



Article Influence of Carbonization Conditions on Structural and Surface Properties of K-Doped Mo₂C Catalysts for the Synthesis of Methyl Mercaptan from CO/H₂/H₂S

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Abstract: The cooperative transition of sulfur-containing pollutants of $H_2S/CO/H_2$ to the high-value chemical methyl mercaptan (CH₃SH) is catalyzed by Mo-based catalysts and has good application prospects. Herein, a series of Al_2O_3 -supported molybdenum carbide catalysts with K doping (denoted herein as K-Mo₂C/Al₂O₃) are fabricated by the impregnation method, with the carbonization process occurring under different atmospheres and different temperatures between 400 and 600 °C. The CH₄-K-Mo₂C/Al₂O₃ catalyst carbonized by CH₄/H₂ at 500 °C displays unprecedented performance in the synthesis of CH₃SH from CO/H₂S/H₂, with 66.1% selectivity and a 0.2990 g·g_{cat}⁻¹·h⁻¹ formation rate of CH₃SH at 325 °C. H₂ temperature-programmed reduction, temperature-programmed desorption, X-ray diffraction and Raman and BET analyses reveal that the CH₄-K-Mo₂C/Al₂O₃ catalyst contains more Mo coordinatively unsaturated surface sites that are responsible for promoting the adsorption of reactants and the desorption of intermediate products, thereby improving the selectivity towards and production of CH₃SH. This study systematically investigates the effects of catalyst carbonization and passivation conditions on catalyst activity, conclusively demonstrating that Mo₂C-based catalyst systems can be highly selective for producing CH₃SH from CO/H₂S/H₂.

Keywords: methyl mercaptan; CO/H₂S/H₂; molybdenum carbide; effect of carbonization conditions

1. Introduction

Coal is the main energy source in China. This produces large quantities of sulfurcontaining pollutants emitted by coal combustion, which has resulted in serious atmospheric environmental pollution [1–3]. Therefore, the removal and utilization of hydrogen sulfide resources have become research hotspots in the coal chemical industry [4,5]. In this industry, the Claus method and the improved Claus method are generally used to recover H₂S to produce sulfur or sulfuric acid, and the added value of the products is low. The preparation of the high-value chemical methyl mercaptan (CH₃SH) from H₂S, along with CO and H₂ in the process of coal gasification, has become a valuable development direction [6–9]. This technology can not only effectively remove H₂S but also provide a new route for downstream product development. The key to realizing the efficient utilization of raw materials and the high yield of products is to build a high-performance catalyst system. Until now, molybdenum sulfide based catalysts have been widely preferred because of their excellent sulfur resistance, but the reactant conversion and product selectivity are poor [10,11], which greatly restricts the development and application of molybdenum sulfide based catalysts.

In the industry, CH₃SH is mainly synthesized from the thiolation of methanol over alkali-promoted transition metal catalysts [12,13], but methanol needs to be prepared with



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). syngas (CO + H₂), which leads to complex processes, massive energy consumption and high economic costs. Olin et al. [14] developed a one-step synthesis method of CH₃SH using syngas raw materials and reduced sulfur species (hydrogen sulfide) generated during coal gasification that will greatly reduce the production cost of CH₃SH. Therefore, the preparation of CH₃SH from CO/H₂/H₂S has received widespread attention in recent years [15–17], and most research has focused on tungsten-based and molybdenum-based catalysts.

Among these, sulfurized K-Mo-based materials have received widespread attention due to their good catalytic activity and excellent sulfur resistance [18–21]. Many studies have been focused on the reactive phase, the reaction path and improving the performance of the catalysts by regulating catalyst carriers, additives, preparation methods and so on. Liu et al. [7] found that the addition of alkali metals (Na, K, Cs) can lead to different sulfidation degrees of Mo oxidized species owing to the different electric effects of alkali metals, which result in the formation of different concentrations of alkali-metal-promoted Mo containing coordinatively unsaturated sites, dramatically improving the CH_3SH selectivity and CO conversion. Lu et al. [22] synthesized mesoporous silica (SBA-15)-supported, 2–4 layered, ordered and K-promoted MoS₂ nanosheets. K promotion played an important role by stabilizing the C-S bond during the adsorption of the intermediate, COS, to avoid its conversion to side products in the gas phase, so the CO conversion and the selectivity towards CH_3SH were obviously improved. Yu et al. [23] also found not only that K can enhance the MoS₂-catalyzed synthesis of methanethiol, whereby synergy increases with alkali cation size, but also that alkali sulfides themselves were the active sites. However, there are still obstacles in CO/H₂/H₂S synthesis of CH₃SH using a molybdenum sulfide based catalyst, such as low reactant conversion and low selectivity towards the product, CH₃SH. Therefore, it is still of great significance to explore high-performance catalysts.

The transition metal carbide (TMC) molybdenum carbide (Mo₂C), which acts as an electron donor, exhibits high catalytic activity and selectivity due to the redistribution of electrons after carbon introduction. It has been widely applied for selective C-C, C-O and C-H bond cleavage and for producing fuel molecules from oxygenated biomass [24–27]. Moreover, it has good sulfur resistance and is expected to replace noble metal catalysts, which are limited by their low abundance and high cost [28,29]. The current synthesis methods of Mo₂C including solid–gas reactions [30,31], solid–liquid reactions [32–34] and solid–solid reactions [35–37], among which solid–gas reactions are the most commonly used and involve the carbonization reaction of molybdenum oxide (MoO₃ or MoO₂) with hydrogen and alkane/aromatics. During the carbonization process, different carbonization atmospheres can lead to the formation of different crystal forms of Mo₂C [27]. At present, there are no reports of the synthesis of CH₃SH from CO/H₂/H₂S over molybdenum carbide based catalysts. Due to their unique structures, molybdenum carbide based materials are expected to become emerging catalysts for the synthesis of CH₃SH from CO/H₂/H₂S.

Here, K-Mo/Al₂O₃ catalysts are prepared by the impregnation method, and a series of characterizations, including H₂ temperature-programmed reduction (H₂-TPR), Brunauer–Emmett–Teller (BET) analysis, temperature-programmed desorption (TPD), powder X-ray diffraction (XRD) and Raman spectroscopy, are conducted to investigate the effects of catalyst carbonization and passivation conditions on catalyst activity. We show that the regulation of carbonization and passivation conditions dramatically impacts the active sites and surface chemistry of the catalysts, and we explain how this can be exploited to greatly propel the production of CH₃SH from CO/H₂/H₂S.

2. Experimental Section

2.1. Catalyst Preparation

K-Mo/Al₂O₃ catalysts with a Mo loading of 10 wt% were prepared by the impregnation method, wherein γ -Al₂O₃ was used as the support and ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) and potassium carbonate (K₂CO₃) were used as the precursors of Mo and K, respectively. Firstly, a certain amount of (NH₄)₆Mo₇O₂₄·4H₂O was fully dissolved in 3.5 mL deionized water, and then K₂CO₃ was added to the solution at a K:Mo molar ratio of 2:1. Next, 2 g support was added to the mixed solution and stirred. The mixture was allowed to stand overnight for aging and was then placed in an oven and dried at 110 °C for 6 h. Finally, the samples were transferred to a muffle furnace and heated from room temperature to 550 °C at 5 °C/min, with calcination in air for 5 h. The resulting catalyst was labelled as K-Mo/Al₂O₃.

2.2. Catalyst Characterization

Powder X-ray diffraction (XRD) of catalysts was performed on a Bruker Germany D8 ADVANCE instrument with Cu K α -radiation (λ = 0.15418 nm) operating at 40 kV and 30 Ma. Raman spectroscopy (Jobin-Yvon France LabRam HR 800) was performed under 532 nm laser excitation, and the collection range was 200–1200 cm⁻¹. BET surface areas and pore structures of catalysts were determined by N₂ physisorption at 77 K using an America Quantachrome NOVA4200e analyzer. The temperature-programmed reduction of the sulfided sample (0.05 g) by hydrogen (H_2 -TPR) was performed using a thermal conductivity detector (TCD) at a heating rate of 10 °C/min until reaching 800 °C. The reduction atmosphere comprised a 10% $H_2/Ar(v/v)$ gas at a flow rate of 30 mL/min. The temperature-programmed desorption of carbon monoxide/hydrogen/hydrogen sulfide $(CO/H_2/H_2S-TPD)$ was conducted in a fixed-bed flow reactor equipped with a thermal conductivity detector (TCD) as the detector. Taking CO-TPD as an example, prior to the analysis, the sample (0.05 g, 40–60 mesh) was first heated to 300 $^{\circ}$ C at a rate of 5 $^{\circ}$ C/min and kept at 300 °C for 0.5 h to remove adsorbed matter from the catalyst surface. After the sample was cooled down to room temperature, the gas stream was switched to 10% CO/He (30 mL/min). The adsorption was carried out at room temperature for 1 h, and then the sample was purged with Ar to remove the physically adsorbed CO. The reactor was heated from room temperature to 900 °C at a rate of 10 °C/min for temperature-programmed desorption. With other conditions remaining unchanged, H2-TPD and H2S-TPD were performed by replacing 10% CO/He with 10% H_2 /Ar and 10% H_2 S/He, respectively.

2.3. Catalyst Activity Test

2.3.1. Catalytic Performance Tests

Before the performance test, 0.8 g K-Mo/Al₂O₃ (40–60 mesh) was placed in a quartz tube and a pre-treatment gas (carbonization gas: CH_4/H_2 , C_2H_6/H_2 , C_3H_8/H_2) was introduced. Taking CH_4/H_2 as an example, the ratio of CH_4 :H₂ was 1:9 (v/v, 40 mL/min); the sample was first heated from room temperature to 300 °C under a carbonization atmosphere at a rate of 1 °C/min and was maintained for 2 h; the sample was then further heated to the carbonization temperature stage (400 °C, 500 °C, 600 °C) at a rate of 1 °C/min and held for 2 h. K-Mo/Al₂O₃ samples were carbonized in CH_4/H_2 , C_2H_6/H_2 or C_3H_8/H_2 atmospheres and named as CH_4 -K-Mo₂C/Al₂O₃ or K-Mo₂C/Al₂O₃, C_2H_6 -K-Mo₂C/Al₂O₃ and C_3H_8 -K-Mo₂C/Al₂O₃, respectively.

The activity evaluation of the catalysts (0.4 g) was carried out on a fixed-bed reactor. A gas mixture of $CO/H_2/H_2S$ (gas volume concentration: CO = 10%, $H_2 = 40\%$, $H_2S = 50\%$) was used. N₂ was used as the equilibrium component and was introduced to the quartz tube with a pressure of 0.2 MPa and a flow rate of 40 mL/min. The catalytic activity was measured in the range of 275–400 °C. After reaching a steady state at each temperature, the products were analyzed online using three gas chromatographs (GC9790, China FULI INSTRUMENTS) equipped with FPD, TCD and FID.

2.3.2. Analysis of the Products

The CO conversion rate and product selectivity were calculated using the following equation:

$$Con_{CO} = \frac{C_{CO,in} - C_{CO,out}}{C_{in}} \times 100\%$$

Sel_X = X_i/ $\sum_{i=1}^{n} X_i \times 100\% = \frac{C_i}{C(CH_3SH) + C(COS) + C(CO_2) + C(CH_4) + C(CS_2)} \times 100\%$

where $C_{CO,in}$ denotes the concentration of CO in the feed gas and $C_{CO,out}$ denotes the concentration of CO in the product; the product selectivity is calculated based on carbon balance, where i is the target product (CH₃SH, COS, CO₂, CH₄, CS₂). C_i is the product concentration.

The CO consumption rate and CH₃SH formation rate were calculated using the following equation:

$$\begin{split} r(CO) &= \frac{M_{CO} \times C_{CO,in} \times conCO \times Q}{V_m \times m_{cat}} \\ r(CH_3SH) &= \frac{M_{CH_3SH} \times C_{CH_3SH} \times Q}{V_m \times m_{cat}} \end{split}$$

where M_{CO} is CO molar mass (g/mol); M_{CH3SH} is the molar mass of CH₃SH (g/mol). Q is the flow rate (L/h), V_m is the molar volume of gas under standard condition (L/mol) and m_{cat} is the catalyst amount (g).

3. Results

3.1. Performance of Catalysts Prepared at Different Carbonization Temperatures

Figure 1 shows the effect of different carbonization temperatures on the catalytic performance of the K-Mo/Al₂O₃ catalyst for the synthesis of CH₃SH from a CO/H₂/H₂S mixture. From Figure 1A,B, it can be seen that the CO consumption rate first increased and then decreased with increasing temperature over 325 °C. Our former studies showed that the equilibrium constant of the CO consumption reaction (CO + $H_2S \rightarrow COS + H_2$) decreases with increasing temperature, which indicates that rising temperature is adverse to the occurrence of the CO consumption reaction. Therefore, the decrease in CO conversion at high temperatures is due to equilibrium limitations [7]. The CH_3SH formation rate also showed a similar tendency to that of CO consumption. It can be obviously seen from the tendency that when the oxidation state material was carbonized at 500 $^{\circ}$ C, the catalyst was found to have the optimum catalytic activity, and the CO conversion (35.5%) and selectivity towards CH_3SH (66.1%) reached maximum values when the reaction temperature was 325 °C. At this temperature, the CO consumption rate reached 0.2660 g \cdot g_{cat}⁻¹ \cdot h⁻¹ and the CH₃SH formation rate reached 0.2990 $g \cdot g_{cat}^{-1} \cdot h^{-1}$. Recently, Lu et al. investigated the synthesis of CH_3SH using $CO/H_2/H_2S$ as reactants over K-Mo-type catalysts. COS was demonstrated to be generated first via the reaction between CO and H_2S (as shown by Equation (1)), and then CH_3SH was formed via two reaction pathways, which were the hydrogenation of COS and CS_2 (as shown in Equations (3) and (4)).

$$CO + H_2 S \to COS + H_2 \tag{1}$$

$$COS + 3H_2 \rightarrow CH_3SH + H_2O \tag{2}$$

$$2COS \to CO_2 + CS_2 \tag{3}$$

$$CS_2 + 3H_2 \rightarrow CH_3SH + H_2S \tag{4}$$

From Figure 1C, it can be seen that there was no significant difference in the main products formed over K-Mo/Al₂O₃ after being carbonized at different temperatures for the preparation of CH₃SH from CO/H₂/H₂S; CH₃SH, COS, CO₂, CH₄ and CS₂ were the main products in this reaction system.

The H₂-TPR curves of K-Mo/Al₂O₃ catalysts treated at different carbonization temperatures are shown in Figure 1D. The three materials with different carbonization temperatures exhibited similar reduction peak characteristics, with a low temperature reduction peak at 200–350 °C and a moderate temperature reduction peak at 450–600 °C. Moreover, the catalyst carbonized at 500 °C exhibited a reduction peak at a high temperature (above 700 °C), which was attributed to the reduction of Mo⁴⁺ to Mo⁰, and the hydrogen consumption peaks were obviously lower than those of the other two materials at the same reduction temperature. These results indicated that K-Mo/Al₂O₃ carbonized at 500 °C was more easily reduced under the same reduction conditions, resulting in more Mo with coordinatively unsaturated surface sites that were conducive to the adsorption of reactants and the desorption of intermediate products such as COS and CH₃SH. Thus, the catalyst obtained by carbonized at 500 °C in subsequent experiments.



Figure 1. K-Mo/Al₂O₃ catalysts prepared with different carbonization temperatures were used to synthesize CH₃SH from CO/H₂/H₂S; (a) K-Mo/Al₂O₃-600 °C; (b) K-Mo/Al₂O₃-500 °C; (c) K-Mo/Al₂O₃-400 °C. Rate of CO consumption (**A**); Rate of CH₃SH formation (**B**); Distribution of CO conversion and main product selectivity (**C**); Curves of H₂-TPR (**D**).

3.2. The Role of Passivation

According to the literature, fresh molybdenum carbide materials are prone to violent reactions with air to form molybdenum oxide [38–40]. Therefore, fresh molybdenum carbide materials need to be passivated. After passivation, a passivation layer is formed on the surface of the material, which makes it more stable (passivation treatment with O_2 /inert

gas). To reveal the role of passivation in the catalytic performance of K-Mo/Al₂O₃ for the synthesis of CH₃SH from CO/H₂/H₂S, the catalytic activity of the catalysts before/after passivation was conducted. As shown in Figure 2, there was a significant change in the CO consumption rate within the reaction temperature range of 275–400 °C after passivation that decreased with increasing temperature. However, the formation rate trend of CH₃SH remained almost unchanged, first increasing and then decreasing with increasing temperature. After comparing with the product analysis diagram, it was found that the formation of main products before/after passivation did not change (CH₃SH, COS, CO₂, CH₄, and CS₂), but the selectivity towards CH₃SH was significantly reduced and the selectivity of by-product COS was increased after passivation. These changes were likely due to the passivation layer on the passivated catalyst surface, which covered the active site for direct hydrogenation of some COS to CH₃SH, resulting in the reduction of selectivity towards CH₃SH. The result revealed that passivation treatment was not effective for the synthesis of CH₃SH from CO/H₂/H₂S, as the existing of the passivation layer would inhibit the formation of CH₃SH.



Figure 2. Catalytic activity of K-Mo₂C/Al₂O₃ catalysts before and after passivation, (a) before passivation, (b) after passivation. Rate of CO consumption (**A**); Rate of CH₃SH formation (**B**); Distribution diagram of unpassivated catalyst products (**C**); Distribution diagram of unpassivated catalyst products (**C**).

3.3. Performance of Catalysts Carbonized under Different Atmospheres

Different carbonization atmospheres can lead to the formation of different crystal forms of molybdenum carbide. For example, MoO_3 will be converted into cubic molybdenum carbide with H_2 /toluene as the reaction gas at 673 K [41]; using H_2 /butane as the reaction gas, MoO_3 is initially converted into face-centered cubic (fcc) molybdenum carbide, then the face-centered cubic molybdenum carbide gradually transforms into a hexagonal closely

packed structure (fcp) with an increase in carbonization temperature [42]. Using alkanes with different carbon atomic numbers as a carbonization gas will generally lead to different carbonation degrees and then generate different numbers of active sites [27]. K-Mo/Al₂O₃ was carbonized by different atmospheres $(CH_4/H_2, C_2H_6/H_2, C_3H_8/H_2)$, and the catalytic performance of different catalysts in the synthesis of CH_3SH from $CO/H_2/H_2S$ is shown in Figure 3. Remarkably, $K-Mo/Al_2O_3$ samples treated with different atmospheres all showed similar tendencies of catalytic performance, whereby the CO consumption rate first increased and then decreased. Catalysts treated with C₃H₈/H₂ had the highest CO consumption rate, followed by catalysts treated with C_2H_6/H_2 , and catalysts treated with CH_4/H_2 had the worst CO consumption rate. From Figure 3B, it can be seen that the CH_3SH generation rate of the catalyst treated with C_3H_8/H_2 , which had the highest CO consumption rate, was not optimum. Combined with the product analysis (Figure 3E), the selectivity towards by-product CO₂ of this catalyst was high, which might have been caused by the hydrolysis of COS or the water-gas shift reaction of CO. Compared with that of the K-Mo₂C/Al₂O₃ catalyst treated with C_3H_8/H_2 , the CO consumption rate of the K-Mo₂C/Al₂O₃ catalyst treated with C_2H_6/H_2 was slightly lower. It can be seen intuitively in Figure 3B that the CH₃SH generation rate decreased sharply at high temperatures. And it was found that the selectivity of by-products of the catalyst was higher at high temperatures (COS, CH_4) and the CH_3SH selectivity was lower, which might be due to easy carbon deposition on the catalyst surface at high temperatures, further leading to a decrease in COS hydrogenation to generate CH₃SH and excessive hydrogenation of CH₃SH to generate CH4; thus, CH3SH selectivity decreased. Although the K-Mo2C/Al2O3 catalyst treated with CH_4/H_2 exhibited a poor CO consumption rate, it had a relatively stable CH₃SH generation rate and high CH₃SH selectivity. To reveal the role of carbonization atmospheres in catalytic performance, the characterization of catalysts was conducted.



Figure 3. Effect of different carbonization atmospheres on the catalytic performance of K- Mo_2C/Al_2O_3 catalysts, (a) CH₄/H₂, (b) C₂H₆/H₂, (c) C₃H₈/H₂. Rate of CO consumption (**A**); Rate of CH₃SH formation (**B**); Distribution diagram of carbonization catalyst products in CH₄/H₂ atmosphere (**C**); Distribution diagram of carbonization catalyst products in C₂H₆/H₂ atmosphere (**D**); Distribution diagram of carbonization catalyst products in C₃H₈/H₂ atmosphere (**E**).

3.4. Characterization of Catalysts Carbonized under Different Atmospheres

The N₂ adsorption–desorption isotherms and physical properties of the catalysts assessed using N₂ physisorption are displayed in Figure 4 and Table 1. As shown in Figure 4, the oxidation state sample was a typical mesoporous structure with an IV curve and an H1 hysteresis ring, and the surface area and pore volume were 116.1 m²/g and 0.269 cc/g, respectively. After carbonization, the specific surface area of all samples decreased slightly, with CH₄-K-Mo₂C/Al₂O₃ decreasing to 103.9 m²/g, C₂H₆-K-Mo₂C/Al₂O₃ decreasing to 101.3 m²/g and C₃H₈-K-Mo₂C/Al₂O₃, decreasing to 113.4 m²/g. However, the average pore volume of CH₄-K-Mo₂C/Al₂O₃, C₂H₆-K-Mo₂C/Al₂O₃ and C₃H₈-K-Mo₂C/Al₂O₃ increased to 0.321 cc/g, 0.290 cc/g and 0.390 cc/g, respectively. It can be therefore be concluded that the small decrease in specific surface area and the increase in pore volume after carbonization were caused by the collapse of some small pores during the carbonization process.



Figure 4. N₂ adsorption–desorption isotherms of oxidation K-Mo/Al₂O₃ and Mo₂C/Al₂O₃ samples treated in different carbonization atmospheres, (a) oxidized, (b) CH_4/H_2 , (c) C_2H_6/H_2 , (d) C_3H_8/H_2 .

Table 1. Textural characteristics of oxidation $K-Mo/Al_2O_3$ and Mo_2C/Al_2O_3 samples treated in different carbonization atmospheres.

Sample	Surface Area (m ² /g)	Pore Volume (cc/g)	Pore Diameter Dv (d) (nm)
K-Mo/Al ₂ O ₃	116.1	0.269	7.853
CH ₄ -K-Mo ₂ C/Al ₂ O ₃	103.9	0.321	9.618
C ₂ H ₆ -K-Mo ₂ C/Al ₂ O ₃	101.3	0.290	8.598
C ₃ H ₈ -K-Mo ₂ C/Al ₂ O ₃	113.4	0.390	11.159

The phase compositions of the catalysts of different carbonization atmospheres were characterized by XRD and Raman spectroscopy. As shown in Figure 5A, the diffraction peaks at $2\theta = 38.1^{\circ}$, 39.4° , 61.7° and 75.7° were attributed to β -Mo₂C (JCPDS card No.65-8766) and correspond to the (002), (101), (110) and (201) crystal planes, respectively. Small diffraction peaks of K₂MoO₄ species (JCPDS card No.29-1021) were also detected. In the Raman spectrum (Figure 5B), diffraction peaks were detected at 325 cm^{-1} , 896 cm^{-1} and 917 cm⁻¹, which were attributed to monomolybdate MoO₄²⁻ species and K₂MoO₄ on the sample surface [43,44], indicating an interaction between the precursor potassium and molybdenum. The diffraction peak was detected at 215 cm⁻¹, assigned to well-dispersed $AIMo_6O_{24}H_6^{3+}$ and erson heteropolymetalate anions ($AIMo_6$) formed by an alumina carrier and molybdenum-based aqueous solution [45-47]. The diffraction peaks at 661 cm⁻¹, 818 cm⁻¹ and 990 cm⁻¹ were also assigned to β -Mo₂C [48,49]; among these, the peaks at 818 cm⁻¹ and 990 cm⁻¹ correspond to the stretching vibrations of Mo-C-Mo and Mo-C, respectively. The results of XRD and Raman spectroscopy showed that there was no significant difference in the phase structure of the catalysts under different carbonization atmospheres.



Figure 5. XRD (**A**) and Raman (**B**) patterns of K-Mo₂C/Al₂O₃ samples under different carbonation atmospheres, (a) CH₄/H₂, (b) C_2H_6/H_2 , (c) C_3H_8/H_2 .

H₂-TPR was carried out on the catalysts under different carbonization atmospheres to investigate redox properties; the results for the catalysts are displayed in Figure 6. It can be seen that all K-Mo₂C/Al₂O₃ catalysts had three obvious hydrogen consumption peaks, two of which appeared at 200–400 °C and 400–600 °C, with larger hydrogen consumption peaks at >600 $^{\circ}$ C. Generally, the hydrogen consumption peak at low temperatures (200–400 $^{\circ}$ C) was the reduction of the passivation layer on the surface of the molybdenum carbide [50]. The moderate temperature reduction peak (400–600 °C) can be attributed to the reduction of Mo⁶⁺ to Mo⁴⁺ or other high-valent Mo species [51]. The high-temperature reduction peak (>600 °C) can be attributed to the reduction of Mo⁴⁺ or Mo²⁺ to Mo atoms [52]. However, the sample was not subjected to passivation treatment, and the presence of Mo⁶⁺ was not detected in the XRD spectrum. According to the literature [39,52], the hydrogen consumption peak at low temperatures (200-400 °C) is the reduction of surface high-valent molybdenum oxides, while the consumption peak at 650-800 °C is the reduction of Mo⁴⁺ or Mo^{2+} to Mo atoms. Therefore, in this work, the three hydrogen consumption peaks of 200–400 °C, 400–600 °C and >600 °C can attributed to the reduction of Mo⁴⁺, the reduction of potassium carbide species and the reduction of Mo^{2+} to Mo atoms, respectively. K-Mo₂C/Al₂O₃ catalysts synthesized under different carbonization atmospheres exhibited similar H₂-TPR reduction peaks, but the CH₄-K-Mo₂C/Al₂O₃ catalyst showed larger hydrogen consumption peaks at low and medium temperatures, indicating that more Mo coordinatively unsaturated surface sites were formed on the catalyst, which is more conducive to the adsorption of reactants and the desorption of products, consistent with the above catalytic performances.



Figure 6. The H₂-TPR spectra of K-Mo₂C/Al₂O₃ samples in different carbonation atmospheres, (a) CH₄/H₂, (b) C₂H₆/H₂, (c) C₃H₈/H₂.

The TPD technique is commonly used to characterize the surface properties and chemical reactions of a material. As an important step in a catalytic reaction, the adsorption of reactant molecules by the catalyst plays a crucial role in the catalytic performance [53,54]. To investigate the adsorption and activation abilities of K-Mo₂C/Al₂O₃ catalysts under different carbonization atmospheres for reactants, the catalysts were characterized by carbon monoxide, hydrogen and hydrogen sulfide adsorption and desorption; the results of CO-TPD, H₂-TPD and H₂S-TPD of the catalysts are displayed in Figure 7. As shown in Figure 7A, the CH₄-K-Mo₂C/Al₂O₃ catalyst exhibited three CO desorption peaks, indicating three different CO adsorption sites and on the catalyst with different adsorption strengths. According to the literature, CH₄-K-Mo₂C/Al₂O₃ has a low-temperature desorption peak at around 120 °C, which was assigned to the desorption of CO and physical adsorption of Mo₂C. In the high-temperature region, the desorption peak was the dissociation adsorption peak formed by the strong chemical adsorption between the catalyst and CO [52]. C₂H₆-K-Mo₂C/Al₂O₃ and C₃H₈-K-Mo₂C/Al₂O₃ showed one and two CO desorption peaks, respectively, which were obviously lower than those of CH_4 -K-Mo₂C/Al₂O₃. According to the related research, the Mo coordinatively unsaturated sites serve as the adsorption sites for the activation of CO [6,7,55]. Therefore, the CH₄/H₂ atmosphere promotes the generation of more Mo coordinatively unsaturated sites on the catalyst and thus facilitates CO adsorption and activation, which also enhances the selectivity of CH₃SH.



Figure 7. CO-TPD (**A**), H₂-TPD (**B**) and H₂S-TPD (**C**) spectra of (a) CH_4 -K-Mo₂C/Al₂O₃, (b) C_2H_6 -K-Mo₂C/Al₂O₃, (c) C_3H_8 -K-Mo₂C/Al₂O₃ samples.

In H₂-TPD, the CH₄-K-Mo₂C/Al₂O₃ catalyst exhibited slightly strong hydrogen activation ability, producing a large amount of desorbed H at medium temperature, and there was an obvious H₂ negative peak, indicating that hydrogen might be dissociated into adsorbed H* at this temperature. Moreover, as shown in the H₂S-TPD results (Figure 7C), the CH₄-K-Mo₂C/Al₂O₃ catalyst showed that it had strong H₂S adsorption and dissociation abilities, very similar to the other two catalysts in the low temperature range but slightly stronger above 500 °C. In short, the use of CH₄/H₂ as a carbonization atmosphere facilitates the adsorption and activation of reactants of K-Mo₂C/Al₂O₃, thus delivering a high activity and selectivity towards CH₃SH.

4. Conclusions

In conclusion, a series of K-Mo₂C/Al₂O₃ catalysts were successfully obtained through the impregnation method with a carbonization process at temperatures of 400–600 °C. Through careful control of the carbonization temperature, passivation process and carbonization atmosphere (500 °C, unpassivated and CH₄/H₂ being optimal), a CH₄-K-Mo₂C/Al₂O₃ catalyst with unusually high activity and selectivity towards CH₃SH produced from CO/H₂/H₂S at 325 °C could be obtained (e.g., 66.1% selectivity and 0.2990 g·g_{cat}⁻¹·h⁻¹ formation rate to CH₃SH). Structural characterization studies revealed that passivation of the catalysts would

lead to a layer formed on the surface of the material, covering the active sites of the reaction and reducing the activity of the catalyst. Under different carbonization temperatures and atmospheres (CH₄/H₂, C₂H₆/H₂, C₃H₈/H₂), the catalyst carbonized by CH₄/H₂ at 500 °C exhibited higher catalytic activity because it was more easily reduced under the same reduction conditions and resulted in more Mo coordinatively unsaturated sites, which was conducive to the adsorption of reactants and the desorption of intermediate products, thus showing the best overall performance. This work identifies K-Mo₂C/Al₂O₃ as a promising new Mo-based catalyst for the production of CH₃SH from CO/H₂/H₂S.

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