

Investigation of the active phases in alkali metal promoted molybdenum sulfide catalysts for the synthesis of methanethiol from syngas and hydrogen sulfide

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545548 Investigation of the Active Phases in Alkali Metal Promoted Molybdenum Sulfide Catalysts for the Synthesis of Methanethiol from Syngas and Hydrogen Sulfide

At-A-Glance

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1. Introduction

Methanethiol (CH_3SH) is an important industrial raw material widely used in the synthesis of valuable organosulfur compounds such as pesticides, pharmaceuticals and petrochemicals [1]. A state-of-art production method for CH_3SH is the thiolation of methanol (CH_3OH) over transition metal sulfide catalysts [2]. Even if the production of CH_3SH is an efficient process involving high CH_3OH conversion and CH_3SH yield, this route needs a multi-step pathway for the synthesis of CH_3SH , which results in high production cost. Considering that CH_3OH is generated from syngas (CO and H_2), Olin et al. [3] proposed to synthesize CH_3SH directly from H_2S -containing syngas. The benchmark catalysts for this reaction are alkali metal promoted molybdenum sulfide (MoS_2) supported on silica or alumina [4].

Most of the earlier works have been focused on the optimization of the reaction conditions, while the active phase itself started to attract attention only recently. Cordova et al. proposed that the active phase related to the direct synthesis of methanethiol from $\text{CO}/\text{H}_2/\text{H}_2\text{S}$ using $\text{K}_2\text{MoO}_4/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{MoS}_4/\text{Al}_2\text{O}_3$ catalysts precursors, consists of layered 1T- MoS_2 crystallites in which potassium ions are intercalated between the layers [4]. This K_xMoS_2 phase was characterized by X-ray photoelectron spectroscopy (XPS) and the amount of this phase was correlated with the CH_3SH productivity.

It should be noted, however, that 1T- MoS_2 has been reported to be unstable compared to 2H- MoS_2 phase: it easily transforms to the 2H phase at high temperature [5]. The correlation between the amount of 1T phase and CH_3SH productivity was solely based on XPS result before the reaction. Therefore, aim of this work was to study the stability of 1T- MoS_2 under reaction conditions to examine whether the 1T- K_xMoS_2 phase is the actual active component for CH_3SH synthesis.

2. Experimental

Potassium-promoted molybdenum sulfide catalysts were prepared by co-impregnation of a 75-125 μm sieve fraction of crushed $\gamma\text{-Al}_2\text{O}_3$ extrudates ($V_p=0.6 \text{ cm}^3/\text{g}$) with an aqueous solution of suitable metal salts, ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, Sigma Aldrich) and potassium nitrate (KNO_3 , Sigma Aldrich). After impregnation, the catalyst precursors were dried at 110°C for 24 h and subsequently calcined at 450°C for 2 h in flowing air for 2 h. The molybdenum loading was 8 wt.%, whereas the loading of potassium was varied to achieve the atomic ratio of K to Mo as 0.5, 1 and 2, which was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The catalysts are denoted as $\text{K}_x\text{Mo}/\text{Al}_2\text{O}_3$, in which x is the atomic ratio of K to Mo. Besides, the catalysts were also characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and operando extended X-ray adsorption fine structure (EXAFS).

The activation of catalyst precursors and CH_3SH synthesis were performed in a fixed-bed reactor. Prior to catalytic test, the precursors were in-situ sulfided with 10 vol% $\text{H}_2\text{S}/\text{H}_2$ under atmospheric pressure and 350°C for 2 h. The same procedure was also applied for “quasi” in situ XPS and TEM measurements. After activation, the feed gas was changed to mixed $\text{CO}/\text{H}_2/\text{H}_2\text{S}$ (molar ratio equals to 1/2/1) with a total flow rate of 60 mL/min and 3 mL/min N_2 as internal standard. The catalytic performance was measured under 10 bar from 280°C to 320°C , the outlet product composition was analyzed by an online compact gas chromatograph (GC).

3. Results

The XPS spectra of Mo 3d core level of $\text{K}_0\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{Mo}/\text{Al}_2\text{O}_3$, which were in-situ sulfided at atmospheric pressure, are shown in Fig. 1a. These spectra can be deconvoluted into four doublets: Mo^{VI} , Mo^{V} , Mo^{IV} and K-Mo^{IV} . The doublet of Mo^{IV} at 228.9 eV and 232.0 eV corresponds to Mo in pristine 2H-MoS_2 , while the doublet of K-Mo^{IV} at 228.0 eV and 231.1 eV corresponds to Mo in 1T-MoS_2 [4]. Obviously, K-Mo^{IV} exists only in the spectrum of $\text{K}_2\text{Mo}/\text{Al}_2\text{O}_3$, which means that the addition of K in MoS_2 can induce its phase conversion from 2H to 1T. By comparing the area of doublet Mo^{VI} and KMo^{VI} , the ratio of 1T to 2H phase in $\text{K}_2\text{Mo}/\text{Al}_2\text{O}_3$ is about 1.2.

The sulfided samples were also analyzed by EXAFS at the Mo K-edge, and the Fourier transforms of $\text{K}_0\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{Mo}/\text{Al}_2\text{O}_3$ are shown in Fig. 1b. In the spectrum of $\text{K}_0\text{Mo}/\text{Al}_2\text{O}_3$, there are two main peaks corresponding to the nearest Mo-S (2.40 Å) and Mo-Mo (3.17 Å) bonds, respectively. On the other hand, there is one extra scatterer at 2.77 Å, which is assigned to a distorted shorter Mo-Mo bond. Previous studies showed that the structure of MoS_2 can be distorted when it changes from 2H-phase to 1T-phase [6], so the shorter Mo-Mo bond peak in EXAFS spectrum can be assigned to the 1T-phase in $\text{K}_2\text{Mo}/\text{Al}_2\text{O}_3$.

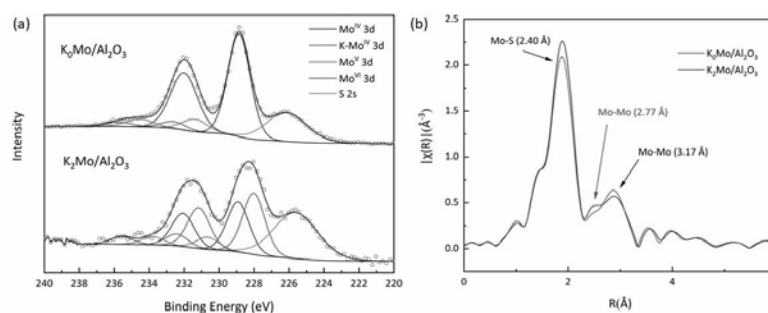


Fig. 1. (a) Mo 3d XP spectra of $\text{K}_0\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{Mo}/\text{Al}_2\text{O}_3$ (b) Fourier transform of Mo K-edge EXAFS spectra of $\text{K}_0\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{Mo}/\text{Al}_2\text{O}_3$

The catalytic performance of all four catalysts at 320°C is shown in Fig. 2a. It is clear that the addition of K can both increase the CO conversion and CH_3SH selectivity. Meanwhile, the XPS spectra of the $\text{K}_2\text{Mo}/\text{Al}_2\text{O}_3$ after 2 h, 5 h, 10 h and 20 h under reaction conditions (10 bar and 350°C) were also measured, and the ratios of 1T to 2H phase were calculated and shown together with CO conversion and CH_3SH selectivity in Fig. 2b.

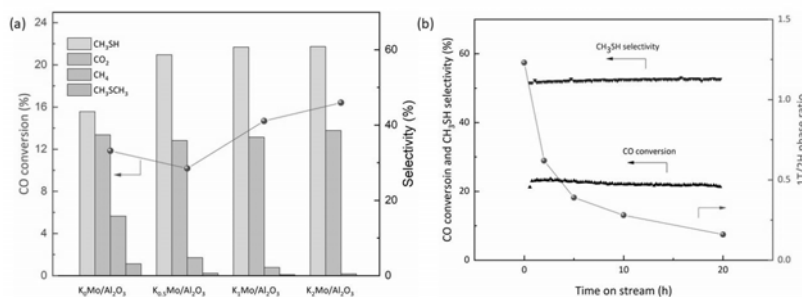


Fig. 2. (a) CO conversion and product selectivity of all four catalysts under 320°C (b) Catalytic performance and 1T/2H ratio of $\text{K}_2\text{Mo}/\text{Al}_2\text{O}_3$ in 20h

4. Discussion

The results from XPS and EXAFS clearly show that the addition of K in MoS_2 drives the conversion of 2H phase to 1T phase. Additionally, the ratios of 1T/2H calculated from XPS and EXAFS (by coordination numbers for different scattering paths) are very similar, which makes XPS a reliable

method to identify the amount of 1T-MoS₂ in this system. The 1T/2H ratio values (Fig. 2b) show that 1T phase converts to 2H phase during the reaction very quickly. Since the reaction temperature is the same as that for the sulfidation, high pressure should be responsible for the 1T to 2H transition. However, even though the ratio of 1T/2H decreases dramatically, the catalytic performance was quite stable for 20 h, suggesting that the structure of 1T-MoS₂ is not an all-important aspect of K-promoted MoS₂ for CH₃SH synthesis.

5. Conclusions

In our work, K-promoted MoS₂ catalysts were prepared. The existence of 1T-MoS₂ was confirmed by XPS and EXAFS. However, 1T-MoS₂ quickly converted to 2H-MoS₂ during the CH₃SH synthesis reaction because of its instability at high pressure. Therefore, we argue that under CH₃SH reaction conditions the 2H-MoS₂ phase is the real active phase.

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