Supporting Information

Title:

Investigation of reaction pathway for synthesizing methyl mercaptan (CH_3SH) from H_2S-containing syngas over K-Mo-type materials

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1. The calculating formula

$$\Delta H_r{}^{\theta}(298K) = \sum \upsilon_i \Delta H_f{}^{\theta}(298K)$$

$$\Delta G_r{}^{\theta}(298K) = \sum \upsilon_i \Delta G_f{}^{\theta}(298K)$$

The Kirchhoff law[1,2]:

$$\Delta H_r(T) = \Delta H_r{}^{\theta}(298K) + \int_{298}^{T} (\sum \upsilon_i C_P dT)$$

$$\Delta S_r(T) = \Delta S_r{}^{\theta}(298K) + \int_{298}^{T} (\sum \upsilon_i C_P / T\, dT)$$

$$C_p = A + B \times T + C \times T^2 + D \times T^3$$

$$C_p = (\Sigma \upsilon_j{}^{(i)} \Delta a_j - 37.93) + (\Sigma \upsilon_j{}^{(i)} \Delta b_j + 0.210) \times T + (\Sigma \upsilon_j{}^{(i)} \Delta c_j - 3.91 \times 10^{-4}) \times T^2 + (\Sigma \upsilon_j{}^{(i)} \Delta d_j + 2.06 \times 10^{-7}) \times T^3$$

The Gibbs-Helmholtz Equation:

$$\Delta G_r^{\theta}(T) = \Delta H_r^{\theta}(T) - T\Delta S_r{}^{\theta}(T) \text{ or } \Delta G_r(T) = \Delta H_r(T) - T\Delta S_r\ (T)$$

The varied Gibbs-Helmholtz Equation[1,2]:

$$\Delta G_r(T) = \Delta G_r{}^{\theta}(298K) \times T/298 + \Delta H_r{}^{\theta}(298K) \times (1 - T/298) + \int_{298}^{T} \Sigma \upsilon_i C_P dT - T \times \int_{298}^{T} \Sigma \upsilon_i C_P / T dT$$

$$K_p = \exp\left[-\Delta G_r(T)/(R \cdot T)\right]$$

2. The calculating results

Table 1-S the fundamental thermodynamics data of partial substances for the synthesis of methanethiol from mixture gas.

No	Species	$\Delta H_f^{\theta}(298K)$[a] kcal/mol	$\Delta G_f^{\theta}(298K)$[a] kcal/mol	C_p (cal·mol^{-1}·K^{-1})[b]=A + B×T + C×T^3 + D×T^4			
				A	B	C	D
1	COS	-33.867	-40.367	5.63E+00	1.91E-02	-1.68E-05	5.86E-09
2	H_2	0	0	6.48E+00	2.22E-03	-3.30E-06	1.83E-09
3	CH_3SH[b]	-5.469	-2.221	3.17E+00	3.48E-02	-2.04E-05	4.96E-09
4	H_2O	-57.797	-54.634	7.70E+00	4.60E-04	2.52E-06	-8.59E-10
5	CO_2	-94.05	-94.255	4.73E+00	1.75E-02	-1.34E-05	4.10E-09
6	H_2S	-4.899	-7.963	7.63E+00	3.43E-04	5.81E-06	-2.81E-09
7	CH_4	-17.829	-12.08	4.60E+00	1.25E-02	2.86E-06	-2.70E-09
8	C_2H_4	12.525	16.336	9.09E-01	3.74E-02	-1.99E-05	4.19E-09
9	C_2H_6	-20.238	-7.853	1.29E+00	4.25E-02	-1.66E-05	2.08E-09

[a] the data obtained from the HSC Chemical software.

[b] the data coming from 1,3.

Table 2-S the calculated enthalpy changes, Gibbs free energy changes, equilibrium constants of reaction for the synthesis or decomposition of methanethiol from mixture gas at different temperature.

Reactions	$\Delta H_r(T)$ (kJ/mol)					$\Delta G_r(T)$ kJ/mol					Kp				
	548K	573K	598K	623K	648K	548K	573K	598K	623K	648K	548K	573K	598K	623K	648K
$COS+3H_2 \rightarrow CH_3SH+H_2O$	**-132.68**	**-133.45**	**-134.19**	**-134.90**	**-135.58**	**-20.24**	**-15.09**	**-9.91**	**-4.70**	**-0.54**	**84.99**	**23.77**	**7.34**	**2.48**	**0.91**
$2COS+3H_2 \rightarrow CH_3SH+H_2S+CO_2$	**-163.96**	**-164.78**	**-165.57**	**-166.31**	**-167.02**	**-49.92**	**-44.70**	**-39.45**	**-34.16**	**-28.84**	**5.74E+04**	**1.19E+04**	**2.79E+03**	**7.31E+02**	**2.11E+02**
$CH_3SH+H_2 \rightarrow CH_4+H_2S$	**-75.11**	**-75.42**	**-75.73**	**-76.04**	**-76.34**	**-75.71**	**-75.73**	**-75.74**	**-75.73**	**-75.71**	**1.65E+07**	**8.01E+06**	**4.13E+06**	**2.24E+06**	**1.27E+06**
$2CH_3SH \rightarrow C_2H_4+2H_2S$	**58.85**	**58.89**	**58.92**	**58.93**	**59.94**	**-8.75**	**-11.84**	**-14.92**	**-18.01**	**-21.10**	**6.83**	**11.99**	**20.12**	**32.37**	**50.22**
$2CH_3SH+H_2 \rightarrow C_2H_6+2H_2S$	**-81.82**	**-82.10**	**-82.38**	**-82.65**	**-82.91**	**-77.80**	**-77.61**	**-77.41**	**-77.20**	**-76.98**	**2.61E+07**	**1.19E+07**	**5.78E+06**	**2.97E+06**	**1.60E+06**
$CS_2+3H_2 \rightarrow CH_3SH+H_2S$	**-165.21**	**-165.42**	**-165.57**	**-165.68**	**-165.74**	**-64.58**	**-59.98**	**-55.38**	**-50.78**	**-46.16**	1.43E+06	2.94E+05	6.88E+04	1.81E+04	5.26E+03

Table 3-S the calculated enthalpy changes, Gibbs free energy changes and equilibrium constants for the CH_3SH-free reaction from mixture gas at different temperature.

Reactions	$\Delta H_r(T)$ (kJ/mol)					$\Delta G_r(T)$ (kJ/mol)					Kp				
	548K	573K	598K	623K	648K	548K	573K	598K	623K	648K	548K	573K	598K	623K	648K
$CO+H_2S \rightarrow COS+H_2$ [A]	-8.25	-7.98	-7.71	-7.45	-7.18	11.11	11.99	12.85	13.71	14.55	8.73E-02	8.08E-02	7.54E-02	7.09E-02	6.72E-02
$CO+H_2S \rightarrow COS+H_2$ [B]	-8.17	-7.88	-7.60	-7.31	-7.02	11.10	11.98	12.84	13.69	14.53	8.73E-02	8.09E-02	7.56E-02	7.11E-02	6.74E-02
$COS+H_2 \rightarrow CO+H_2S$ [A]	8.25	7.98	7.71	7.45	7.18	-11.11	-11.99	-12.85	-13.71	-14.55	1.15E+01	1.24E+01	1.33E+01	1.41E+01	1.49E+01
$COS+H_2 \rightarrow CO+H_2S$ [B]	8.17	7.88	7.60	7.31	7.02	-11.10	-11.98	-12.84	-13.69	-14.53	1.15E+01	1.24E+01	1.32E+01	1.41E+01	1.48E+01
$COS+H_2O \rightarrow CO_2+H_2S$ [A]	-31.20	-31.24	-31.27	-31.30	-31.32	-29.68	-29.61	-29.54	-29.46	-29.39	6.75E+02	5.00E+02	3.80E+02	2.96E+02	2.34E+02
$COS+H_2O \rightarrow CO_2+H_2S$ [B]	-28.00	-27.71	-27.43	-27.14	-26.86	-30.75	-30.88	-31.02	-31.18	-31.35	8.53E+02	6.53E+02	5.13E+02	4.11E+02	3.36E+02
$CO+H_2O \rightarrow CO_2+H_2$ [A]	-39.45	-39.22	-38.99	-38.75	-38.5	-18.57	-17.62	-16.69	-15.76	-14.84	5.89E+01	4.04E+01	2.87E+01	2.10E+01	1.57E+01
$CO+H_2O \rightarrow CO_2+H_2$ [B]	-38.67	-38.38	-38.10	-37.81	-37.53	-18.87	-17.97	-17.09	-16.22	-15.36	6.29E+01	4.35E+01	3.11E+01	2.29E+01	1.73E+01
$CS_2+2H_2O \rightarrow CO_2+2H_2S$ [A]	-68.80	-68.85	-68.9	-68.94	-68.96	-72.40	-72.56	-72.72	-72.88	-73.04	7.97E+06	4.12E+06	2.25E+06	1.29E+06	7.72E+05
$CS_2+2H_2O \rightarrow CO_2+2H_2S$ [B]	-65.10	-64.81	-64.53	-64.25	-63.96	-73.71	-74.11	-74.52	-74.94	-75.38	1.06E+07	5.70E+06	3.23E+06	1.92E+06	1.19E+06
$CO_2+H_2 \rightarrow CO+H_2O$ [A]	39.45	39.22	38.99	38.75	38.5	18.57	17.62	16.69	15.76	14.84	1.70E-02	2.47E-02	3.49E-02	4.77E-02	6.36E-02
$CO_2+H_2 \rightarrow CO+H_2O$ [B]	38.67	38.38	38.10	37.81	37.53	18.87	17.97	17.09	16.22	15.36	1.59E-02	2.30E-02	3.22E-02	4.37E-02	5.78E-02
$CO_2+H_2S \rightarrow COS+H_2O$ [A]	31.20	31.24	31.27	31.30	31.32	29.68	29.61	29.54	29.46	29.39	1.48E-03	2.00E-03	2.63E-03	3.39E-03	4.27E-03
$CO_2+H_2S \rightarrow COS+H_2O$ [B]	28.00	27.71	27.43	27.14	26.86	30.75	30.88	31.02	31.18	31.35	1.17E-03	1.53E-03	1.95E-03	2.43E-03	2.97E-03

[A] The data calculated *by using HSC Chemistry software;*

[B] The data calculated *by thermodynamics equations.*

3. The GC atlas of the standard gas, reactant gas, intermediate products and the final products

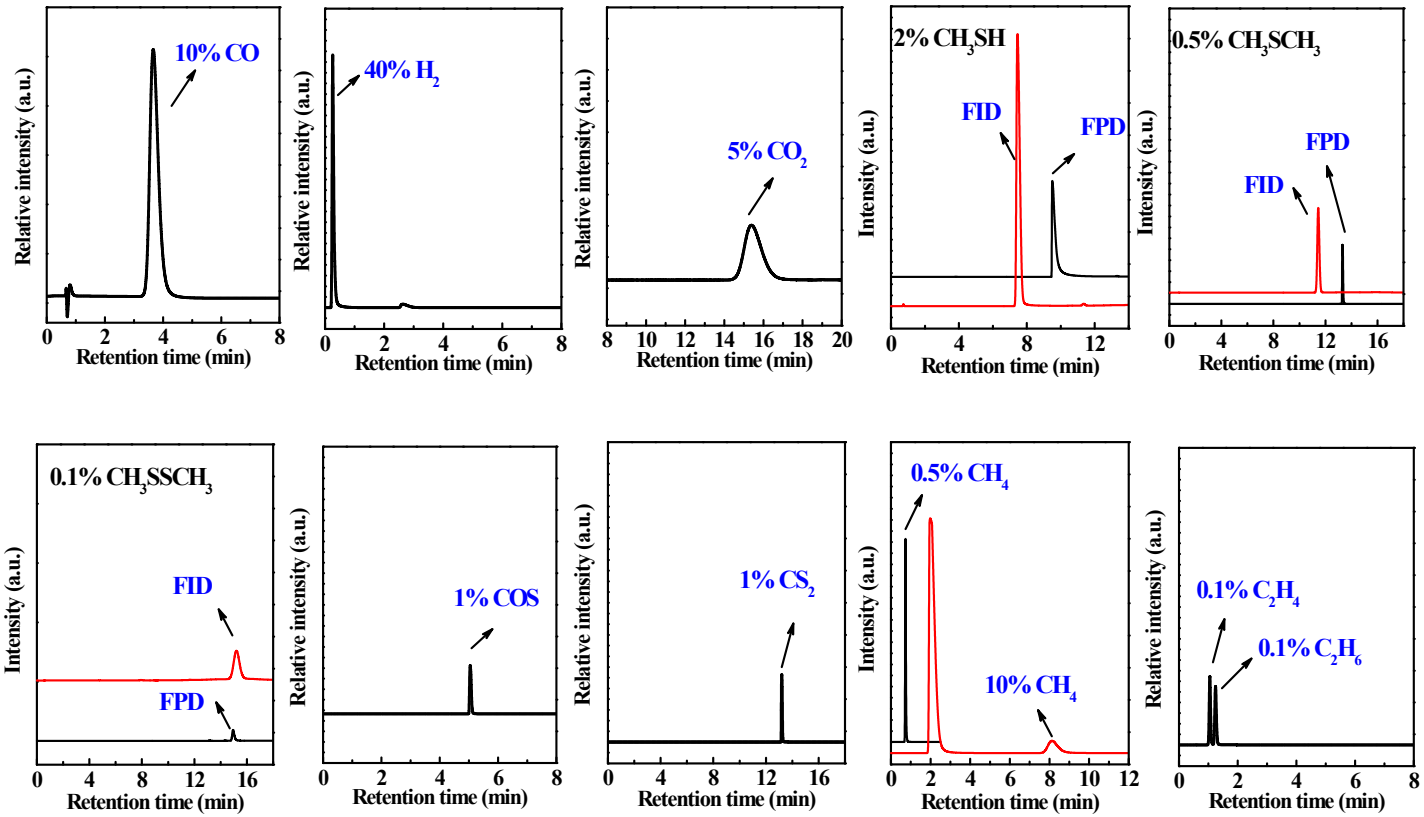

Figure 1-S The GC atlas of the standard gas (CO, H_2, CO_2, CH_3SH, CH_3SCH_3, CH_3SSCH_3, COS, CS_2, CH_4, C_2H_4 and C_2H_6).

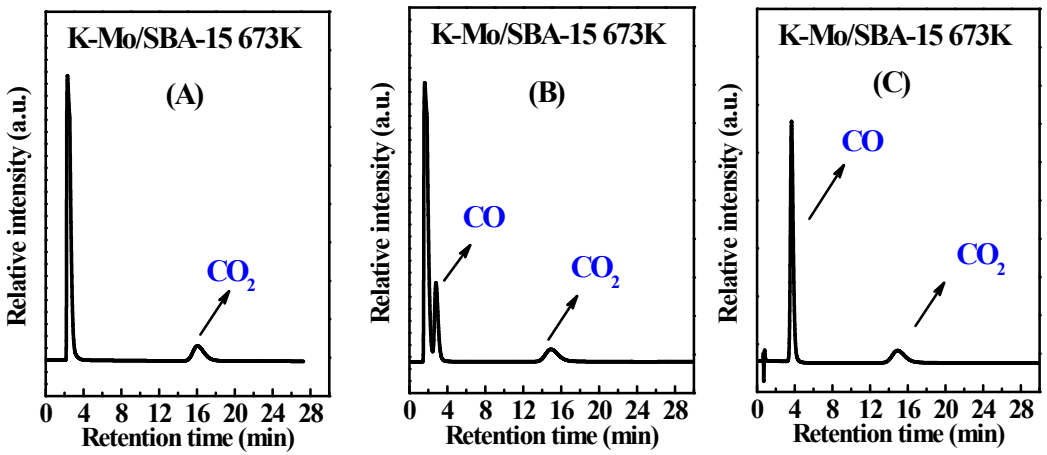

Figure 2-S (A) The GC atlas of the reactant gas (CO_2) over K-Mo/SBA-15 catalysts at 673K with the reactant gas of $CO_2/H_2S/N_2$=1:1:8. (B) The GC atlas of the reactant gas (CO, CO_2) over K-Mo/SBA-15 catalysts at 673K with the reactant gas of $CO_2/H_2/CO/N_2$=1:1:1:7. (C) The GC atlas of the reactant gas (CO) and final product (CO_2) over K-Mo/SBA-15 catalysts at 673K with the reactant gas of CO/H_2=1:4.

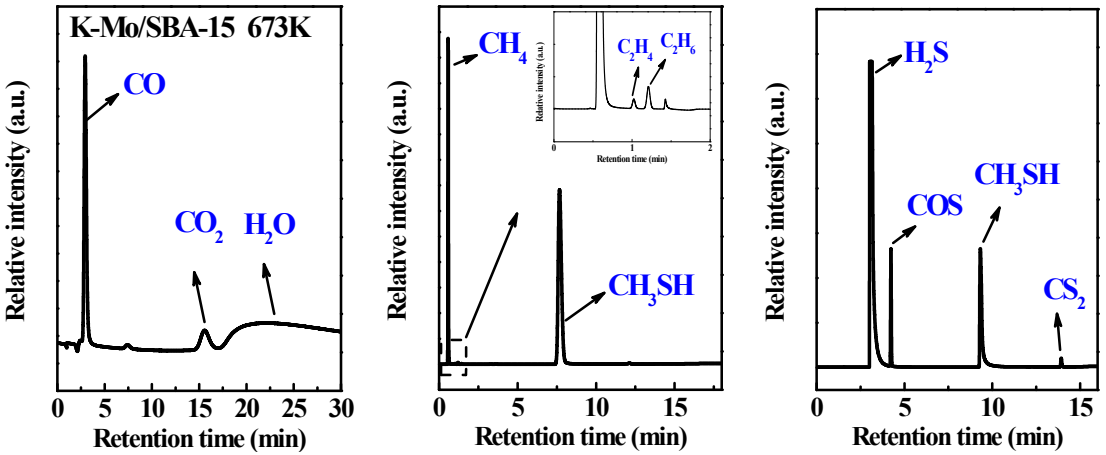

Figure 3-S The GC atlas of the reactant gas (CO), intermediate products (COS, CS_2, H_2O) and the final products (CH_3SH, CH_4, C_2H_4, C_2H_6 and CO_2) over K-Mo/SBA-15 catalysts at 673K with the reactant gas of $CO/H_2S/H_2$=1:5:4.

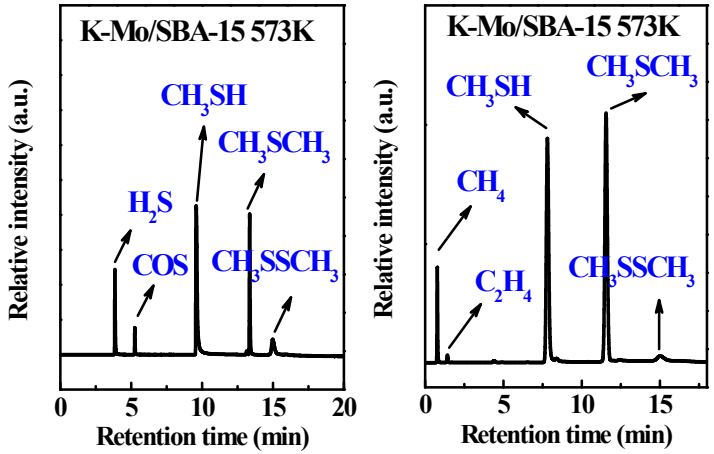

Figure 4-S The GC atlas of the reactant gas (CH_3SH), intermediate products (CH_3SCH_3, CH_3SSCH_3) and the final products (CH_4, COS, C_2H_4, and H_2S) over K-Mo/SBA-15 catalysts at 573K with the reactant gas of CH_3SH.

Reference

[1] J. W. Tester, M. Modell, Thermodynamics and its Applications, 3rd Edition, *Prentice-Hall*, 1997.

[2] B. E. Poling, J. M. Prausnitz, J. P. O'Connell, The Properties of Gases and Liquids, Fifth Edition, *McGRAW-HILL*, 2001.

[3] D. R. Lide, et. al. CRC Handbook of Chemical and Physics, 84th edition, 2003-2004.