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# The Promoting Effect of Tellurium on $K_2MoO_4/SiO_2$ Catalyst for Methanethiol Synthesis from High $H_2S$-Containing Syngas

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**Abstract** Tellurium used as promoter was investigated in the preparation of $K_2MoO_4/SiO_2$ catalyst for methanethiol synthesis from high $H_2S$-containing syngas. The experimental results showed that the addition of Te to $K_2MoO_4/SiO_2$ improved the activity of catalysts and the selectivity of methanethiol. ESR results reveal that the addition of Te decreases the content of "oxo-$Mo^{5+}$" species and increase that of the "oxysulfo-$Mo^{5+}$" species, simultaneously increase the low valence states of sulfur species. XPS results reveal that the addition of Te to $K_2MoO_4/SiO_2$ increase the amount of low valence states of molybdenum and sulfur species, which are related to the formation of methanethiol.

**Keywords** Tellurium · Methanethiol · Mo-based catalyst · Syngas · ESR · XPS

## 1 Introduction

As an important chemical raw material and organic synthesis intermediate, methanethiol is extensively used in the synthesis of methionine, pesticide, medicine, plastics etc. At present, it is made commercially by the reaction of methanol with hydrogen sulfide, which requires the synthesis of methanol from syngas. Obviously, one-step synthesis of methanethiol from $H_2S$-containing syngas is very promising in industrial application. Very recently, Mul et al. [1] have investigated the synthesis of methanethiol from CO and $H_2S$ over sulfided vanadium catalysts based on $TiO_2$ and $Al_2O_3$ at 340 °C, 1.0 MPa, 600 $h^{-1}$, and the optimized methanethiol yield amounts to 0.35 $mmolh^{-1} \cdot g^{-1}_{cat}$. Zhang et al. [2, 3] have reported the synthesis route of methanethiol from the reaction of $CO/H_2/H_2S$ over $\alpha$-$Al_2O_3$ at 340 °C, 2.0 MPa, 200 $h^{-1}$, and the selectivity of methanethiol was reported to be over 98%. However, the silica-supported K–Mo catalysts were found to be the most excellent catalysts for direct synthesis of methanethiol at relative low reaction temperature (300 °C) and high space velocity (3000 $h^{-1}$), rare-earth oxides and transition metal oxides used as promoters were investigated [4–6].

Nonmetallic tellurium is often added as a promoter to Mo–V-based catalysts for allylic selective oxidation and ammoxidation of olefins [7, 8]. In the present study, Te was introduced into the $K_2MoO_4/SiO_2$ catalyst and the performance of the catalysts was investigated. ESR and XPS were used to characterize the modified catalysts.

## 2 Experimental

### 2.1 Catalysts Preparation

The Te-promoted $K_2MoO_4/SiO_2$ catalysts were prepared by multi-step impregnation. Firstly, a given quantity of telluric acid ($H_6TeO_6$) was dissolved under heating and stirring to produce an aqueous solution, with which 5.00 g of $SiO_2$ ($S_{BET}$ = 260 $m^2$/g, 20–45 meshes) was impregnated for 12 h, then dried at 120 °C to get precursor. The precursor prepared above was secondly impregnated in an ammonia solution with 2.07 g of $K_2MoO_4$, then dried, followed by calcination at 400 °C in air for 3 h. The catalysts thus prepared were expressed as $K_2MoTe_xO/SiO_2$. (x was the ratio of Te to Mo; the catalyst was expressed as $K_2MoO_4/SiO_2$ when x was zero).

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### 2.2 Activity Assay of the Catalysts

The activity evaluation was carried out in a tubular fixed-bed flow stainless steel microreactor by using 0.5 mL of catalyst per pass. The evaluation experiments were performed under reaction conditions of 0.2 MPa, 300 °C, feed gas mixture $CO:H_2:H_2S = 1:1:2$ (by volume) and GHSV = 2000 h$^{-1}$. The hydrocarbon, sulfur-containing products, CO were analysed by on-line GC equipped with flame ionization detector (GDX-103 column, 1.5 m × ϕ8 mm), flame photometric detector (HP-Plot/Q capillary column, 30 m × 0.539 mm × 40.00 μm) and thermal conductivity detector (carbon molecular sieves column, 1.5 m × ϕ8 mm), respectively.

### 2.3 Catalysts Characterization

ESR measurements were carried out with a Bruker ER2000-SRC spectrometer at microwave frequency of 9.06 GHz with 5 mW of power. The modulating frequency was 100 kHz and modulating amplitude was 6.0 Gpp. The *g* values were calculated from accurate measurement of both the magnetic field strength and the microwave frequency. XPS spectra were recorded on a PHI Quantum 2000X spectrometer operating with Al Kα radiation source. The binding energy in the spectra were calibrated against the adventitious carbon C1*s* ($E_b$ = 284.7 eV) singlet.

## 3 Results and Discussion

### 3.1 Catalytic Performance

The activity assay results of $K_2MoO_4/SiO_2$ catalysts modified with different amount of Te for methanethiol synthesis from high $H_2S$-containing syngas are listed in Table 1. As it can be seen, the addition of a small amount of Te to $K_2MoO_4/SiO_2$ catalyst increases evidently the activity of the catalysts, which can find expression in the significant change of conversion of CO and the yield of $CH_3SH$, hereafter the activity of the catalysts increases slightly with the increase of Te. When the molar ratio of Te to Mo is 0.5, the conversion of CO reaches a maximum with 62.1% and a yield of methanethiol of 0.60 g $mL_{cat}^{-1} \cdot h^{-1}$. Hereafter, the conversion of CO decreases with the increase of Te addition. Obviously, Te also can be taken as an effective promoter of K-Mo/$SiO_2$ catalysts for the synthesis of methanethiol from high $H_2S$-containing syngas.

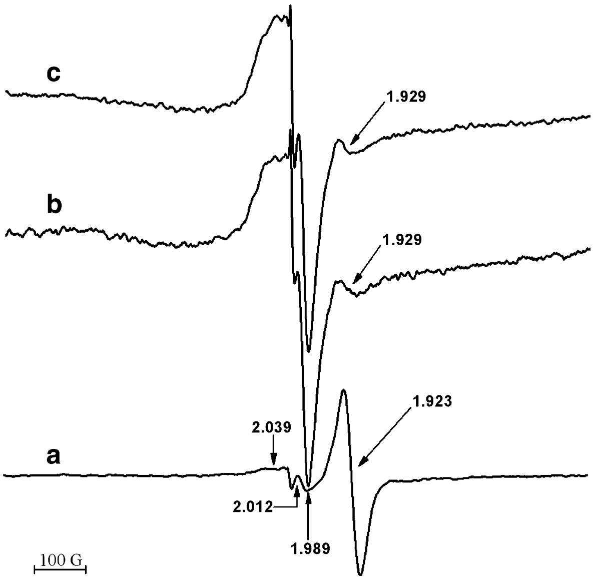

**Fig. 1** ESR spectra of sulfided catalysts: (**a**) $K_2MoO_4/SiO_2$, (**b**) $K_2MoTe_{0.2}O/SiO_2$, (**c**) $K_2MoTe_{0.5}O/SiO_2$ 160 × 154 mm (150 × 150 DPI)

**Table 1** The promoting effect of Te on the catalytic performance of $K_2MoO_4/SiO_2$[a]

| Catalysts | CO conversion (%) | Selectivity (%) | | | | | | | Yield of $CH_3SH$ ($g \cdot mL_{cat}^{-1} \cdot h^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| | | Hydrocarbon | | $CO_2$ | S-containing products | | | | |
| | | $C_1$ | $C_2$ | | COS | $CH_3SH$ | $C_2SH$ | $CS_2$ | |
| $K_2MoO_4/SiO_2$ | 43.5 | 0.2 | T[b] | 34.5 | 25.3 | 40.1 | T | T | 0.34 |
| $K_2MoTe_{0.2}O/SiO_2$ | 58.8 | 0.2 | T | 32.8 | 18.6 | 48.4 | – | – | 0.56 |
| $K_2MoTe_{0.3}O/SiO_2$ | 60.5 | 0.1 | T | 31.3 | 19.7 | 48.7 | – | – | 0.57 |
| $K_2MoTe_{0.4}O/SiO_2$ | 61.0 | 0.2 | T | 31.2 | 20.0 | 48.6 | – | T | 0.58 |
| $K_2MoTe_{0.5}O/SiO_2$ | 62.1 | 0.2 | T | 30.1 | 20.6 | 49.1 | – | – | 0.60 |
| $K_2MoTe_{0.7}O/SiO_2$ | 58.0 | 0.2 | T | 28.4 | 23.8 | 47.6 | T | – | 0.53 |

[a] Reaction conditions: 300 °C,$CO:H_2:H_2S = 1:1:2$, 2000 h$^{-1}$, 0.2 MPa

[b] T = Trace < 0.1%

**Fig. 2** Mo (3d) XPS spectra of sulfided catalysts: (**a**) $K_2MoO_4/SiO_2$, (**b**) $K_2MoTe_{0.2}O/SiO_2$, (**c**) $K_2MoTe_{0.5}O/SiO_2$ 166 × 139 mm (96 × 96 DPI)

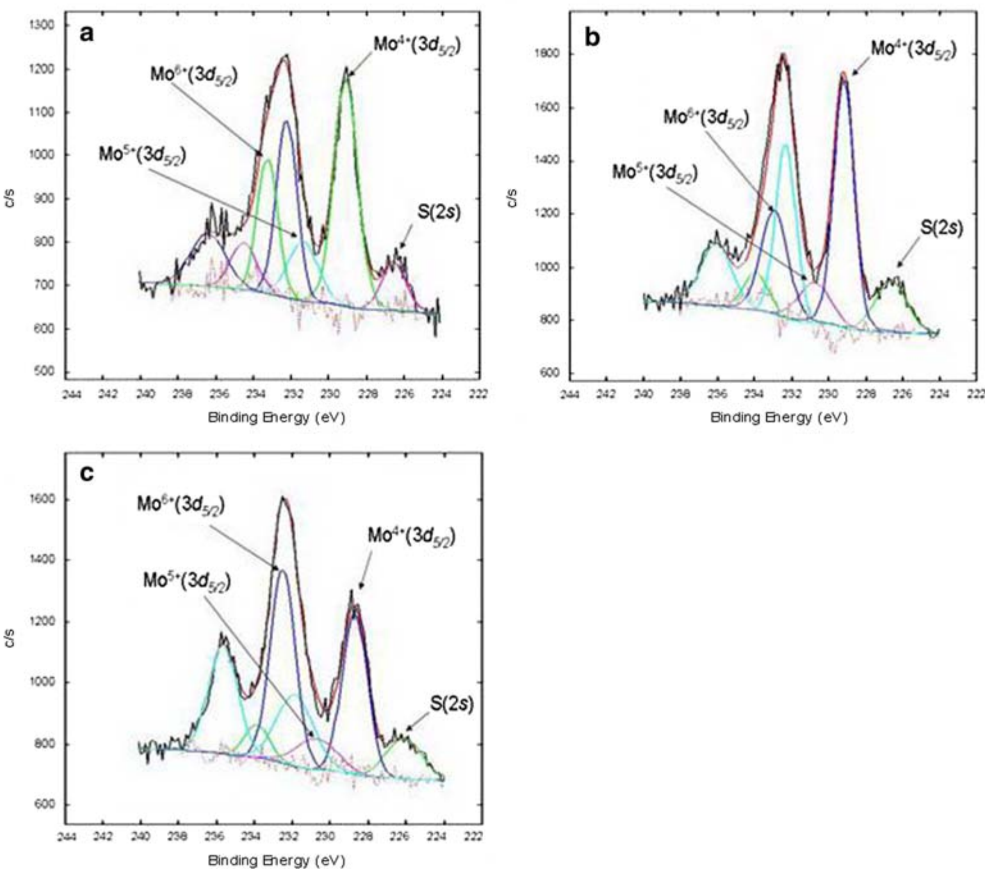

**Table 2** The binding energy and atomic ratio of Mo species

| Catalyst | Binding energy (eV) | | | Content (%) | | |
|---|---|---|---|---|---|---|
| | $Mo^{4+}$ | $Mo^{5+}$ | $Mo^{6+}$ | $Mo^{4+}$ | $Mo^{5+}$ | $Mo^{6+}$ |
| $K_2MoO_4/SiO_2$ | 229.1 | 231.4 | 233.3 | 49.4[a] | 14.2 | 26.4 |
| $K_2MoTe_{0.2}O/SiO_2$ | 229.2 | 230.8 | 233.0 | 54.7 | 21.1 | 24.2 |
| $K_2MoTe_{0.5}O/SiO_2$ | 228.7 | 230.7 | 232.8 | 55.5 | 22.2 | 22.3 |

[a] $Mo^{4+}/(Mo^{4+} + Mo^{5+} + Mo^{6+})$

## 3.2 ESR Study

Figure 1 shows the ESR spectra of sulfided catalysts with different concentrations of $TeO_2$. Four signals appeared at $g = 1.923$, 1.989, 2.012 and 2.039 can be detected in ESR measurements. The resonant signal at $g = 1.923$ corresponds to oxo-$Mo^{5+}$ species, i.e., $Mo^{5+}$ ion surrounded by oxygen [9]. Furthermore, a shift of the $g$ value of oxo-$Mo^{5+}$ toward lower fields with the addition of Te is observed. The signal at $g = 1.989$ is due to oxysulfo-$Mo^{5+}$ species, i.e., $Mo^{5+}$ ion in a O,S-surrounding sites due to the partial exchange of the oxygen with sulfur [10–12]. Signal of $g = 2.012$ and 2.039 can be attributed to paramagnetic sulfur species according to [12–14], these species may be disulfur radicals and polysulfur species produced during the reaction.

From Fig. 1a–c, it can be seen that owing to the addition of Te to $K_2MoO_4/SiO_2$, the intensity of signal of $g = 1.923$ decreases, which suggests that the content of oxo-$Mo^{5+}$ species decrease. An explanation might be that the Te added partly weaken the interaction between Mo species and support, leading to the oxygen atoms of oxo-$Mo^{5+}$ are easily replaced by sulfur. The increase in intensity of oxysulfo-$Mo^{5+}$ accompanied by an increase of paramagnetic sulfur species, indicating that the Te addition favors the increase of oxysulfo-$Mo^{5+}$ species and paramagnetic sulfur at the expense of oxo-$Mo^{5+}$ species. The connection between the results of ESR and activity assay shows that the

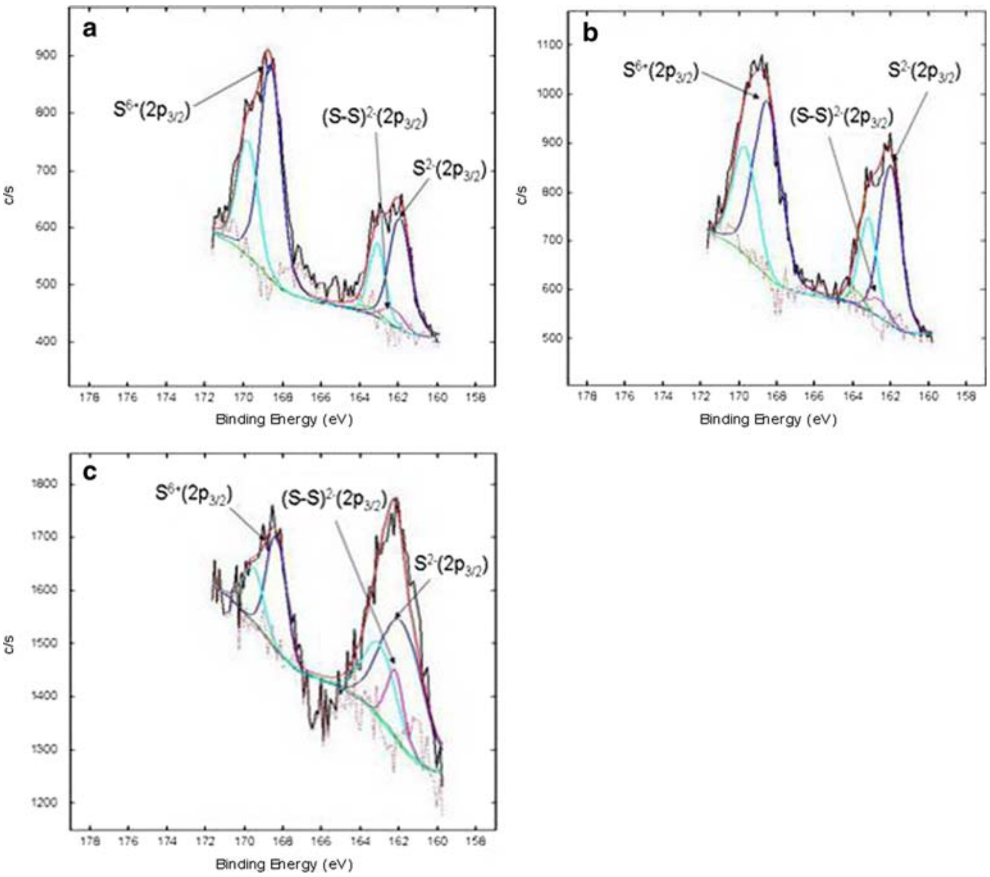

**Fig. 3** S (2p) XPS spectra of sulfided catalysts :(**a**) $K_2MoO_4/SiO_2$, (**b**) $K_2MoTe_{0.2}O/SiO_2$, (**c**) $K_2MoTe_{0.5}O/SiO_2$
164 × 139 mm (96 × 96 DPI)

oxysulfo-$Mo^{5+}$ and low valence states sulfur species may benefit the formation of the desirous product of $CH_3SH$.

### 3.3 XPS Study

Figure 2 shows Mo(3d) spectra of the sulfided catalyst modified with different amounts of Te. For a quantitative analysis, the curves were fitted by using Multipak V6.1A software in accordance with the following assumption: $\Delta E_b = E_b(Mo3d_{3/2}) - Eb(Mo3d_{5/2}) = 3.1$, an area ratio of 3:2 between the $Mo3d_{5/2}$ and $Mo3d_{3/2}$, and a mixed Gaussian-Lorentzian function after a Shirley background subtraction [5, 15, 16]. The $Mo3d_{5/2}$ of binding energy at ~229, ~231 and ~233 eV may be due to the oxidation state of +4, +5 and +6, respectively, binding energy at 226.6 eV may be ascribed to S(2s) peak hided in Mo(3d) spectra [17, 18]. The results of deconvolution of the spectra and surface atomic ratio are listed in Table 2. As it can be seen, there are higher relative concentrations of $Mo^{4+}$ and $Mo^{5+}$ on the surface of the Te-promoted catalysts as compared to $K_2MoO_4/SiO_2$, accompanied by lower concentrations of $Mo^{6+}$ at the same time. The Te added is conducive to the reduction of $Mo^{6+}$ to $Mo^{5+}$ or $Mo^{4+}$, suggesting that Te may participate in the electron transform of redox processes of Mo species.

Figure 3 shows the S(2p) XPS spectra of the sulfided catalysts. The peaks at 161.5, 162.5 and 168.5eV can be assigned to $S^{2-}$, $[S\text{–}S]^{2-}$ and $S^{6+}$, respectively[5, 18]. Obviously, the area in the spectra which corresponds to the low valence states increases with the addition of Te from 0.2 to 0.5. The importance of low valence sulfur ion, both $S^{2-}$ and $S_2^{2-}$, on $MoS_2$-based catalysts to activate $H_2$ has been proved [19, 20]. The activation of $H_2$ may proceed in two pathways, namely the coordinating activation by $[S\text{–}S]^{2-}$ and heteropolar rupture on $Mo^{4+}\text{–}S^{2-}$ [21]. Consequently, higher concentrations of low valence states of Mo and S species in the sulfided catalysts lead to the higher yield of $CH_3SH$.

Figure 4 shows the Te (3d) XPS spectrum of the sulfided catalyst. The Te $3d_{5/2}$ binding energy of ~576 eV indicates an oxidation state of +4 and the shoulder peak at 573 eV corresponds to the presence of zero-valent Te [22]. López Nieto et al. [23] found that the performance of Mo–V–Te–Nb–O catalysts strongly depended on the Te-compounds used as precursors in the oxidation of propane to acrylic acid, high activity was observed on the catalysts prepared from $Te^{6+}$ precursors while low activity was observed if the catalysts were prepared from $Te^{4+}$ precursors. Bart et al. [24] reported that the Mo, Te and O could form the compound $Te_2MoO_7$ and the activation of

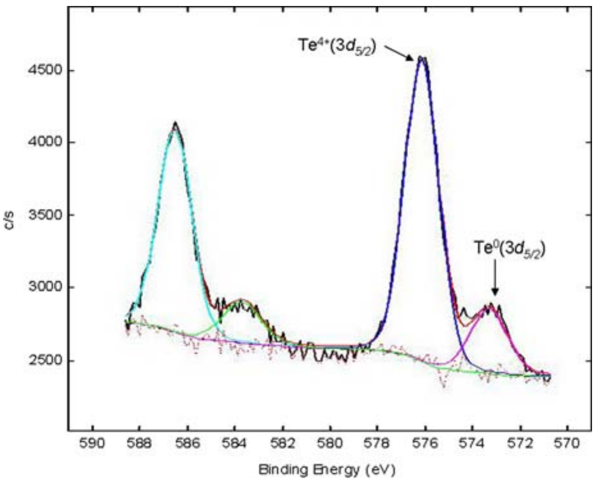

**Fig. 4** Te (3d) XPS spectrum of sulfided $K_2MoTe_{0.5}O/SiO_2$ 170 × 136 mm (96 × 96 DPI)

propylene takes place on $Te^{4+}$ sites in the reaction of the ammoxidation of propylene to acrylonitrile. In this study, $Te^{4+}$ species are mainly present in the sulfided KMoTeO/$SiO_2$ catalysts, which exhibit higher activity than K–Mo/$SiO_2$ catalysts, so it can be inferred that the intermediate valence of $Te^{4+}$ species could participate in the redox process of $Mo^{6+}/Mo^{5+}$, $Mo^{4+}$ on one hand, or be as the active sites of some elementary reactions for synthesis methanethiol on the other hand. Consequently, the high valence states of molybdenum and sulfur species may be more easily reduced to low valence states after the Te addition to $K_2MoO_4/SiO_2$. This makes the reduction and sulfidation of catalysts more easily, leading to the improvement in the activity of the catalysts and selectivity of methanethiol.

## 4 Conclusion

It has been found that Te has a promoting effect on the $K_2MoO_4/SiO_2$ catalyst for the synthesis of methanethiol from high $H_2S$-containing syngas. High activities and selectivities for methanethiol were obtained when the molar ratio of Te promoter to Mo equaled 0.5. The results of ESR characterization show that the Te addition was able to decrease the amount of “oxo-$Mo^{5+}$” while the amount of “oxysulfo-$Mo^{5+}$” and low valence states of sulfur species increase. XPS investigations indicate that Te exists mainly in oxidation state of +4 in sulfided catalysts, and the addition of Te to $K_2MoO_4/SiO_2$ increases the concentration of low valence states of molybdenum and sulfur species, which may be close related to the formation of methanethiol.

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