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Catalytic Synthesis of Methanethiol from H_2S-rich Syngas Over Sulfided SiO_2-supported Mo-based Catalysts

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Abstract The synthesis of methanethiol from H_2S-rich syngas was investigated over sulfided Mo-based catalysts supported on SiO_2. At $CO/H_2/H_2S = 1/1/2$, 0.2 MPa, 3,000 h^{-1}, and 300 °C, mainly CH_3SH, COS, and CO_2 were formed, along with small amounts of hydrocarbons and thioethers over potassium-promoted Mo-based catalysts. Studies of the reaction pathway show that COS is a primary product, which is hydrogenated to CH_3SH and H_2O. Most of CO_2 originates from water-gas shift reaction. The hydrocarbons and thioethers originate from the hydrogenation of CH_3SH.

Keywords Methanethiol synthesis · Hydrogen sulfide · Syngas · Mo-based catalysts

1 Introduction

Supported Mo-based catalysts have been extensively studied in Fischer–Tropsch (F–T) reaction for the synthesis of mixed alcohols from syngas ($CO + H_2$) [1–6]. In contrast, the studies of the reactions of the syngas in the existence of H_2S are very limited. Previously, we have studied the effects of H_2S concentration in syngas on the performance of Mo-based catalysts. In this case, we accidentally found that mixed alcohols disappeared and methanethiol became the dominant product when the concentration of H_2S in the syngas was over 1.6% [7, 8]. Methanethiol, also referred to as methyl mercaptan, is a well-known intermediate used in the synthesis of organosulfur compounds, such as methionine, dimethyl sulfoxide, and dimethyl sulfone [9]. Methanethiol is industrially produced by the reaction of methanol and hydrogen sulfide over supported metal oxide catalysts, such as K_2WO_4/Al_2O_3 and Cs_2WO_4/Al_2O_3 [10]. Obviously, compared to the CH_3OH-H_2S route for the production of methanethiol, it would be attractive and promising if a simple feedstock, such as H_2S-rich syngas (i.e., high H_2S-containing syngas or $CO/H_2/H_2S$ mixtures), could be used.

Based on different product distribution and catalysts, different pathways for the synthesis of methanethiol have been proposed. Based on results of the co-adsorption of CO and H_2S over anatase and rutile, Beck et al. [11] proposed a reaction pathway for the formation of CH_3SH from the hydrogenation of carbonyl sulfide (COS), which proceeded via a thioformic acid ($HSCHO_{ads}$) and a surface methylthiolate (CH_3S_{ads}) intermediate. Moreover, Barrault et al. [12] investigated the synthesis of methanethiol from carbon oxides (CO and CO_2), H_2S and H_2 over tungsten-based catalysts. They proposed that carbon oxides react with H_2S to produce COS and that COS was hydrogenated to CH_3SH. Recently, Mul et al. [13] reported a similar pathway for the CH_3SH synthesis from CO and H_2S over vanadium-based catalysts. However, based on an approximate Anderson–Schulz–Flory product distribution, Zhang et al. [14, 15] proposed a modified mechanism of the F–T process incorporating a reaction of a C_1 intermediate with a surface –SH group for the synthesis of CH_3SH over unmodified α-Al_2O_3 catalysts.

In this paper, the SiO_2-supported Mo-based catalysts were chosed for the direct synthesis of methanethiol from H_2S-rich syngas. The catalysts modified with potassium and cobalt exhibit a higher catalytic activity than those reported in recent literature and patents. The products were

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identified, for the first time, on the K–Mo–Co/SiO_2 catalyst. The source of desired products and by-products and the pathway of the CH_3SH synthesis from H_2S-rich syngas are discussed.

2 Experimental

2.1 Catalyst Preparation

Catalysts were prepared by the incipient wetness impregnation method and SiO_2 (commercial sample, $S_{BET} = 261\ m^2/g$, 20–45 mesh) was used as the support. In a typical preparation of the K_2O–MoO_3–CoO/SiO_2 catalyst, the required quantities of K_2CO_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and $Co(NO_3)_2\cdot 6H_2O$ were dissolved in distilled water, to which ammonia was added until the precipitate was dissolved under stirring to yield an aqueous solution. Subsequently, SiO_2 was impregnated for 12 h, followed by drying and calcining at 400 °C for 4 h. The amount of precursors was expressed as that of corresponding oxides. For the sake of brevity, the samples thus prepared K_2O/SiO_2 (15/100, wt/wt), CoO/SiO_2 (5/100, wt/wt), K_2O–CoO/SiO_2 (15–5/100, wt/wt), MoO_3/SiO_2 (25/100, wt/wt), MoO_3–CoO/SiO_2 (25–5/100, wt/wt), K_2O–MoO_3/SiO_2 (15–25/100, wt/wt), and K_2O–MoO_3–CoO/SiO_2 (15–25–5/100, wt/wt) are denoted as K/SiO_2, Co/SiO_2, KCo/SiO_2, Mo/SiO_2, MoCo/SiO_2, KMo/SiO_2, and KMoCo/SiO_2, respectively.

2.2 Reaction Conditions

The reaction was carried out in a stainless-steel tubular fixed-bed flow microreactor with 0.5 ml of catalyst. Before evaluation, the catalysts were reduced with hydrogen at 420 °C for 4 h followed by sulfidation with the feedstock ($H_2S/H_2/CO = 2/1/1$, v/v) at 300 °C for 4 h. The feedstock of H_2S, CO, and H_2 was mixed into a cylinder beforehand, to which 2–3% (volume %) of N_2 was added as internal standard. N_2, CO, and CO_2 were analyzed by an on-line gas chromatographs (GC) fitted with thermal conductivity detector (TCD) (carrier: H_2; a carbon molecular sieve column: 1.5 m × 8 mm; 120 °C (5 min) to 180 °C (9 min) at 10 °C/min). The hydrocarbons were analyzed by an on-line GC equipped with a flame ionization detector (FID) (carrier: N_2; a Porapak Q column: 1.5 m × 8 mm; 120 °C (5 min) to 180 °C (9 min) at 10 °C/min). The sulfur-containing compounds were analyzed by an on-line GC fitted with a flame photometric detector (FPD) (carrier: N_2; a HP-Plot/Q capillary column: 30 m × 0.539 mm × 40.00 μm; 80 °C (5 min) to 180 °C (5 min) at 10 °C/min). The three detectors were installed in series. All lines from the reactor to the gas sampling valves were kept at ~150 °C by using a thermostated heating belt to prevent product condensation. CO and CO_2 were quantitatively analyzed by an internal standard method. CH_4, C_2H_4, C_2H_6, CH_3SH, H_2S, COS, and CS_2 were measured by an external standard method. The mass balances were closed within 3%. All the activity and selectivity data were taken when the steady state was achieved.

The reaction products were collected with an ice-salt bath and analyzed off-line with a Varian GC3900/SATUM 2100w GC-MS spectrometer (carrier: He; a HP-2MS capillary column: 30 m × 0.25 mm × 0.25 μm; 40 °C (10 min) to 150 °C at 20 °C/min; mass scan range: 40–300 AMU; acetone was as a standard).

3 Results

3.1 Product Distribution

Table 1 shows the distribution of carbon-containing and sulfur-containing products in the reaction of $CO/H_2/H_2S$ at 300 °C and 0.2 MPa over different catalysts. The reaction of CO and H_2S even took place in the empty reactor (blank test) to form exclusively COS, but the conversion of CO is very low (1.2%). With unmodified SiO_2, K/SiO_2, Co/SiO_2,

Table 1 Product distribution and catalyst activity for the synthesis of methanethiol from H_2S-rich syngas[a]

Catalysts	Selectivity (%) (H_2O excluded)								Conversion of CO (%)
	CH_4	C_2H_4	C_2H_6	COS	CO_2	CH_3SH	CS_2	Thioethers[b]	
Blank	Trace	–	–	100	–	–	–	–	1.2
SiO_2	3.8	–	–	94.7	Trace	1.5	–	–	1.7
K/SiO_2	1.8	–	–	96.0	Trace	2.2	–	–	3.7
Co/SiO_2	2.2	–	–	95.0	Trace	2.8	–	–	3.2
KCo/SiO_2	1.6	–	–	93.2	Trace	5.2	–	–	3.1
Mo/SiO_2	1.5	–	–	96.2	Trace	2.3	–	–	4.6
MoCo/SiO_2	2.7	Trace	–	94.6	Trace	2.7	–	–	8.3
KMo/SiO_2	0.3	0.1	Trace	19.1	31.7	48.5	0.2	0.1	42.7
KMoCo/SiO_2	0.6	0.1	Trace	16.6	36.6	45.7	0.3	0.1	62.4

[a] Reaction conditions: $CO/H_2/H_2S = 1/1/2$ (v/v), 0.2 MPa, 300 °C, 3,000 h^{-1}

[b] $CH_3SCH_3 + CH_3SSCH_3 + CH_3SSSCH_3$

KCo/SiO_2, Mo/SiO_2 and $MoCo/SiO_2$, a slight increase of CO conversion and the following order of CO conversion was found: $MoCo/SiO_2 > Mo/SiO_2 > KCo/SiO_2 > K/SiO_2 > Co/SiO_2 > SiO_2$. Moreover, COS was still the dominant product (selectivity > 90%), along with small amounts of CH_3SH and CH_4. However, the CO conversion increased markedly over the potassium-promoted Mo-based catalysts (KMo/SiO_2 and $KMoCo/SiO_2$). Meanwhile, the product distribution changed significantly. It was found that COS, CO_2, and CH_3SH become the main products, with a decrease of the selectivity of CH_4. Surprisingly, C_2H_4, C_2H_6, CS_2, H_2O, and some unidentified products (could not be separated in the GC chromatogram) were also detected in the reaction tail gas. To identify the nature of the species in the overlapping peaks, the products were collected in an ice–salt cooling trap, and analyzed with GC-MS. The overlapping peaks could be separated and ascribed to dimethyl sulfide (CH_3SCH_3), dimethyl disulfide (CH_3SSCH_3), and dimethyl trisulfide (CH_3SSSCH_3). No C_3^+ Fischer–Tropsch products, higher thioethers, or higher thiols were observed under these reaction conditions. To the best of our knowledge, there are no reports showing that CH_3SSCH_3 and CH_3SSSCH_3 are produced from the H_2S-rich syngas under our reaction conditions. The data in Table 1 also show that methane is a more dominant byproduct (selectivity, $CH_4 > C_2$ or thioethers). The comparison of the performance of the KMo/SiO_2 and $KMoCo/SiO_2$ catalysts shows that the addition of cobalt increases the conversion of CO and the selectivity of CH_4, while it decreases the selectivity of COS and CH_3SH slightly. This observation is obviously due to the hydrogena function of the cobalt promoter. The yield of methanethiol over KMo/SiO_2 and $KMoCo/SiO_2$ is 0.49 g h^{-1} ml_{cat}^{-1} and 0.77 g h^{-1} ml_{cat}^{-1}, respectively.

3.2 Study of the Reaction Pathway

Keeping the molar ratio of H_2S/CO in a constant, the effect of the variation of the H_2 concentration in the feedstock on activity and selectivity over $KMoCo/SiO_2$ was studied. The results are presented in Fig. 1. A higher concentration of H_2 in the feedstock lowered the conversion of CO but favored the formation of CH_4. When H_2 was absent from the feedstock, the selectivities of CH_3SH, COS, and CO_2 were 31%, 33%, and 35%, respectively. No water was detected in this case. These observations are consistent with a previous study [13]. With the concentration of H_2 increasing from 15% to 50%, the selectivities of CH_3SH and CO_2 increased slightly while that of COS decreased slightly.

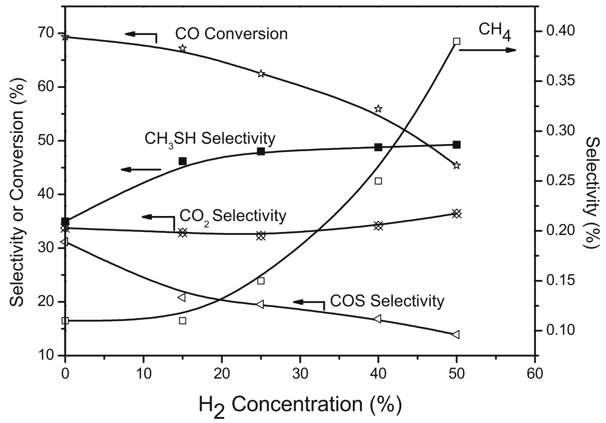

Fig. 1 Effect of H_2 concentration on the catalyst activity and the product selectivity. Conditions: Catalyst = $KMoCo/SiO_2$, Temperature = 300 °C, Total pressure = 0.2 MPa, GHSV = 3,000 h^{-1}, H_2S/CO Molar ratio = 2/1

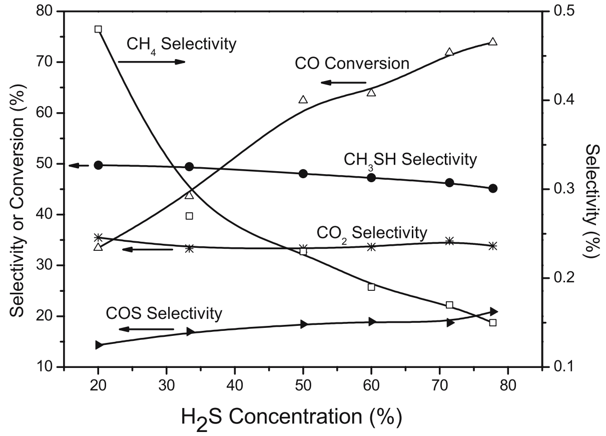

Fig. 2 Effect of H_2S concentration on the catalyst activity and the product selectivity. Conditions: Catalyst = $KMoCo/SiO_2$, Temperature = 300 °C, Total pressure = 0.2 MPa, GHSV = 3,000 h^{-1}, CO/H_2 molar ratio = 1/1

A similar experiment was carried out by changing the concentration of H_2S and the results are shown in Fig. 2. Contrary to H_2, a higher concentration of H_2S favored the conversion of CO but decreased the selectivity of CH_4. Meanwhile, the selectivity of CH_3SH decreased slightly when the concentration of H_2S increased from 20% to 78%.

The measurements of catalytic activity were carried out by varying the reaction temperatures (Table 2) and the total pressures (Fig. 3). As shown in Table 2, the conversion of CO increased with increasing temperature and reached a maximum at 340 °C. At higher temperatures, the CO conversion and CH_3SH selectivity decreased. Moreover, the higher temperature was beneficial for the formation of hydrocarbons, CS_2, and thioethers byproducts. The optimal temperature for the synthesis of methanethiol from H_2S-rich syngas was about at 320–340 °C. At higher reaction temperature, a decrease in the selectivity of methanethiol was observed. As shown in Fig. 3, the CO conversion increased with increasing pressure. The results of the variations of temperature and pressure show that the

Table 2 Effect of temperature on activity and selectivity over KMoCo/SiO$_2^a$

Temperature (°C)	Selectivity (%) (H_2O excluded)								Conversion of CO (%)
	CH_4	C_2H_4	C_2H_6	COS	CO_2	CH_3SH	CS_2	Thioethers[b]	
260	0.1	–	–	23.4	32.8	43.7	–	–	31.3
300	0.6	0.1	Trace	16.6	36.6	45.7	0.3	0.1	62.4
320	0.8	0.1	Trace	15.9	32.2	50.2	0.3	0.2	64.3
340	1.6	0.1	Trace	15.8	32.8	49.0	0.4	0.3	64.8
360	2.3	0.2	Trace	15.7	33.7	47.5	0.3	0.3	62.6
420	6.5	0.8	0.5	10.5	36.9	43.3	0.9	0.6	55.6

[a] Reaction conditions: $CO/H_2/H_2S = 1/1/2$ (v/v), 0.2 MPa, 3,000 h^{-1}

[b] $CH_3SCH_3 + CH_3SSCH_3 + CH_3SSSCH_3$

decrease of the COS selectivity is concomitant with the increase of the CH_3SH selectivity. Moreover, hydrocarbons and thioethers were observed to a minor extent at low temperature or low pressure, while their concentration increased with increasing temperature or pressure.

The decrease of the gas hourly space velocity (GHSV), i.e., the increase of the contact time, led to an increase of the CO conversion. Figure 4 shows the relationship between the selectivity of the main products and the conversion of CO. A shorter contact time favored the selectivity of COS, whereas a longer contact time benefited the formation of CH_3SH and CO_2. Especially, the selectivities of CO_2 and CH_3SH were close to zero at very low CO conversion. This observation suggests that COS is a primary product, and that CO_2 and CH_3SH are the secondary products. Moreover, the rate of COS consumption is higher than that of CH_3SH formation with increasing contact time, as is reflected in the slopes of the curves in Fig. 4. It implies that the rate of COS formation from H_2S and CO is higher than that of CH_3SH formation from COS and H_2. These features are consistent with those reported in the literature [12, 13]. Accordingly, the lower GHSV favors the formation of CH_3SH.

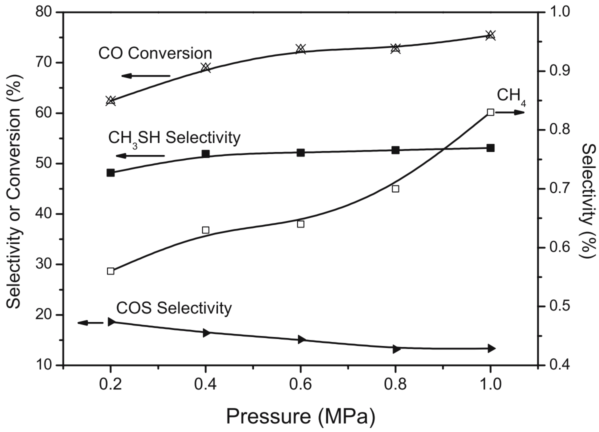

Fig. 3 Effect of pressure on the catalyst activity and the product selectivity. Conditions: Catalyst = KMoCo/SiO$_2$, Temperature = 300 °C, GHSV = 3,000 h^{-1}, $CO/H_2/H_2S$ molar ratio = 1/1/2

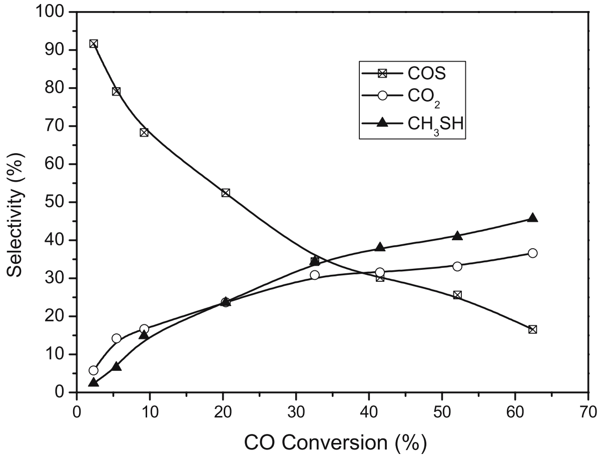

Fig. 4 Effect of CO conversion on the selectivities of the main products. Conditions: Catalyst = KMoCo/SiO$_2$, temperature = 300 °C, total pressure = 0.2 MPa, $H_2/CO/H_2S$ molar ratio = 1/1/2

4 Discussion

Although methanol could be produced from the reaction of CO and H_2 over sulfided KMo-based catalysts, no methanol was detected at our reaction temperatures (Table 2) and low CO conversion (Fig. 4). It suggests that the synthesis of methanethiol is impossibly formed by the reaction of CH_3OH and H_2S. Whereas our experimental results suggest that COS is an intermediate from the reaction of CO and H_2S, and that the subsequent hydrogenation of COS forms CH_3SH. The pathway of the synthesis of methanethiol from H_2S-rich syngas over sulfided KMoCo/SiO$_2$ catalyst may be as follows:

$$CO + H_2S \leftrightarrow COS + H_2 \qquad (1)$$

$$COS + 3H_2 \leftrightarrow CH_3SH + H_2O \qquad (2)$$

Reaction (1) can easily take place over the transition-metal sulfide catalyst [16]. CO has electron-donor property and electrons may transfer from CO to sulfur ion belonging to the coordination sphere of Mo or Co:

$$M^{n+} - S^{2-} + CO \rightarrow COS_{ads} - M^{(n-2)+} \qquad (3)$$

(M stands for a metal ion)

The hydrogenation of COS_{ads} to CH_3SH, i.e. reaction (2), proceeds via a thioformic acid intermediate ($HSCOH_{ads}$) and a surface methylthiolate intermediate (CH_3S_{ads}) [11]. In this study, experiments by varying H_2 and H_2S concentration in the feedstock were carried out. According to Le Chatelier's principle, increasing the concentration of H_2 will suppress reaction (1) and lead to a decrease of the conversion of CO, while increasing the concentration of H_2S will increase the conversion of CO, and a high pressure favors the synthesis of CH_3SH. All the theoretical expectations were verified in our experiments (Figs. 1–3). Moreover, the decrease of the concentration of COS should coincide with the increase of that of CH_3SH. This expectation was also confirmed in our experiments (Fig. 4). Furthermore, the decrease of COS leads to a simultaneous increase of CO_2, suggesting that CO_2 is also the derivative of COS. Our experimental results support the pathway for the synthesis of CH_3SH from the intermediate product of COS over SiO_2-supported K–Mo–Co catalyst.

CO_2 may be produced by the disproportionation or hydrolysis of COS or by the water-gas shift reaction:

$$2COS \leftrightarrow CO_2 + CS_2 \quad (4)$$

$$COS + H_2O \leftrightarrow CO_2 + H_2S \quad (5)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (6)$$

Reactions (4), (5), and (6) are favored over acid–base catalysts [11, 12, 17]. As shown in Table 1, the selectivity of CS_2 is only 0.3% over the $KMoCo/SiO_2$ catalyst. This observation shows that most of the CO_2 can not originate from reaction (5), otherwise the selectivity of CS_2 would be close to that of CO_2. However, it just indicates that CS_2 mainly comes from reaction (4). Since the high concentration of H_2S in the reaction system will restrain the hydrolysis of COS, it is impossible that most of the CO_2 originates from reaction (5). It is reasonable to conclude that most of CO_2 should be from the water gas shift reaction, i.e., reaction (6). On the one hand, the Co–Mo–K catalyst is a good catalyst for water–gas shift reaction; On the other hand, reaction (6) is more favorable in agreement with the results of thermodynamic calculations [12].

As for the hydrocarbons and thioethers, i.e., CH_4, C_2H_6, C_2H_4, CH_3SCH_3, CH_3SSCH_3, and CH_3SSSH_3, it is considered that these species result from secondary reactions of CH_3SH but not from parallel reactions occurring in the formation of CH_3SH [11, 15]. This viewpoint is clearly demonstrated by the observations of CH_3SSCH_3 and CH_3SSSCH_3 in this research (Tables 1 and 2).

There are two types of dissociative adsorption of CH_3SH on the surface of the catalysts: one cleaves the S–H bond, leaving an adsorbed $–SCH_3$ group and adsorbed –H; the other cleaves the S–C bond, leaving adsorbed $–CH_3$ and –SH groups. The reactions between these surface species lead to the formation of the hydrocarbons and thioethers [18–20]. Possible reactions are as follows:

$$CH_3SH + H_2 \leftrightarrow CH_4 + H_2S \quad (7)$$

$$2CH_3SH + H_2 \leftrightarrow CH_3CH_3 + 2H_2S \quad (8)$$

$$2CH_3SH \leftrightarrow C_2H_4 + 2H_2S \quad (9)$$

$$2CH_3SH \leftrightarrow (CH_3)_2S + H_2S \quad (10)$$

$$2CH_3SH \leftrightarrow 2CH_3SSCH_3 + H_2 \quad (11)$$

$$3CH_3SH \leftrightarrow CH_3SSSCH_3 + CH_4 + H_2S \quad (12)$$

C_3^+ hydrocarbons and the thioethers containing more than three sulfur atoms were not observed in the products. Methane is a dominant byproduct, which may be due to a large quantity of active H on the sulfided surface and thus benefiting the hydrogenation of CH_3SH. Only a small amount of C_2H_6, C_2H_4, CH_3SCH_3, CH_3SSCH_3, and CH_3SSSCH_3 in reaction products may attribute to the kinetic limitations.

5 Conclusions

In this paper, the synthesis of methanethiol from H_2S-rich syngas over Mo-based catalysts was investigated. It is shown that potassium-promoted Mo-based catalysts exhibit a high activity for CH_3SH synthesis. The incorporation of cobalt into the $K–Mo/SiO_2$ catalyst increases the catalytic activity, but slightly decreases the selectivity of methanethiol. The results of the pathway study show that COS forms from the reaction of H_2S and CO primarily. And that the hydrogenation of COS forms CH_3SH and H_2O. The water–gas shift reaction is the main source of CO_2. The disproportionation of COS leads to the formation of CS_2. The hydrogenation of CH_3SH leads to the formation of small amounts of $C_{1\sim2}$ hydrocarbons (CH_4, C_2H_4 and C_2H_6) and thioethers (CH_3SCH_3, CH_3SSCH_3 and CH_3SSSCH_3). The optimized reaction temperature is 320–340 °C. Higher temperatures will lead to higher selectivity of hydrocarbons and S-containing by-products.

This paper gives a more clear illustration for the pathway of the CH_3SH synthesis from H_2S-rich syngas but the nature of active site and the elementary steps are not completely clear. Therefore, additional works such as surface science studies and structure-activity analysis are required and in progress.

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