The catalytic properties of supported K_2MoS_4/SiO_2 catalyst for methanethiol synthesis from high H_2S-content syngas

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Methanethiol has been synthesized by one-step catalytic reaction from H_2S-content syngas on K_2MoS_4/SiO_2 catalyst with selectivity over 95% under the optimum reaction conditions of 563 K, 2.0–3.0 MPa and 5–6% H_2S content in the feed syngas. The results of XRD and XPS showed that Mo–S–K phase on the surface of the catalyst K_2MoS_4/SiO_2 was responsible for the high activity and selectivity to methanethiol, and which may be restrained by the existence of $(S–S)^{2-}$ species.

Keywords: K_2MoS_4/SiO_2 catalyst, methanethiol, H_2S-content syngas

1. Introduction

Alkali-promoted MoS_x-based catalysts have been reported for their possible application as sulfur-resistant catalysts for synthesis of mixed alcohol from CO–H_2 [1–4]. However, it has been scarcely known in the literature that methanethiol can be synthesized from H_2S-content syngas over alkali-promoted MoS_x-based catalysts. Methanethiol, which is normally produced through a reaction of CH_3OH with H_2S [5,6], is a key intermediate in the manufacture of jet fuels, pesticides, fungicides, plastics and methionine. In the present paper, we report a novel one-step preparation process for methanethiol synthesis from high H_2S-content syngas on supported MoS_x-based catalysts. The effects of the catalyst preparation, the H_2S content and the reaction conditions (temperature and pressure) on the catalysis of K_2MoS_4/SiO_2 and $MoS_2/K_2CO_3/SiO_2$ were investigated. The results provide an important technical reference for the production of methanethiol industrially.

2. Experimental

2.1. Catalyst preparation

K_2MoS_4 and $(NH_4)_2MoS_4$ were prepared according to the known methods. Dimethylformamide (DMF) was purified by drying over 3A molecular sieve, redistillating and deoxygenating by passing through MnO-based deoxygenate. Catalysts were prepared by the method of incipient wetness by depositing a DMF solution of K_2MoS_4 or $(NH_4)MoS_4$ on SiO_2 (BET area $= 280$ m^2/g) or K_2CO_3-doped SiO_2 (BET area $= 179$ m^2/g). K_2MoS_4-derived samples were dried by evacuation at room temperature for 5 h and then heated at 393 K for 2 h, followed by reduction-pretreatment in a flow stream of feed syngas ($CO/H_2 = 1$ v/v) at 578 K for 24 h. $(NH_4)_2MoS_4$-derived samples were dried by evacuation at 723 K for 2 h. All experiments of catalyst preparation were carried out in an atmosphere of purified argon.

2.2. Assay of catalyst activity

The catalytic reaction for methanethiol synthesis was carried out in a stainless steel tubular flow reactor by employing 1.0 ml of catalyst each time. The activity was measured under reaction conditions of 1.0 MPa, 568 K, $CO/H_2 = 1$ (v/v), and GHSV $= 3000$ h^{-1}. Products were analyzed by a gas chromatograph with a GDX103 column of 2.5 m. All data were taken after 16 h of operation when steady state was achieved.

2.3. Characterization

X-ray diffraction (XRD) patterns were taken in a Rigaku Ru-200x diffractometer with Cu K_α at a radiation rate of 6°/min in the 2θ range of 20–80°.

XPS measurements were performed by using a VG Escalab Mark-II machine with Mg K_α radiation (1253.6 eV, 10 kV, 20 mA) and UHV (1×10^{-7} Pa). Si(2p) of SiO_2 at 103.6 eV was chosen as the internal reference. All procedures of transferring samples in the spectroscopic experiments were carried out under an atmosphere of purified nitrogen.

3. Results and discussion

Table 1 summarizes the catalytic results of Mo–S–K based catalysts for methanethiol synthesis from high H_2S-content syngas. On $MoS_2/K_2CO_3/SiO_2$ (0.32/0.15/1,

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Table 1
The results of activity assay for methanethiol synthesis from high H_2S-content syngas over Mo–S–K based catalysts.[a]

Catalyst (wt/wt)	CO conversion (%)	Selectivity (CO_2 excluded)				Methanethiol space time yield ($mg\,h^{-1}\,g_{cat}^{-1}$)
		Hydrocarbon		Methanethiol and ethanethiol		
		C_1	C_2	C_1	C_2	
MoS_2	0.2	62.1	37.9	–	–	–
MoS_2/SiO_2 (0.32/1)	1.3	43.9	56.1	–	–	–
$MoS_2/K_2CO_3/SiO_2$ (0.32/0.15/1)	0.8	42.6	31.6	22.2	3.6	4.5
K_2MoS_4/SiO_2						
A(0.28/1)	3.2	1.6	0.01	97.1	1.2	99.0
B(0.56/1)	2.2	1.0	0.08	98.3	0.4	135.5
C(0.84/1)	2.1	1.0	0.11	98.5	0.5	147.5
K_2MoS_4	0.3	5.0	0.7	94.1	0.2	25.6

[a] Reaction conditions: 563 K, 1.0 MPa, $CO/H_2/N_2/H_2S$= 2/2/0.9/0.1 (v/v), GHSV = 3000 h^{-1}.

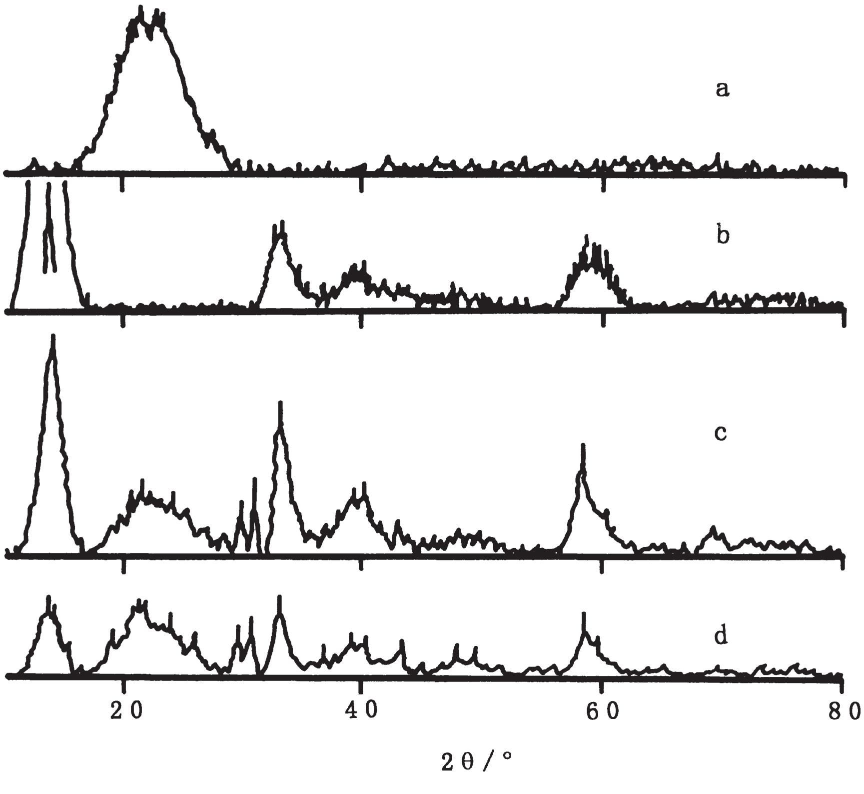

Figure 1. XRD patterns of the catalysts in the functioning state. (a) SiO_2. (b) MoS_2. (c) $MoS_2/K_2CO_3/SiO_2$ (0.32/0.15/1.00, wt/wt). (d) K_2MoO_4/SiO_2 (0.28/1.00, wt/wt).

wt/wt), the methanethiol selectivity, space time yield and hydrocarbon selectivity were 22.2%, 4.5 $mg\,h^{-1}g_{cat}^{-1}$ and 74.2%, respectively, while on K_2MoS_4/SiO_2 (0.28/1, wt/wt, catalyst A), they were 97.1%, 99.0 $mg\,h^{-1}\,g_{cat}^{-1}$ and 1.6%, respectively. The results showed that K_2MoS_4/SiO_2 is more effective than $MoS_2/K_2CO_3/SiO_2$ in one-step preparation of methanethiol from high H_2S-content syngas.

Figure 1 shows the XRD patterns of the two catalysts. It is known [7] that the peak at $2\theta = 21.4°$ belongs to SiO_2 and peaks at $2\theta = 14.0°$, 33.3°, 39.5° and 59.0° belong to MoS_2. Peaks at $2\theta = 29.8°$ and 30.8° were assignable to a new Mo–S–K phase [8,9]. The characterization of the XRD patterns of the two catalysts was almost the same but the relative intensity ratios of the peaks of MoS_2 and Mo–S–K phases are different from each other. For $MoS_2/K_2CO_3/SiO_2$, the ratio $I_{\text{Mo-S-K}(30.8°)}/I_{\text{MoS}_2(140°)}$ is found to be $69/212 = 0.33$. In the case of K_2MoS_4/SiO_2, the ratio $I_{\text{Mo-S-K}(30.8°)}/I_{\text{MoS}_2(140°)}$ is $99/134 = 0.74$. The results indicate that the Mo–S–K phase content in the sample of K_2MoS_4/SiO_2 is 2.2 times higher than that in $MoS_2/K_2CO_3/SiO_2$.

Figure 2 shows the S(2p) XPS spectra of the functioning catalysts. It was found from figure 2 that for the unsupported MoS_2 catalyst the S^{2-}(2p) species was

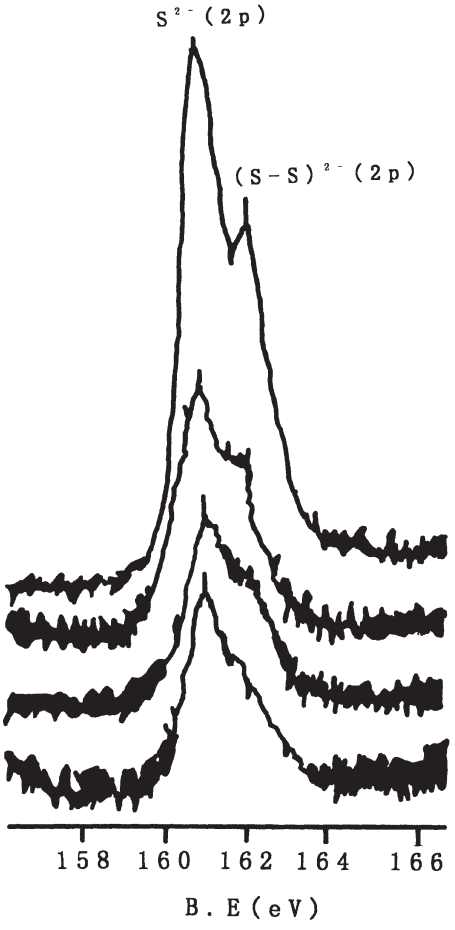

Figure 2. S(2p) XPS spectra of the catalysts in the functioning state. (a) MoS_2. (b) $MoS_2/K_2CO_3/SiO_2$ (0.32/0.10/1.00, wt/wt). (c) $MoS_2/K_2CO_3/SiO_2$ (0.32/0.20/1.00, wt/wt). (d) K_2MoS_4/SiO_2 (0.28/1.00, wt/wt).

present at 161.4 eV, accompanying a shoulder peak at 162.5 eV which may be assigned to $(S\text{–}S)^{2-}$(2p) species. In $MoS_2/K_2CO_3/SiO_2$, the intensity of $(S\text{–}S)^{2-}$ species was decreasing with the increment of K_2CO_3 amounts. In the catalyst K_2MoS_4/SiO_2, the $(S\text{–}S)^{2-}$ peak was undetectable. Taking the XRD result that the Mo–S–K phase content in the K_2MoS_4/SiO_2 catalyst was 2.2 times higher than that in the catalyst $MoS_2/K_2CO_3/SiO_2$ into account, we conclude that the existence of $(S\text{–}S)^{2-}$(2p) species may restrain the generation of M–S–K active phase on the catalyst surfaces.

It was also found from table 1 that the space time yield and selectivity of methanethiol increased with the increase of K_2MoS_4 content in K_2MoS_4/SiO_2, the yield of methanethiol was improved by 52% and its selectivity was improved by 1.2% when the weight of K_2MoS_4 was added twice to the catalyst (catalyst B). The yield of methanethiol was improved by 66% and the selectivity was further improved by 1.4% when the weight of K_2MoS_4 was three times that in catalyst A (see catalyst C). However, on pure K_2MoS_4 the yield was only 18.9% of that on catalyst B, and the selectivity was only 94.1% of that on catalyst B. The results suggests that the optimum ratio of K_2MoS_4 to SiO_2 in K_2MoS_4/SiO_2 may be around 0.56/1 (wt/wt).

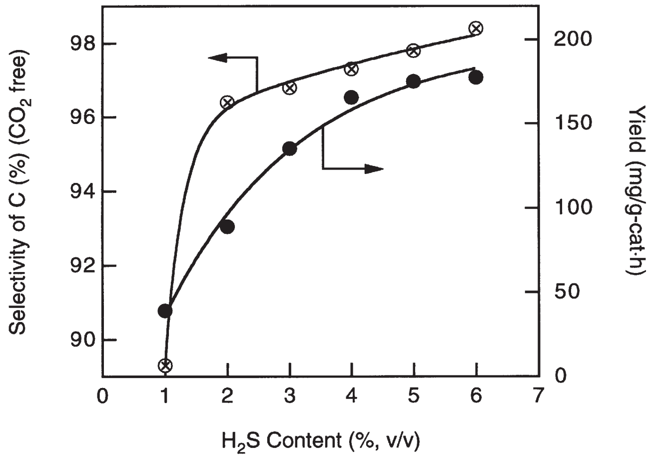

Figure 3. The effect of high H_2S content in syngas on the synthesis of methanethiol over K_2MoS_4/SiO_2.

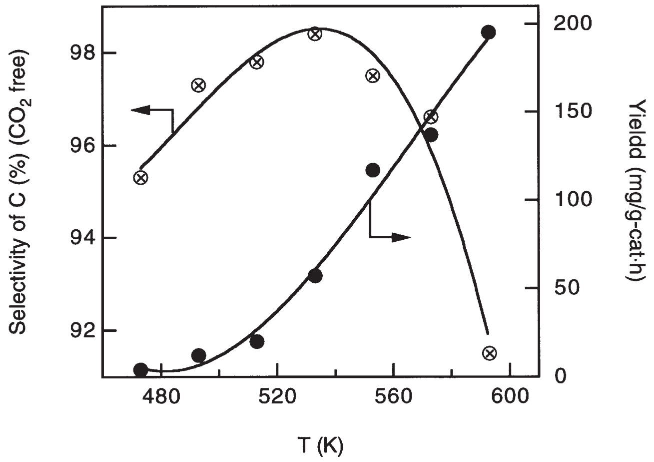

Figure 4. The effect of temperature on the synthesis of methanethiol over K_2MoS_4/SiO_2.

Figure 3 shows the effect of the content of H_2S (1–6%) in syngas on the synthesis of methanethiol over K_2MoS_4/SiO_2. The yield and selectivity of methanethiol increased with the increase of H_2S-content in syngas. The selectivity reached 97.1% and the yield reached 99 $\mathrm{mg\,h^{-1}\,g_{cat}^{-1}}$ when the H_2S-content in syngas was 2%. The selectivity and yield were further improved to 98.5% and 177.6 $\mathrm{mg\,h^{-1}\,g_{cat}^{-1}}$ respectively when the H_2S-content syngas was 6%. The results showed that the H_2S-content in syngas can be controlled among 5–6%.

Figure 4 shows the effect of temperature on the synthesis of methanethiol over K_2MoS_4/SiO_2. In the range of 473–593 K, with the increase of temperature, the yield increased rapidly, while the selectivity reduced rapidly after rising at first. Under the conditions of 1.0 MPa, 563 K and $CO/H_2/N_2/H_2S = 4/4/1.7/0.3$, the yield was 133.5 $\mathrm{mg\,h^{-1}\,g_{cat}^{-1}}$ and the selectivity was 97.5%. When the temperature reached above 575 K, the selectivity dropped rapidly but the yield was still improving. It is suitable to conduct the reaction at a temperature of 562–568 K. The effect of pressure on the synthesis of methanethiol over

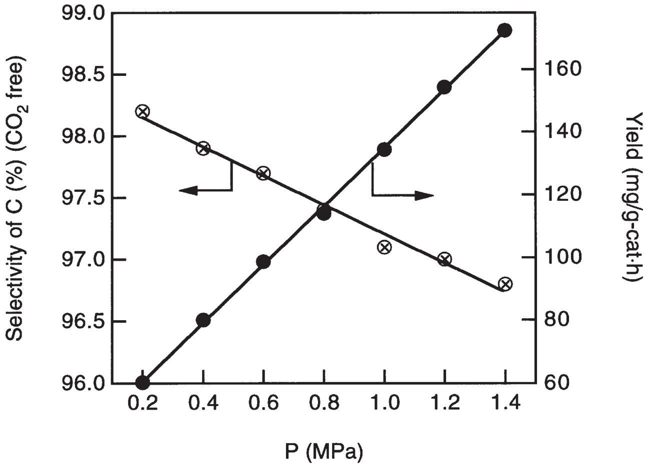

Figure 5. The effect of pressure on the methanethiol synthesis over K_2MoS_4/SiO_2.

K_2MoS_4/SiO_2 is shown in figure 5. It is clear that the yield increased with the increase of reaction pressure, meantime, the selectivity of methanethiol decreased with the increase of the pressure. According to the results, the yield and selectivity of methanethiol were found to be 228 $\mathrm{mg\,h^{-1}\,g_{cat}^{-1}}$, 96.1% respectively under 2.0 MPa and 321 $\mathrm{mg\,h^{-1}\,g_{cat}^{-1}}$, 94.9% respectively under 3.0 MPa. Therefore, the appropriate pressure range should be 2.0–3.0 MPa to maximize the space time yield of methanethiol while maintaining a product selectivity of at least 95%.

4. Conclusion

The existence of $(S–S)^{2-}(2p)$ species in the catalysts inhibits the generation of Mo–S–K, which may be responsible for high yield and selectivity of methanethiol in the one-step synthesis from high H_2S-content syngas. The absence of $(S–S)^{2-}(2p)$ on the catalyst K_2MoS_4/SiO_2 resulted in a higher content of Mo–S–K active phases than that on the catalyst $MoS_2/K_2CO_3/SiO_2$, leading to the catalytic performance of the catalyst K_2MoS_4/SiO_2 being superior to that of the catalyst $MoS_2/K_2CO_3/SiO_2$ for methanethiol synthesis from high H_2S-content syngas. Over the K_2MoS_4/SiO_2 catalyst the optimum reaction conditions for the synthesis of methanethiol were found to be 563 K, 2.0–3.0 MPa, 3000–4000 h^{-1} and 5–6% H_2S-content in the feed syngas.

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