

On methanethiol synthesis from H₂S-containing syngas over K₂MoS₄/SiO₂ catalysts promoted with transition metal oxides

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The catalysts K₂MoS₄/SiO₂ promoted with transition metal oxides Fe₂O₃, CoO, NiO and MnO₂ were prepared and used to catalyze the synthesis of methanethiol from H₂S-containing syngas. The results of activity assay show that the catalysts promoted with Fe₂O₃, CoO and NiO can remarkably increase the hour space yield of methanethiol. Nevertheless, MnO₂ was found to have a disadvantageous effect on the selectivity of methanethiol. The results of XRD and XPS characterization indicate that the addition of the transition metal oxides promoters is in favor of the formation of a Mo–S–K active phase and also retards the decomposition of K₂MoS₄ to MoS₂, thereby suppressing both the deep reduction of Mo species and the formation of (S–S)^{2–} species, which are reflected by the increment of the concentration ratios of both Mo⁶⁺/Mo⁴⁺ and S^{2–}/(S–S)^{2–}.

Keywords: methanethiol, Mo–S-based catalyst, H₂S-containing syngas, transition metal oxide

1. Introduction

As an important material used to produce medicine, pesticides and methionine, methanethiol was conventionally prepared by the reaction of H₂S with halogenated methane. Recently, several publications of preparation ways based on the reaction of H₂S with ethanol or diethyl ether, hydrogenation of dimethyl sulfide, and, in particular, the reaction of H₂S with carbon monoxide over the NiO/TiO₂ or MoO₃/TiO₂ catalyst appeared [1–3]. Our preceding work disclosed that, under the conditions of mixed alcohol synthesis from H₂S-containing syngas over the Mo–S–K-based catalyst, the mixed alcohol of low carbon disappeared and methanethiol was found to be the main product when the concentration of H₂S in syngas was over 1.6%, which started a series of investigations to develop Mo–S–K-based catalysts for methanethiol synthesis from H₂S-containing syngas [4,5]. In the present paper, the effect of the incorporation of several transition metal oxides, Fe₂O₃, CoO, NiO and MnO₂, into K₂MoS₄/SiO₂ to constitute the catalysts K₂MoS₄/MO_x/SiO₂ on the catalytic performance of the catalysts for methanethiol synthesis from H₂S-containing syngas was studied. The results of XRD and XPS characterization of the catalysts promoted with transition metal oxides disclosed the nature of the active sites on the catalysts. It seems useful to provide further information about the nature of the active sites on the catalysts to optimize the technological procedure of the methanethiol production.

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2. Experimental

2.1. Catalyst preparation

K₂MoS₄ and K₂MoS₄/SiO₂ were prepared according to literature methods [4,5]. The preparation of K₂MoS₄/MO_x/SiO₂ is as follows: firstly, a calculated amount of SiO₂ with 80–100 mesh was soaked in an aqueous solution of a metal nitrate, then dried at 110 °C for 2 h, followed by calcining at 500 °C for 3 h to generate MO_x/SiO₂; secondly, the MO_x/SiO₂ thus obtained was impregnated with a dimethylformamide (DMF) solution of K₂MoS₄, then dried under vacuum and DMF was removed by extracting with anhydrous ethyl ether; finally, the samples prepared above were evacuated again to remove undesirable solvents to obtain K₂MoS₄/MO_x/SiO₂.

2.2. Activity assay of the catalysts

The catalytic reaction of methanethiol synthesis was carried out in a stainless-steel tubular reactor with 1.0 ml of the catalyst per pass. The activity was measured under the reaction conditions of 0.2 MPa, 295 °C, CO/H₂/H₂S = 5/14/1 (v/v) and GHSV = 3000 h^{–1}. The products were analyzed on a gas chromatograph with a GDX103 column of 2.5 m. All data were taken after 8 h of operation when the steady state was achieved.

2.3. Characterization

X-ray diffraction (XRD) patterns were taken by using a Rigaku Ru-200x diffractometer with Cu Kα at radiation rate 6°/min in the 2θ range of 10–80°.

XPS measurements were performed by using a VG Escalab Mark-II machine with Mg $K\alpha$ radiation (1253.6 eV, 10 kV, 20 mA) and UHV (1×10^{-7}). Si(2p) of SiO_2 at BE = 103.4 eV was chosen as an internal reference. All procedures of transferring samples into the XPS chamber were conducted in an atmosphere of purified nitrogen.

3. Results and discussion

The results of activity assay of the catalysts K_2MoS_4/SiO_2 promoted with the transition metal oxides for methanethiol synthesis are listed in table 1. It can be seen from table 1 that the yields of methanethiol over the functioning catalysts promoted with Fe_2O_3 , CoO or NiO are twice that on the functioning catalyst without promoter $K_2MoS_4/SiO_2(F)$ and that the selectivities increase by 3%. As for the catalyst promoted with MnO_2 , the yield of methanethiol increases by 73%, but the selectivity of methanethiol decreases by 1.6%, implying a marked increase of catalytic activity for the reaction. It seems that the proper amount of transition metal oxides added may be 3 wt% based on that of the carrier SiO_2 under the present reaction conditions.

Figure 1 shows the XRD patterns of the catalysts. In figure 1(a), the characteristic peak of SiO_2 appears at $2\theta = 21.4^\circ$; in figure 1(b), the peaks at $2\theta = 14, 33.3,$

39.5 and 59° belong to MoS_2 [6]. The XRD patterns of the catalysts both in the oxidative state $K_2MoS_4/SiO_2(O)$ and in the functioning state, including $K_2MoS_4/SiO_2(F)$ and $K_2MoS_4/MO_x/SiO_2$, are shown in figure 1 (c) and (d)–(h), respectively. Comparison of the pattern in figure 1 (c) with those in (d)–(h) shows that two new peaks at $2\theta = 29.8$ and 30.0° , which can be assigned to a “Mo–S–K” active phase [7,8], appeared for the functioning catalysts, meanwhile the intensity ratios of the peaks of the Mo–S–K phase to that of MoS_2 for the functioning catalysts were found to be 1.18, 2.91, 3.08, 2.90 and 1.88. The intensity ratios of the peaks of the functioning catalysts with transition metal oxides, in particular with CoO, Fe_2O_3 and NiO, were remarkably higher than that of $K_2MoS_4/SiO_2(F)$, indicating that the concentration of Mo–S–K active sites on the catalysts with transition metal oxides increased, which can be attributed to that the addition of transition metal oxides retarded the decomposition of K_2MoS_4 to MoS_2 . It is well known that microcrystalline MoS_2 and sulfided supported Mo catalysts are able to take up a considerable amount of H_2 . However, the uptake of H_2 on alkali-salt-promoted systems, in comparison with that on unsupported or neutral potassium salts (e.g., KCl) promoted systems, was greatly reduced. Under the conditions of the synthesis of mixed alcohol from syngas, the principal product on the MoS_2/SiO_2

Table 1
The effect of promoters on catalytic performance of K_2MoS_4/SiO_2 .^a

Catalysts (wt/wt)	Selectivity (%)					Yield of CH ₃ SH (g h ⁻¹ g _{cat} ⁻¹)
	Hydrocarbon			Mercaptan		
	C ₁	C ₂	C ₃	C ₁	C ₂	
MoS ₂ ^b	80.1	16.3	3.6	–	–	–
K ₂ MoS ₄ /SiO ₂ (0.15/1.00) ^c	3.3	0.9	0.8	92.2	2.8	0.15
K ₂ MoS ₄ /Fe ₂ O ₃ /SiO ₂ (0.15/0.04/1.00)	2.4	0.2	0.1	95.8	2.4	0.36
(0.15/0.03/1.00)	2.3	0.2	0.1	95.8	2.3	0.36
(0.15/0.02/1.00)	2.5	0.4	0.3	95.2	2.4	0.33
(0.15/0.01/1.00)	2.7	0.5	0.4	94.7	2.5	0.30
K ₂ MoS ₄ /CoO/SiO ₂ (0.15/0.04/1.00)	1.7	0.2	0.1	95.9	2.2	0.37
(0.15/0.03/1.00)	1.7	0.3	0.1	95.8	2.2	0.37
(0.15/0.02/1.00)	2.0	0.4	0.2	95.2	2.3	0.34
(0.15/0.01/1.00)	2.5	0.6	0.5	93.7	2.5	0.30
K ₂ MoS ₄ /NiO/SiO ₂ (0.15/0.04/1.00)	2.5	0.3	0.1	95.1	2.0	0.32
(0.15/0.03/1.00)	2.4	0.3	0.1	95.2	2.0	0.33
(0.15/0.02/1.00)	2.6	0.5	0.3	94.8	2.3	0.30
(0.15/0.01/1.00)	3.0	0.6	0.6	93.5	2.6	0.28
K ₂ MoS ₄ /MnO ₂ /SiO ₂ (0.15/0.04/1.00)	5.8	1.1	0.3	90.5	2.7	0.25
(0.15/0.03/1.00)	5.7	1.0	0.3	90.6	2.7	0.26
(0.15/0.02/1.00)	5.5	1.1	0.6	91.3	2.9	0.25
(0.15/0.01/1.00)	5.1	1.0	0.7	92.0	2.8	0.22

^a Reaction conditions: 290 °C, 0.2 MPa, $CO/H_2/H_2S = 5/14/1$, 3000 h^{-1} .

^b Derived from the precursor of $(NH_4)_2MoS_4$.

^c The amount of MoS_2 was taken to express that of K_2MoS_4 .

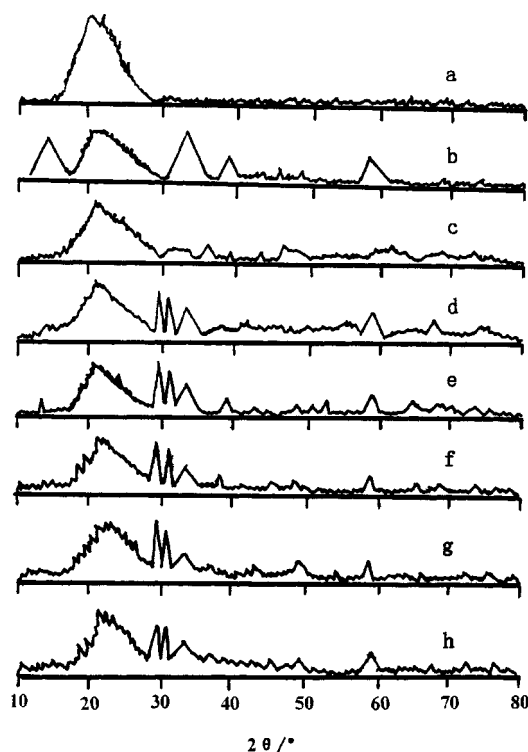


Figure 1. XRD patterns of the catalysts: (a) SiO_2 , (b) MoS_2/SiO_2 (0.15/1.00), (c) K_2MoS_4/SiO_2 (0.15/1.00 oxidative state), (d) K_2MoS_4/SiO_2 (0.15/1.00), (e) $K_2MoS_4/Fe_2O_3/SiO_2$ (0.15/0.03/1.00), (f) $K_2MoS_4/CoO/SiO_2$ (0.15/0.03/1.00), (g) $K_2MoS_4/NiO/SiO_2$ (0.15/0.03/1.00), (h) $K_2MoS_4/MnO_2/SiO_2$ (0.15/0.03/1.00).

catalyst without alkali potassium salt promoter was found to be hydrocarbon, nevertheless mixed alcohol became the main product on MoS_2-K^+/SiO_2 catalyst [9]. This marked differences can likely be attributed to the distinction of the reaction pathway on the two catalyst systems owing to the modification of alkali salt. According to the experimental results on potassium-promoted Mo–S-based catalysts for the synthesis of mixed alcohol from syngas, Lin et al. [7] discovered that on the Mo–S-based catalyst systems doped with basic potassium, such as K_2CO_3 or KF , there is a strong interaction between potassium content and molybdenum component, which led to the proposing of a Mo–S–K phase on the surface of the catalysts.

Figures 2 and 3 show the XPS spectra of the catalysts. The assignments of the main peaks observed are listed in table 2. In the Mo(3d) range of the XPS spectra of MoS_2 shown in figure 2(a), the peaks at 228.5 and 231.6 eV can be assigned to $Mo^{4+}(3d_{5/2})$ and $Mo^{4+}(3d_{3/2})$. In figure 2 (b)–(f) is shown the Mo(3d) range of XPS spectra of the functioning catalysts, in which range, the peaks at 228.0, 231.5, 232.5 and 235.5 eV (BE) can be ascribed to $Mo^{4+}(3d_{5/2})$, $Mo^{4+}(3d_{3/2})$, $Mo^{6+}(3d_{5/2})$ and $Mo^{6+}(3d_{3/2})$ [10], indicating that two kinds of valence state of Mo, namely Mo^{4+} and Mo^{6+} , exist on the surface of the functioning catalysts. The intensity ratios of Mo^{6+}/Mo^{4+} were found to be 0.27, 0.71, 0.80, 0.79 and 0.43. It is clear that the concentration of Mo^{6+} on the surface of the catalysts promoted with the transition metal oxides is higher

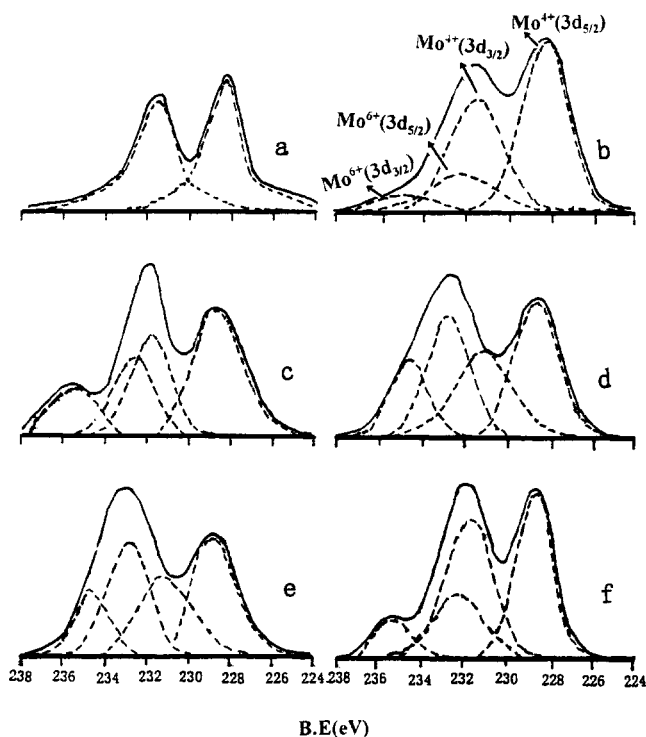


Figure 2. XPS spectra of functioning catalysts at Mo(3d) range: (a) MoS_2 , (b) K_2MoS_4/SiO_2 (0.15/1.00), (c) $K_2MoS_4/Fe_2O_3/SiO_2$ (0.15/0.03/1.00), (d) $K_2MoS_4/CoO/SiO_2$ (0.15/0.03/1.00), (e) $K_2MoS_4/NiO/SiO_2$ (0.15/0.03/1.00), (f) $K_2MoS_4/MnO_2/SiO_2$ (0.15/0.03/1.00).

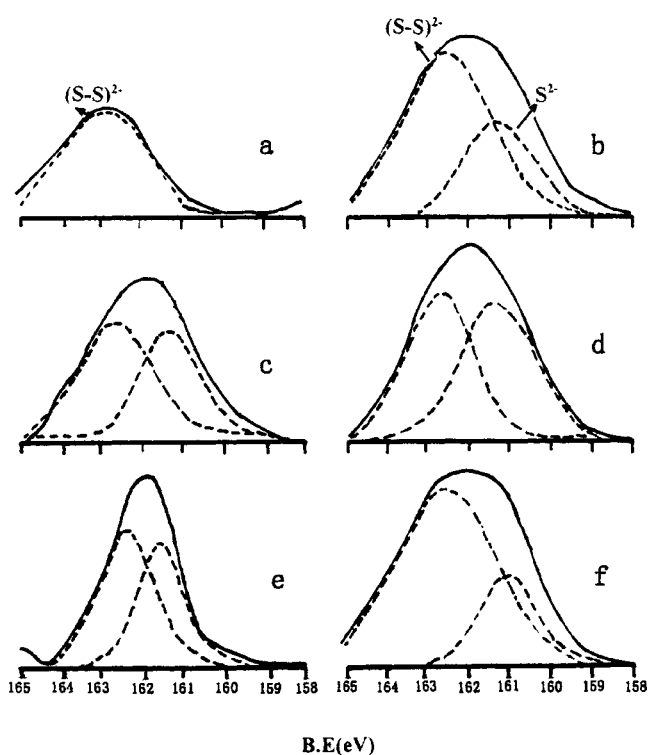


Figure 3. XPS spectra of functioning catalysts at S(2p) range: (a) MoS_2 , (b) K_2MoS_4/SiO_2 (0.15/1.00), (c) $K_2MoS_4/Fe_2O_3/SiO_2$ (0.15/0.03/1.00), (d) $K_2MoS_4/CoO/SiO_2$ (0.15/0.03/1.00), (e) $K_2MoS_4/NiO/SiO_2$ (0.15/0.03/1.00), (f) $K_2MoS_4/MnO_2/SiO_2$ (0.15/0.03/1.00).

than that on the catalysts without promoters. This observation enables us rationally to confirm that the addition of the transition metal oxides can restrain the deep reduction of Mo species, thereby keeping the Mo^{6+}/Mo^{4+} ratio on a higher level.

In the S(2p) range of MoS_2 shown in figure 3(a), the peak at 162.6 eV belongs to $(S-S)^{2-}$. The $(S-S)^{2-}$ anion on the MoS_2 -based catalysts has been detected by Schrader et al. [11] and Duchet et al. [12] by using *in situ* LRS and XPS, respectively. The XPS and LRS observations in our preceding works [13] have also provided experimental evidence for the presence of low-valence sulfur species, i.e., S^{2-} or $(S-S)^{2-}$, on the functioning surface of the MoS_2 -based catalysts. In the S(2p) range of the functioning catalysts shown in figure 3 (b)–(f), the peaks at 161.5 and 162.5 eV can be assigned to S^{2-} and $(S-S)^{2-}$ [12], respectively. The intensity ratios of the peaks of S^{2-} to $(S-S)^{2-}$ were found to be 0.25, 0.85, 0.9, 0.79 and 0.15. Obviously, the addition of Fe_2O_3 , CoO, and NiO strongly enhances the intensity of the peaks of S^{2-} at S(2p). It has been proved that species S^{2-} is in favor of the formation of methanethiol, while $(S-S)^{2-}$ is in favor of the generation of hydrocarbon [14]. Combining these observations with the experimental results that both the intensity ratio of the peak of S^{2-} to that of $(S-S)^{2-}$ in the S(2p) range of MnO_2 -added catalyst and the selectivity of methanethiol over the catalyst are lower, it seems reasonable to relate high yield and selectivity of methanethiol with high intensity ratio of the peaks of S^{2-} to $(S-S)^{2-}$ in the S(2p) range.

It is worth mentioning that Co and Ni are well known promoters of the catalyst MoS_2 for hydrodesulfurization (HDS) of organic sulfides. The addition of Co or Ni to MoS_2 constitutes so-called “synergic pairs” Co/Mo or Ni/Mo catalysts, which are more effective for HDS than single sulfide MoS_2 . This is a most common method to obtain modified MoS_2 for HDS, no matter whether the synergistic pair is supported or unsupported [15]. The origin of this promoting effect has been attributed to the presence of Co_9S_8 or Ni_3S_2 phases [15,16] or the Co–Mo–S phase [17] on the surface of MoS_2 . Iron sulfides do not promote molybdenum sulfide catalyst [18]. In the present work, transition metal oxides CoO, NiO, Fe_2O_3 and MnO_2 were, respectively, added to Mo–S-based catalyst, but, after sulfuring, neither Co_9S_8 or Ni_3S_2 species nor Mo–Co–S phase were detected by XRD and XPS measurements. It is clear that in figure 1 (d)–(h) the XRD patterns for all functioning catalysts have much the same feature, the peaks at $2\theta = 29.8$ and 30.0° appeared at both the samples with transition metal promoters and that without promoter, indicating that the peaks at $2\theta = 29.8$ and 30.0° have nothing to do with the transition metal promoters. It seems to us that the alkali potassium salt doped is responsible for the difference in the active site between the synergistic catalyst system for HDS and the Mo–S–K-based catalyst system doped with transition metals for methanethiol synthesis. As to the existing shape of the transition metals doped on the surface of the Mo–S–K-based catalysts, it remains yet to be solved.

4. Conclusion

The incorporation of transition metal oxides Fe_2O_3 , CoO and NiO into K_2MoS_4/SiO_2 to generate $K_2MoS_4/MO_x/SiO_2$ catalyst systems can notably increase the yield and selectivity of methanethiol under the conditions of methanethiol synthesis from H_2S -containing syngas. The results of XRD characterization show that the promoting effect of the transition metal oxides was achieved by raising the concentration of the Mo–S–K active sites on the surface of the catalysts. The XPS characterization displays further that the addition of the transition metal oxides to the catalyst K_2MoS_4/SiO_2 not only can retard the decomposition of K_2MoS_4 to MoS_2 , thereby increasing the concentration of Mo^{6+} on the surface of the catalysts, but also increases the concentration of the S^{2-} species. It has been confirmed that both Mo^{6+} and S^{2-} species on the surface of the catalysts are responsible for high yield and selectivity of methanethiol under the conditions of methanethiol synthesis from H_2S -containing syngas.

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References

- [1] R.T. Clark and J.A. Elkins, Eur. Patent 564706A1 (1994).
- [2] E. Cadot, M. Lacroix and A. Commarien, Fr. Patent 2711366A1.
- [3] EXXON and Eng. Co., Eur. Patent 167354 (1986).
- [4] Y.Q. Yang, Y.Z. Yan and H.B. Zang, J. Xiamen Univ. (Nat. Sci.) 32 (1993) 447.
- [5] Y.Q. Yang, Y.Z. Yuan and S.J. Dai, Catal. Lett. 54 (1998) 65.
- [6] H. McMurdiel, Powder Diffraction J. 1 (1986) 269.
- [7] G.D. Lin and Y.Q. Yang, Chinese J. Mol. Catal. 6 (1992) 321.
- [8] Y.Q. Yang, H.P. Wang, G.D. Lin and H.B. Zhang, Chinese J. Fuel Chem. 21 (1993) 1.
- [9] H.B. Zhang, *The Catalysis in C₁ Chemistry* (Chemical Industry Press, Beijing, 1995) pp. 187–215.
- [10] J. Abart, E. Delgado, G. Ertl, H. Jeziorowski, H. Knözinger, N. Thiele and X.Zh. Wang, Appl. Catal. 2 (1982) 155.
- [11] G.L. Schrader and C.P. Cheng, J. Catal. 80 (1983) 369.
- [12] J.C. Duchet, E.M. Van Oers, V.H.J. De Beer and R. Prins, J. Catal. 80 (1983) 386.
- [13] H.B. Zhang, in: *New Frontiers in Catalysis*, Proceedings of the 10th International Congress on Catalysis, Budapest, Hungary, 19–24 July 1992.
- [14] K. Klier, R.G. Herman and G.W. Simons, in: *Synthesis Gas Conversion to Liquid Fuels and Upgrading*, Proc. 7th DOE Indirect Liquefaction Contractors Meeting, Pittsburgh, Vol. 1 (1987) pp. 258–379.
- [15] R.R. Chianelli, Catal. Rev. Sci. Eng. 26 (1984) 361.
- [16] R.R. Chianelli, T.A. Pecoraro, T.R. Halbert, W.-H. Pan and E.I. Stiefel, J. Catal. 86 (1984) 226.
- [17] H. Topsøe and B.S. Clausen, Catal. Rev. Sci. Eng. 26 (1984) 395.
- [18] O. Weissner and S. Landa, *Sulfide Catalysts: Their Properties and Applications* (Pergamon, Oxford, 1973).