Study of the supported K_2MoO_4 catalyst for methanethiol synthesis by one step from high H_2S-containing syngas

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ESR and XPS are used to study the Mo-based catalysts $MoO_3/K_2CO_3/SiO_2$ and K_2MoO_4/SiO_2 prepared with two kinds of precursors, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and K_2MoO_4. The catalytic properties of the catalysts for methanethiol synthesis from high H_2S-containing syngas are explored. The activity assay shows that the two catalysts have much the same activity for the reaction. By the ESR characterization of both functioning catalysts, the resonant signals of "oxo-Mo(V)" ($g = 1.93$), "thio-Mo(V)" ($g = 1.98$) and S ($g = 2.01$ or 2.04) can be detected. In the catalyst MoO_3/SiO_2 modified with K_2CO_3, as increasing amounts of K_2CO_3 are added, the content of "oxo-Mo(V)" increases, but "thio-Mo(V)" decreases. The XPS characterization indicates that Mo has mixed valence states of Mo^{4+}, Mo^{5+} and Mo^{6+}, and that S includes three kinds of species: S^{2-} (161.5 eV), $[S\text{–}S]^{2-}$ (162.5 eV) and S^{6+} (168.5 eV). Adding K_2CO_3 promoter to the catalysts, the Mo species of high valence state is easily sulphided and reduced to Mo_2S and "oxo-M(V)", and the derivation of $[S\text{–}S]^{2-}$ and S^{2-} species from S is promoted simultaneously. The methanethiol synthesis is favored if the mole ratio of $(Mo^{6+} + Mo^{5+})/Mo^{4+} \leqslant 0.8$ and $S^{2-}/[S\text{–}S]^{2-}$ is kept at a value of about 1.

KEY WORDS: K_2MoO_4/SiO_2; methanethiol; H_2S-containing syngas

1. Introduction

As an important material used to produce medicine, pesticide and methionine, methanethiol was conventionally prepared by several methods such as catalytic thermo-condensation of H_2S under pressure, the reaction of KHS with halogenated methane, the hydrogenation of dimethyl sulfide and so on [1]. When examining the effects of H_2S on the catalytic performance of Mo–S–K/SiO_2 for the synthesis of mixed low-carbon alcohols, our laboratory firstly found that the mixed low-carbon alcohol disappeared and the methanethiol selectivity was over 90% when the concentration of H_2S in syngas was over 1.6% [2]. We have extended this research to a series of methanethiol syntheses based on catalysts prepared from $(NH_4)_2MoS_4$ and K_2MoS_4. The preparation method of this kind of Mo–S-based catalyst consists of numerous steps. In particular, impregnation with a DMF $[(CH_3)_2NCOH]$ solution is used. In order to simplify the preparation and obtain some ideal catalysts, catalysts of the composition $MoO_3/K_2CO_3/SiO_2$ prepared from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were used as a chemical probe to study the active phase of K_2MoO_4/SiO_2 catalyst systems and their catalytic properties. ESR and XPS techniques were used to characterize these catalysts. The paper aims to get a better understanding of the catalysts and provide an important reference for starting a new technological procedure of methanethiol production from high H_2S-containing syngas.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by the method of incipient wetness. The catalyst K_2MoO_4/SiO_2 was prepared by depositing K_2MoO_4 in an aqueous solution on SiO_2, then dried at 120 °C; $MoO_3/K_2CO_3/SiO_2$ was prepared by depositing K_2CO_3 and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ on SiO_2 in sequence, then dried at 120 °C, and followed by calcining at 300 °C.

2.2. Activity assay of the catalyst

The catalytic reaction for methanethiol synthesis was carried out in a two-cell fixed-bed reactor with 0.5 ml of catalyst per pass. The activity was measured under the reaction conditions of 0.2 MPa, 295 °C, GHSV $= 3000\ h^{-1}$, $V(CO):V(H_2):V(H_2S) = 2:7:1$. The reaction products (hydrocarbon and mercaptan) were analyzed by a gas chromatograph (GD-102) with a GDX-103 column of 2.5 m at 120 °C, and methane was used as an external reference. All the data were taken after 12 h reduction of hydrogen and 8 h of reaction when the steady state was achieved.

2.3. Characterization

ESR measurements were performed by using a Bruker ER200D-SRC spectrometer; the output power is 20.4 mW, microwave frequency is 9.71 GHz, modulating amplitude 6.3 Gpp, modulating frequency 12.5 kHz. XPS characterization was carried out by using a VG Escalab Mark-II ap-

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Table 1
The results of activity assays for methanethiol synthesis over K_2MoO_4/SiO_2 catalysts.[a]

Catalyst (m/m)	Surf. area ($m^2\,g^{-1}$)	CO conv. (%)	Selectivity (%) Hydrocarbon C_1	Hydrocarbon C_2	Hydrocarbon C_3	Mercaptan C_1	Mercaptan C_2	Yield of CH_3SH ($g\,h^{-1}\,g_{cat}^{-1}$)
K_2MoO_4/SiO_2[a]								
2/20	–	18.5	0.5	0.1	0.1	99.2	–	0.23
3/20	–	30.4	0.9	0.1	0.1	98.9	–	0.38
4/20	–	37.6	1.1	0.1	0.1	98.8	–	0.47
5/20	67.2	46.0	0.7	0.1	0.1	99.1	–	0.58
6/20	–	39.8	0.8	0.1	0.1	99.1	–	0.50
7/20	–	36.9	1.2	0.1	0.1	98.6	–	0.46
8/20		30.5	1.2	0.1	0.1	98.7	–	0.38
K_2MoS_4/SiO_2[b]								
5.6/20	51.1	3.2	1.6	0.01	–	97.1	1.2	0.1

[a] Reaction conditions: 295 °C, 0.2 MPa, 3000 h^{-1}. The amount of MoO_3 was taken to express that of K_2MoO_4.

[b] From [3]. The amount of MoS_2 was taken to express that of K_2MoS_4.

Table 2
The results of activity assays for methanethiol synthesis over $MoO_3/K_2CO_3/SiO_2$ derived from $(NH_4)_6Mo_7O_{24}\cdot H_2O/SiO_2$.[a]

Catalyst (m/m)	Surf. area ($m^2\,g^{-1}$)	CO conv. (%)	Selectivity (%) Hydrocarbon C_1	Hydrocarbon C_2	Hydrocarbon C_3	Mercaptan C_1	Mercaptan C_2	Yield of CH_3SH ($g\,h^{-1}\,g_{cat}^{-1}$)
MoO_3/SiO_2 (5/20)	56.1	0.3	64.3	25.5	10.2	–	–	–
$MoO_3/K_2CO_3/SiO_2$								
5/2/20	–	17.5	3.5	0.15	0.15	96.2	0.1	0.21
5/3/20	53.8	29.8	2.2	0.1	0.1	97.7	–	0.37
5/4/20	–	22.6	1.7	0.1	0.1	98.1	–	0.28
5/5/20	–	21.9	1.4	0.1	0.1	98.4	–	0.27
5/6/20	–	11.5	1.1	0.2	0.2	98.5	–	0.14
MoS_2/SiO_2 (6/20)[b]		0.3	43.9	56.1	–	–	–	–
$MoS_2/K_2CO_3/SiO_2$[a]	49.1							
6/3/20	46.2	0.8	12.6	31.6	3.4	22.2	0.2	0.005

[a] Reaction conditions: 295 °C, 0.2 MPa, 3000 h^{-1}. The amount of K_2O was taken to express that of K_2CO_3.

[b] From [3].

paratus with Mg Kα radiation. C at BE = 284.7 eV was chosen as an internal reference. All procedures of transferring samples into the XPS chamber were conducted in an atmosphere of purified nitrogen. The peak deconvolution and fitting was performed by using software of SpXzeigR2.1 running with Igor Pro and Gaussian–Lorentzian line shape, fixing both spin–orbit splitting and the relative intensity of spin–orbit components.

3. Results and discussion

The results of activity assay of the K_2MoO_4/SiO_2 catalyst prepared from K_2MoO_4 for methanethiol synthesis are listed in table 1. It can be seen from table 1 that the methanethiol selectivities on K_2MoO_4/SiO_2 catalysts are as high as 98–99%, in particular, on the K_2MoO_4/SiO_2 (5/20) catalyst, the selectivity is found to reach 99.1% and the space yield of methanethiol is found to be 0.58 $g\,h^{-1}\,g_{cat}^{-1}$ being four times higher than that on the catalyst K_2MoS_4/SiO_2 (5.6/20) prepared from K_2MoS_4. No significant deactivation has been found after 100 h running in the present study.

Previous studies of the phase dependence of catalytic activity for materials prepared from $(NH_4)_2MoS_4$ and K_2MoS_4 indicated the formation of a new "Mo–S–K" phase generated during the reaction of alkali potassium salt [3]. The content of Mo–S–K was closely related to the formation of methanethiol. The same product distribution over both the sulfided catalysts K_2MoO_4/SiO_2 and K_2MoS_4/SiO_2 appeared to be related to the "Mo–S–K" phase on the surface. In order to test the assumption of the existence of a "Mo–S–K" phase, the catalyst, $MoO_3/K_2CO_3/SiO_2$, was prepared by impregnating $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ on the SiO_2, which was pre-modified with K_2CO_3. The results of activity assay are listed in table 2.

Table 2 shows that the catalyst MoO_3/SiO_2 is similar to MoS_2/SiO_2 in that they have no ability to catalytically produce mercaptan. However, for the catalyst

Table 3
The results of activity assays for methanethiol over the catalyst regenerated from deactivated K_2MoO_4/SiO_2 (5/20).[a]

The regeneration conditions of the deactivated catalyst	Reaction time (h)	CO conv. (%)	Selectivity (%)				Yield of CH_3SH ($g\,h^{-1}\,g_{cat}^{-1}$)
			Hydrocarbon			CH_3SH	
			C_1	C_2	C_3		
Calcining at 300 °C under N_2 for 3 h	2	–	6.5	1.5	1.9	91.2	0.36
	4	–	4.1	1.0	1.1	93.7	0.45
	8	46	2.6	0.1	0.1	97.1	0.57
After 48 h of drop temperature to 25 °C in feeding syngas	2	–	6.3	0.9	0.5	92.3	0.29
	4	–	4.4	0.6	0.4	94.5	0.45
	8	44	4.3	0.5	0.4	94.8	0.52
Calcining for 3 h under air at 295 °C, then reducing with H_2 for 12 h	2	–	32.7	15.2	8.0	44.1	0.01
	4	–	29.5	13.8	7.7	48.9	0.01
	8	1.7	26.7	12.7	6.9	53.8	0.02
Adding 15% K_2CO_3 to the catalyst calcined for 3 h under air at 295 °C, then reducing with H_2 for 12 h	2	–	7.9	8.8	7.4	75.7	0.06
	4	–	5.4	7.5	4.5	82.6	0.07
	8	7.0	4.9	6.5	4.2	84.3	0.08

[a] Reaction conditions: 295 °C, 0.2 MPa, 3000 h^{-1}.

$MoO_3/K_2CO_3/SiO_2$ with 10–30% of K_2CO_3 the selectivity for main product CH_3SH is found to be up to 96–98%. The selectivity for methanethiol on the catalyst $MoO_3/K_2CO_3/SiO_2$ (25/15/100) with excellent catalytic activity is found to reach 97.7%, and the yield of methanethiol is found to be 0.37 $g\,h^{-1}\,g_{cat}^{-1}$. A product distribution similar to that on the $MoS_2/K_2CO_3/SiO_2$ catalyst is observed (table 1). It can be reasonably inferred that the catalysts prepared from the two precursors may have the same catalytically active phase.

Table 3 shows the results of the activity assays for methanethiol synthesis over the catalyst regenerated from deactivated K_2MoO_4/SiO_2. From table 3 we can conclude that after calcining at 300 °C under N_2 for 3 h or for 48 h of drop temperature to 25 °C in feeding syngas, the activity of the catalyst can recover, only 3–9% dropping of both selectivity and the yield of CH_3SH was found. However, after calcining for 3 h under air at 295 °C, the catalyst almost deactivated. Though adding 15% K_2CO_3 to treat the deactivated catalyst the selectivity for CH_3SH can increase to 84.3%, the yield of CH_3SH and conversion of CO maintained at very low level. If it is necessary to stop the reaction, the functioning catalyst should be protected by N_2 then drop temperature.

Figure 1 shows the relation of $\log V$ (V stands for the reaction rate) and $1/T$ of the K_2MoO_4/SiO_2 catalyst at temperature range of 255–295 °C. According to the Arrhenius formula the reaction activation energies can be figured out:

$$E = -\frac{2.303\times 8.314\times[-2.10-(-2.40)]}{(1.802-1.870)\times 10^{-3}} = 84.5\ \mathrm{kJ\,mol^{-1}}.$$

Figure 2 represents the ESR spectra of functioning Mo-based catalysts. It can be seen from figure 2 that g-resonant signals appeared at 1.93, 1.98, 2.01 and 2.04. Konings *et al.* [4–6] assigned the resonant signal of $g = 1.93$ to the "oxo-Mo(V)" caused by reaction of Mo species with carrier and surrounded by O atoms, and that of $g = 1.98$ to the "thio-Mo(V)" ($g_{\parallel} = 2.06$, $g_{\perp} = 1.98$) in the environment of S. They also concluded that the resonance signals are generated by the phases of MoS_2 like and unconcerned in the carriers. Silbernagel *et al.* [7,8] obtained these signals ($g_{\parallel} = 2.04$, $g_{\perp} = 2.004$) also and considered that these signals are generated by the "thio-Mo(V)" which lies on the edge of MoS_2 crystal with low symmetry. Derouane *et al.* [9] assigned $g = 2.01$ and $g = 2.04$ to the resonant signals of S.

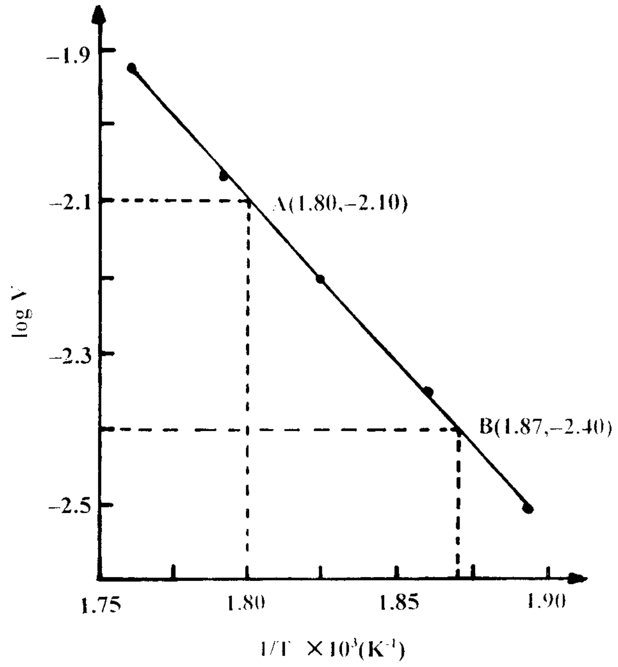

Figure 1. Curve of log V *versus* $1/T$ for the synthesis of methanethiol over K_2MoO_4/SiO_2 catalyst.

From figure 2 (a)–(c), it can be seen that as more K_2CO_3 is added, the resonance signal of $g = 1.93$ increases, indicating on increases of the content of "oxo-Mo(V)". The "oxo-Mo(V)" content of K_2MoO_4/SiO_2 (figure 2(d)) is found

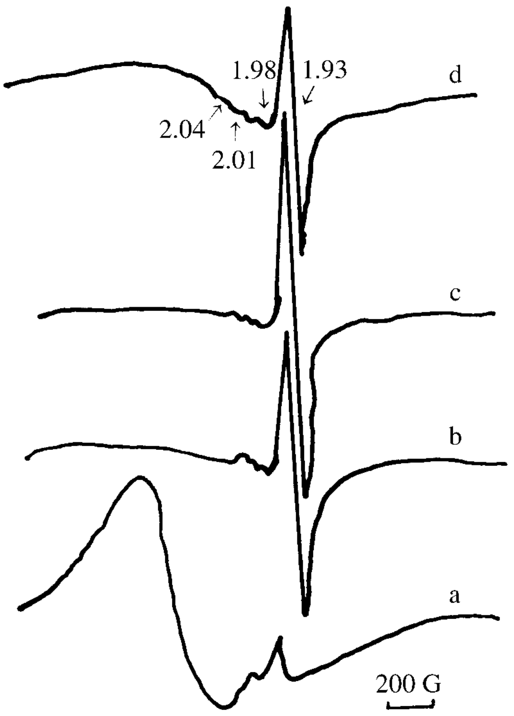

Figure 2. ESR spectra of the Mo-based catalysts in the functioning state: (a) MoO_3/SiO_2 (5/20), (b) $MoO_3/K_2CO_3/Si_2$ (5/3/20), (c) $MoO_3/K_2CO_3/SiO_2$ (5/4/20) and (d) K_2MoO_4/SiO_2 (5/20).

to be equal to that of $MoO_3/K_2CO_3/SiO_2$ (5/3/20), which has a higher catalytic activity. It shows a close relationship between the existence of "oxo-Mo(V)" and the addition of K_2O, in agreement with the inference proposed by Kantschewa and Delanney [10], namely, the existence of K favors the formation of stable Mo(V). Probably it is for the sake of that both K_2O and O-terminate on carrier restrained the deep reduction of Mo. Figure 2 also shows that the resonant signal ($g = 1.98$) of "thio-Mo(V)" decreased as the amount of K_2CO_3 added increased, and that the signal is much more weaker than that of "oxo-Mo(V)". The interpretation of this observation may be as follows: through the S-bridge, the electrons of potassium are delocalized to Mo, thus weakening the interaction of Mo–O–Si. This leads to easy sulfidation and the subsequent reduction of Mo^{6+} to Mo^{4+} [11,12], forming the new "Mo–S–K" phase.

Figure 3 shows the Mo(3d) XPS spectra of Mo-based catalysts. The peaks at 229, 232 and 233 eV may be ascribed to the mixed valence states of Mo^{4+}, Mo^{5+} and Mo^{6+} [13,14]. From figure 3 (a)–(c), it can be seen that the content of Mo^{6+} decreases gradually, and those of Mo^{5+} and Mo^{4+} increase as the amount of K_2CO_3 added to MoO_3/SiO_2 is increased. This indicates that the addition of K_2CO_3 favors the formation of Mo^{5+} and Mo^{4+}. The literature [15] suggests that, for the species of Mo^{6+}, Mo^{5+} and Mo^{4+}, $\Delta E_b = E_b(\text{Mo } 3d_{3/2}) - E_b(\text{Mo } 3d_{5/2}) = 3.1$ eV, and for the same Mo^{n+} $I(\text{Mo } 3d_{5/2})/I(\text{Mo } 3d_{3/2}) = 1.5$, where $I(\text{Mo } 3d_{5/2})$ and $I(\text{Mo } 3d_{3/2})$ stand for the intensity of the spectra peaks of $3d_{5/2}$ and $3d_{3/2}$, respectively. Based on this assumption, the decomposition of the spectra is listed in table 4. From table 4 the mole ratio, $(Mo^{6+} + Mo^{5+})/Mo^{4+}$, of $MoO_3/K_2CO_3/SiO_2$ (5/3/20) with excellent catalytic activity was counted to be 0.8, and this is close to that of K_2MoO_4/SiO_2 (figure 3(d)).

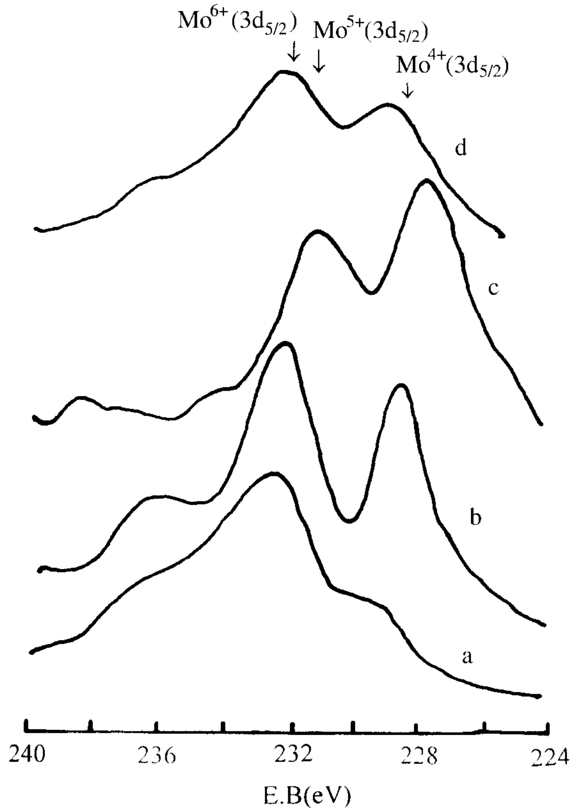

Figure 3. Mo(3d) XPS spectra of the Mo-based catalysts in the functioning state: (a) MoO_3/SiO_2 (5/20), (b) $MoO_3/K_2CO_3/SiO_2$ (5/3/20), (c) $MoO_3/K_2CO_3/SiO_2$ (5/4/20) and (d) K_2MoO_4/SiO_2 (5/20).

Table 4
Bonding energies of the functioning Mo-based catalysts.

Catalyst	EB (Mo $3d_{5/2}$) (eV)			Content (%)		
(m/m)	Mo^{6+}	Mo^{5+}	Mo^{4+}	Mo^{6+}	Mo^{5+}	Mo^{4+}
K_2MoO_4/SiO_2						
5/20	233.5	231.9	229.1	20.5	24.3	56.2
$MoO_3/K_2CO_3/SiO_2$						
5/0/20	233.7	232.1	229.1	48.3	15.6	36.1
5/3/20	233.3	231.9	228.8	21.7	22.6	55.7
5/4/20	232.9	231.7	228.0	12.0	21.6	66.4

Figure 4 shows the S(2p) XPS spectra of functioning Mo-based catalysts. In figure 4, the peaks at 161.5 and 162.5 eV can be assigned to S^{2-} [11] and $[S–S]^{2-}$ [15]; the broad peak at 168.5 eV can be ascribed to overlapping of $S_2O_3^{2-}$ (168.5 eV), SO_3^{2-} (166.6 eV) and SO_4^{2-} (169.1 eV) [16, 17]. On MoO_3/SiO_2 (figure 4(a)), the broad peak at about 168.5 eV is known to be the main peak, implying that the S species may exist as $S_2O_3^{2-}$, SO_3^{2-} or SO_4^{2-}. However, when K_2CO_3 is incorporated into MoO_3/SiO_2 (figure 4 (b) and (c)), the peaks of both S^{2-} and $[S–S]^{2-}$ become main peaks. Similar results are observed for K_2MoO_4/SiO_2 (figure 4(d)). For the MoO_3/SiO_2 catalyst, with less reactivating, the peaks

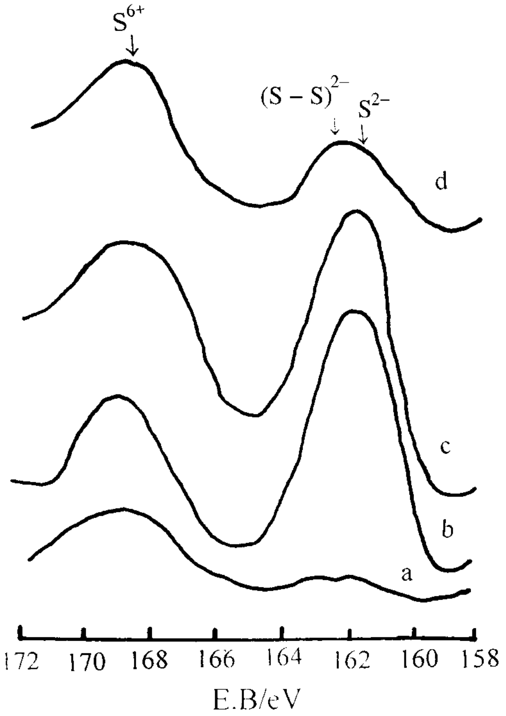

Figure 4. S(2p) XPS spectra of the Mo-based catalysts in the functioning state: (a) MoO_3/SiO_2 (5/20), (b) $MoO_3/K_2CO_3/Si_2$ (5/3/20), (c) $MoO_3/K_2CO_3/SiO_2$ (5/4/20) and (d) K_2MoO_4/SiO_2 (5/20).

of both species look ambiguous. Large, symmetric peaks are observed for the catalysts $MoO_3/K_2CO_3/SiO_2$ (5/3/20) and K_2MoO_4/SiO_2 (5/20), which are more reactive than the MoO_3/SiO_2 catalyst. We conclude that the active catalysts have abundant S^{2-} and $[S–S]^{2-}$ species and they occur in equal mole ratios. These species may be responsible for the high ability to create alcohol.

The importance of the existence of sulfur ions with low valence, both S^{2-} and $[S–S]^{2-}$, on MoS_2-based catalysts for the activation of H_2 has been proved [15,18,19]. Two pathways to activate H_2 have been conceived, namely the coordinating activation by $[S–S]^{2-}$ on the surface of the catalysts,

$$[S-S]^{2-} + H_2 \rightleftharpoons 2SH^-$$

or the heteropolar rupture of H_2 on the Mo–S,

$$Mo^{4+}-S^{2-} \rightleftharpoons \overset{\substack{H\\|}}{Mo}-\overset{\substack{H\\|}}{S}$$

thus providing the resource of active H for the synthesis of thiol.

4. Conclusion

(1) Only the catalyst MoO_3/SiO_2 derived from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ converts H_2S-containing syngas to hydrocarbon; little mercaptan is detected under the reaction conditions. The incorporation of K_2CO_3 into MoO_3/SiO_2 leads to the formation of mercaptan as a main product under the same conditions, and the product distribution is found to be the same as that on the catalyst K_2MoO_4/SiO_2 prepared with K_2MoO_4. The active sites for these conversions appears to be the new "Mo–S–K" phase.

(2) The ESR characterization shows that there exist relatively more "oxo-Mo(V)" which does nothing to the formation of methanethiol and less "thio-Mo(V)" which favors the formation of mercaptan in both K_2MoO_4/SiO_2 and $MoO_3/K_2CO_3/SiO_2$. As the more K_2CO_3 is added, "oxo-Mo(V)" increases and "thio-Mo(V)" decreases.

(3) XPS characterization indicates that the addition of K_2CO_3 to Mo-based catalysts is in favor of the formation of Mo^{5+}, Mo^{4+}, S^{2-} and $[S–S]^{2-}$ species, and it will benefit the methanethiol synthesis to keep $(Mo^{6+} + Mo^{5+})/Mo^{4+} \leqslant 0.8$ and $S^{2-}/[S–S]^{2-}$ close to 1.

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