattering paths were calculated by FEFF6 from relevant crystal structures obtained from the ICSD database. Fitted parameters were the energy shift (ΔE₀), coordination number (CN), change in bond distance (ΔR), and the relative mean square displacement (σ²).

Quasi in situ high-resolution transmission electron microscopy (HRTEM) was performed using a monochromated FEI Titan 80-300 microscope.
Tecnai transmission electron microscope operated at an accelerating voltage of 200 keV. Samples were sulfided as described in section 2.3 and then transported to a nitrogen-filled glovebox (H2O < 1 ppm, O2 < 1 ppm) in sealed glass ampules. An ampule was opened inside the glovebox, and a suspension of the sample was made in n-hexane, of which a few droplets were placed on a microgrid carbon film (Quantifoil) supported on a Cu TEM grid. The grid was transported to the TEM without exposure to air using a homemade protective atmosphere TEM sample holder.33 The particle size and stacking of at least 500 particles were measured from ≥10 micrographs using ImageJ software. The mean particle size \( \bar{N} \) was determined by fitting a log-normal function to the particle size distribution, as described previously.34 The average stacking degree \( \bar{N} \) was calculated according to

\[
\bar{N} = \frac{\sum N_i n_i}{\sum n_i}
\]

where \( N_i \) is the number of stacked MoS2 layers (i.e., the number of MoS2 platelets in the stack) and \( n_i \) is the amount of individual MoS2 particles counted for a given stacking number \( N_i \).

2.3. Catalytic Performance. The activation of the catalyst precursors and CH3SH synthesis were performed in a fixed-bed reactor. Prior to catalytic experiments, 0.2 g of the precursors was sulfided in a flow of 10 vol % H2S/H2 under atmospheric pressure at 350 °C for 2 h. The same procedure was applied to prepare samples for XPS and TEM characterization. After activation, the pressure was increased to 10 bar and the temperature decreased to 300 °C. The feed gas was then changed to a mixture of CO:H2:H2S (molar ratio of 1:2:1) at a total flow rate of 60 mL/min, to which a flow of 3 mL/min \( N_2 \) was added as internal standard. The catalytic \( \bar{N} \) was determined on a carbon number basis.

3. RESULTS AND DISCUSSIONS

The elemental composition and structural properties of K2Mo catalysts are summarized in Table 1. The distribution of the MoS2 particle size and the MoS2 stacking degree for sulfided K2Mo catalysts are shown in Figure 1. Figure 2 shows representative TEM images of sulfided K2Mo and K4Mo catalysts. As the Mo loading with respect to the alumina support material was always the same, the final Mo loadings of the final catalysts containing K were slightly lower due to the addition of K. However, the atomic K/Mo ratio was well-controlled. The XRD patterns of the oxide precursors of K2Mo catalysts are shown in Figure S1a. The absence of XRD peaks other than the peaks related to the γ-Al2O3 support means that the oxide precursors are well dispersed on the support before sulfidation. The mean particle size of the sulfided K2Mo sample was 2.1 nm with an average stacking degree of 1.6 layers per particle. The mean particle size and stacking degree increase when the atomic K/Mo ratio is higher than 0.5, which is consistent with previous studies.15 As it is reported that K can intercalate between MoS2 layers, K+ ions might act as “bridges” during sulfidation and connect separated MoS2 layers. This leads to a more stacked structure with a lower fraction of single MoS2 layers in K2Mo (30%) compared to K4Mo (53%).

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Mo (wt %)</th>
<th>K (wt %)</th>
<th>K/Mo</th>
<th>particle size (nm)</th>
<th>stacking degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>K2Mo</td>
<td>7.5</td>
<td>1.4</td>
<td>0.5</td>
<td>2.1</td>
<td>1.6</td>
</tr>
<tr>
<td>K4Mo</td>
<td>7.2</td>
<td>0.5</td>
<td>1.4</td>
<td>2.4</td>
<td>1.6</td>
</tr>
<tr>
<td>K4Mo</td>
<td>7.2</td>
<td>0.5</td>
<td>1.4</td>
<td>2.4</td>
<td>1.6</td>
</tr>
<tr>
<td>K4Mo</td>
<td>6.7</td>
<td>0.5</td>
<td>1.4</td>
<td>2.4</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table 1. Elemental Composition and Structural Properties of K2Mo Catalysts

*Mo and K loading derived from ICP-AES. bMolar ratio. Derived from TEM of sulfided K2Mo catalysts.
MoS\(_2\) phase. A similar trend is obtained from the deconvolution of the S 2p XP spectra (Table S1). This demonstrates that the addition of K can indeed induce the formation of 1T-MoS\(_2\).

However, even without the phase transition, intercalated K can donate electrons to MoS\(_2\), resulting in lower apparent oxidation state of Mo\(^{37}\) which might affect the accuracy of the 1T-MoS\(_2\) quantification. XRD patterns of sulided K\(_x\)Mo catalysts were recorded and shown in Figure S1b. Unfortunately, no characteristic peaks from 2H or 1T-MoS\(_2\) could be detected due to the high dispersion of MoS\(_2\) particles. At this stage, further characterization was needed to confirm the phase composition of the K\(_x\)Mo catalysts. Recent studies on thin films of 1T-MoS\(_2\) show that simultaneous with the 1T-MoS\(_2\), also a more stable distorted 1T\(^\prime\)-MoS\(_2\) with 2\(\times\)1 real-space periodicity is obtained.\(^{30,38-40}\) The pure 1T structure is unstable and will spontaneously transform to 1T\(^\prime\)-MoS\(_2\).\(^{40,41}\) 1T\(^\prime\)-MoS\(_2\) can be further stabilized in the presence of hydrogen atoms.\(^{40,42}\) While in the 1T-MoS\(_2\), the Mo–Mo bond distance is the same as in the 2H phase (3.16 Å), the distortion in the Mo layer of 1T\(^\prime\)-MoS\(_2\) results in a different Mo–Mo bond distance, which is about 0.4 Å shorter. This has been confirmed by scanning transmission electron microscopy (STEM)\(^{43-47}\) and EXAFS.\(^{46-51}\) The 1T\(^\prime\)-MoS\(_2\) has not been observed yet in supported MoS\(_2\) samples. In order to further elucidate the phase composition of MoS\(_2\), the sulided catalysts were therefore studied using Mo K-edge EXAFS.

The Fourier-transformed EXAFS spectra of 2H- and 1T-MoS\(_2\) reference powders and sulided K\(_x\)Mo and K\(_2\)Mo catalysts are shown in Figure 4. The corresponding fitted spectra and fit parameters are given in Figure S3 and Table S2. In the FT-spectra of the 2H-MoS\(_2\) reference, the two main features can be assigned to the nearest Mo–S (2.40 Å) and Mo–Mo (3.16 Å) bonds, respectively. For the 1T-MoS\(_2\) reference, the shift of the first Mo–Mo distance from 3.16 to 2.73 Å indicates the existence of the distorted 1T\(^\prime\)-MoS\(_2\) structure. In sulided K\(_0\)Mo catalysts, only the usual Mo–Mo bond distance of 3.16 Å was observed. The Mo–S and Mo–Mo bond distances are similar to the corresponding distances in the 2H-MoS\(_2\) reference. In contrast, the sulided K\(_2\)Mo contains both the conventional and distorted Mo–Mo bonds. The bond distance for the distorted Mo–Mo shell is 0.4 Å shorter than the conventional Mo–Mo distance. This demonstrates that, in the sulided K\(_2\)Mo catalyst, Mo\(_{\text{S}}\) exists as a mixture of 2H and 1T phases. Furthermore, the distorted Mo–Mo coordination number (CN) was higher than the conventional Mo–Mo CN, suggesting that there was more 1T-than 2H-MoS\(_2\) in sulided K\(_2\)Mo, in accordance with the XPS results. Overall, XPS and EXAFS spectra of sulided K\(_2\)Mo
catalysts confirm that the addition of K can induce the formation of the 1T phase of MoS2. For the sulfded K2Mo catalyst, Mo is predominantly present as 1T-MoS2. The catalytic performance of the KxMo catalysts in the conversion of synthesis gas in the presence of H2S was evaluated by determining the CO conversion, the product distribution, and the CH3SH productivity. The major products include CH3SH, CH4, COS, CO2, and CH3SCH3. Only negligible amounts of CS2 were detected, which can be explained by the rapid hydrogenation of CS2 to CH3SH and H2S, consistent with a previous kinetic study.9 The catalytic performance at different feed flow rates and particle size of the K2Mo catalysts was also determined. The corresponding CH3SH productivities are shown in Figure S4. These results show that external and internal diffusion limitations are absent.

Figure 5 shows the CO conversion and the product distribution for all four catalysts from 300 to 400 °C. It can be seen that the CO conversion increases with temperature. Generally, the addition of K to MoS2 catalysts is beneficial to the CO conversion. Nevertheless, the CO conversion of K0Mo is lower than that of the Mo-only catalyst at all investigated temperatures. On the other hand, the effect of K on the product distribution shows a more consistent trend. For the K0Mo sample, the selectivity to CH3SH and COS decreased strongly with increasing temperature as more CO was converted into CH4 and CO2. For the K-promoted MoS2 samples, the changes in the COS and CO2 selectivity were very similar to those for the K2Mo sample. However, the presence of K generally improves the CH3SH selectivity at the expense of CH4 selectivity. The CH3SH selectivity of the K2Mo catalyst at 350 °C was 45%, which is much higher than the selectivity of K0Mo at the same temperature (14%), and even slightly higher than that of K2Mo at 300 °C (41%). Compared to the

Table 2. Binding Energies and Atomic Percentage of Different Mo Species in Sulfded KxMo Catalysts

<table>
<thead>
<tr>
<th>sample</th>
<th>Mo5+ 3d5/2</th>
<th>Mo6+ 3d5/2</th>
<th>Mo4+ 3d3/2</th>
<th>1T-Mo4+ 3d3/2</th>
<th>S2− 2s</th>
<th>binding energy (eV)</th>
<th>fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K0Mo</td>
<td>228.8</td>
<td>230.7</td>
<td>232.7</td>
<td>226.2</td>
<td>80</td>
<td>80</td>
<td>14</td>
</tr>
<tr>
<td>K0.5Mo</td>
<td>228.8</td>
<td>230.1</td>
<td>232.4</td>
<td>226.1</td>
<td>83</td>
<td>83</td>
<td>12</td>
</tr>
<tr>
<td>K1Mo</td>
<td>228.7</td>
<td>230.6</td>
<td>232.6</td>
<td>227.8</td>
<td>80</td>
<td>80</td>
<td>9</td>
</tr>
<tr>
<td>K2Mo</td>
<td>228.9</td>
<td>230.7</td>
<td>232.4</td>
<td>228.0</td>
<td>86</td>
<td>37</td>
<td>9</td>
</tr>
</tbody>
</table>
CH₄ selectivity of K₀Mo at 350 °C (28%), only 2% CH₄ was formed over K₂Mo.

Furthermore, the CH₃SH and CH₄ productivities normalized to the molar amount of Mo as a function of the temperature are shown in Figure 6. Addition of K improves the CH₃SH productivity and lowers the CH₄ productivity. There is an optimum temperature with respect to CH₃SH productivity. With increasing K/Mo ratio, this optimum temperature and also the productivity at this maximum increase. On the other hand, the CH₄ productivities of all samples substantially increased with temperature. While K₂Mo catalyst produced only little CH₄ at 350 °C, the CH₄ productivity increased about 8 times from 350 to 400 °C.

Based on these results, the promotional effect of K to MoS₂ catalyst on CH₃SH synthesis is due to the suppression of CH₄ formation and an enhanced rate of CH₃SH formation. For instance, although the CO conversion of K₀.5Mo was lower than that of K₀Mo, CH₃SH productivity of K₀.5Mo was higher over the whole temperature range. The decrease of CO conversion is therefore related to the fact that the CH₄ formation pathway is hindered by adding K. Furthermore, at increased K/Mo ratio the CH₄ productivity was further suppressed, while CO conversion improved because of the increased CH₃SH productivity.

As the sulfided K₀Mo catalyst contained the highest amount of 1T-MoS₂ and also exhibited the best catalytic performance, it is reasonable to assume that the better performance in CH₃SH synthesis relates to this phase. We performed prolonged catalytic experiments to evaluate the stability of this phase. CH₃SH productivity during 20 h reaction is shown in Figure 7. The catalytic performance of the K₀Mo catalyst was stable and the CH₃SH productivity only decreased 8.6% after 20 h. Using XPS, the composition of the MoS₂ phase was determined after catalytic reaction at 350 °C and 10 bar for 2, 5, 10, and 20 h. The samples are referred to as KₓMo_xh, where x represents the reaction time. The Mo 3d and S 2s regions of the XP spectra and the corresponding fit results are shown in Figure 8 and Table S3, respectively (S 2p XP spectra and fit results in Figure S5 and Table S4).

With increasing reaction time, the doublet related to Mo species narrows and shifts to higher binding energy. This suggests a decrease of the amount of 1T-MoS₂ in the used catalysts, which is supported by the fit results. The amount of 1T-MoS₂ decreased from ~45% in the freshly sulfided sample to ~12% after 20 h of reaction. The analysis of S 2p XP spectra also demonstrates a similar decrease from ~45% to ~17%. Thus, XPS clearly shows that 1T-MoS₂ is not stable and

![Figure 6](https://dx.doi.org/10.1021/acscatal.9b03178)

**Figure 6.** (a) CH₃SH productivity and (b) CH₄ productivity of KₓMo catalysts in catalytic experiments. Reaction conditions: T = 300−400 °C, P = 10 bar, CO:H₂:H₂S = 1:2:1 with a total flow rate of 60 mL/min.

![Figure 7](https://dx.doi.org/10.1021/acscatal.9b03178)

**Figure 7.** Stability of CH₃SH productivity and 1T-MoS₂/Mo ratio under 350 °C and 10 bar for 20 h.

![Figure 8](https://dx.doi.org/10.1021/acscatal.9b03178)

**Figure 8.** Mo 3d and S 2s XP spectra of KₓMo samples after different reaction times: (a) 0, (b) 2, (c) 5, (d) 10, and (e) 20 h. Reaction conditions: T = 350 °C, P = 10 bar, CO:H₂:H₂S = 1:2:1 with a total flow rate of 60 mL/min. Experimental data are represented by open circles and fit by a black curve. The fits are composed of Mo⁴⁺ (blue), Mo⁵⁺ (olive), Mo⁶⁺ (violet), 1T-Mo⁴⁺ (red), as well as the S²⁻ 2s signal (dark yellow).
transforms into the more stable 2H-MoS₂ under reaction conditions. However, neither CO conversion nor CH₃SH selectivity were substantially affected by the decreasing amount of 1T-MoS₂. Clearly, there is no correlation between the CH₃SH productivity and the amount of 1T phase in MoS₂ catalysts, which is contrary to a previous study.¹⁵

All used catalysts were studied by XPS. The Mo 3d and S 2s XP spectra of freshly sulfided and used catalysts are shown in Figure 9. The fit results for the used catalysts are collected in Table S5. The corresponding S 2p XP spectra and fit results are shown in Figure S6 and Table S6. For all samples, the 1T-MoS₂ transformed completely to 2H-MoS₂ during the standard catalytic experiments, further demonstrating that 1T-MoS₂ is unstable not only at elevated pressure, but also at elevated temperature. After only 3 h all 1T-MoS₂ was converted at 400 °C, while 12% 1T-MoS₂ remained after 20 h reaction at 350 °C for the K₂Mo sample. The influence of temperature on the stability of 1T-MoS₂ was further confirmed by a lower amount of 1T-MoS₂ in the K₂Mo catalysts sulfided at 400 °C as compared to the sample sulfided at 350 °C (corresponding XPS data are shown in Figure S7 and Table S7).

The instability of 1T-MoS₂ was further confirmed by EXAFS spectroscopy of used K₂Mo catalysts. Next to analyzing the used catalyst after standard catalytic experiments, also an in situ experiment was performed for the K₂Mo sample. Spectra of both samples (transferred via a glovebox and in situ) are compared with fresh catalysts in Figure 10. Corresponding fitted spectra and fit parameters are shown in Figure S8 and Table S2. It is obvious that the feature of the distorted structure in 1T-MoS₂ disappeared in the used catalysts, which is in accordance with the XPS results. It is worth mentioning that, for the in situ experiment, the reaction time was only 3 h and the total pressure was set as 10 bar but for safety reasons the partial pressure of CO was much lower (0.9 bar vs 2.5 bar) than that in the actual catalytic experiment. Even under these milder conditions, however, 1T-MoS₂ transformed to 2H-MoS₂. The result further underpins the instability of 1T-MoS₂ during reaction conditions.

Overall, due to the instability of 1T-MoS₂ in K-promoted MoS₂ catalysts under reaction conditions, the enhancement of catalytic performance cannot be attributed to the different phase composition of MoS₂. We notice that the amount of 1T-MoS₂ in sulfided K₂Mo catalysts is not proportional to K/Mo, which suggests that K prefers to adsorb on the edge sites of MoS₂ before intercalating between the MoS₂ layers. The presence of K⁺ ions at the edge sites was shown to lead to charge transfer to Mo atoms.⁵² This is consistent with the decreased binding energy of Mo⁴⁺ in used catalysts with higher K/Mo ratio as shown in Table S5. Due to this, the work function of the MoS₂ surface is decreased and its hydrogenation ability is suppressed, while the mode of CO activation shifts from hydrogen-assisted CO dissociation to non-dissociative adsorption. This phenomenon could explain why the formation of CH₃SH becomes much more favorable than CH₄ over K-promoted MoS₂ catalysts. Furthermore, K-promotion decreases the surface poisoning with CH₄ species and results in higher reaction rates.⁵²,⁵³ Consequently, we hypothesize that the K-modified edge sites are the active sites for the CH₃SH synthesis, while the actual structure of MoS₂ phase is less important.

4. CONCLUSION

K-promoted MoS₂ supported on a γ-Al₂O₃ with different K/Mo ratios was prepared as catalysts for the synthesis of CH₃SH from synthesis gas and H₂S. The effect of K on the structure and phase composition of MoS₂ was characterized in detail. TEM analysis showed that the particle size and stacking degree of MoS₂ slightly increased when the K/Mo ratio was larger than 0.5. XPS and EXAFS were applied to examine the phase composition of K₂Mo catalysts. In Mo 3d XP spectra of sulfided catalysts, an additional doublet, which was ~0.9 eV lower than the binding energy of Mo⁴⁺ in 2H-MoS₂, was observed and assigned to 1T-MoS₂. In EXAFS, a 0.4 Å shorter Mo–Mo bond representing the distorted structure in 1T’-MoS₂ was observed together with the Mo–Mo bond in 2H-MoS₂. XPS and EXAFS results both indicate that in sulfided K₂Mo catalysts, MoS₂ exists as a mixture of 2H and 1T phases. The addition of K to MoS₂ results in a higher CO conversion and a higher CH₃SH selectivity in catalytic experiments performed in the 300–400 °C temperature range at a pressure...
of 10 bar. This enhancement is stable for prolonged time for the K₂Mo catalysts, despite the loss of the 1T-MoS₂ phase as observed by XPS and EXAFS of used catalysts. The characteristic features of 1T-MoS₂ in the freshly sulfided sample disappeared during the catalytic reaction, showing that 1T-MoS₂ is not stable and transforms into the more stable 2H-MoS₂. This result proves that there is no correlation between the CH₃SH productivity and the amount of 1T-MoS₂ in K-promoted MoS₂ catalysts. It is likely that the presence of K at the MoS₂ edges is key to selective formation of CH₃SH.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.9b03178. XRD patterns, detailed XP and EXAF spectra, and corresponding fitting information (PDF)

## AUTHOR INFORMATION

### Corresponding Author

Emiel J. M. Hensen — Eindhoven University of Technology, Eindhoven, The Netherlands; orcid.org/0000-0002-9754-2417; Email: e.j.m.hensen@tue.nl

### Other Authors

Miao Yu — Eindhoven University of Technology, Eindhoven, The Netherlands; orcid.org/0000-0002-3155-5901

Nikolay Kosinov — Eindhoven University of Technology, Eindhoven, The Netherlands; orcid.org/0000-0001-8520-4886

Lennart van Haandel — Eindhoven University of Technology, Eindhoven, The Netherlands

Patricia J. Kooyman — University of Cape Town, Cape Town, South Africa; orcid.org/0000-0003-1252-5296

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acscatal.9b03178

## Notes

The authors declare no competing financial interest.

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## REFERENCES