

Supplementary Information

The role of weak Lewis acid sites for methanol thiolation

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S.1. Characterization

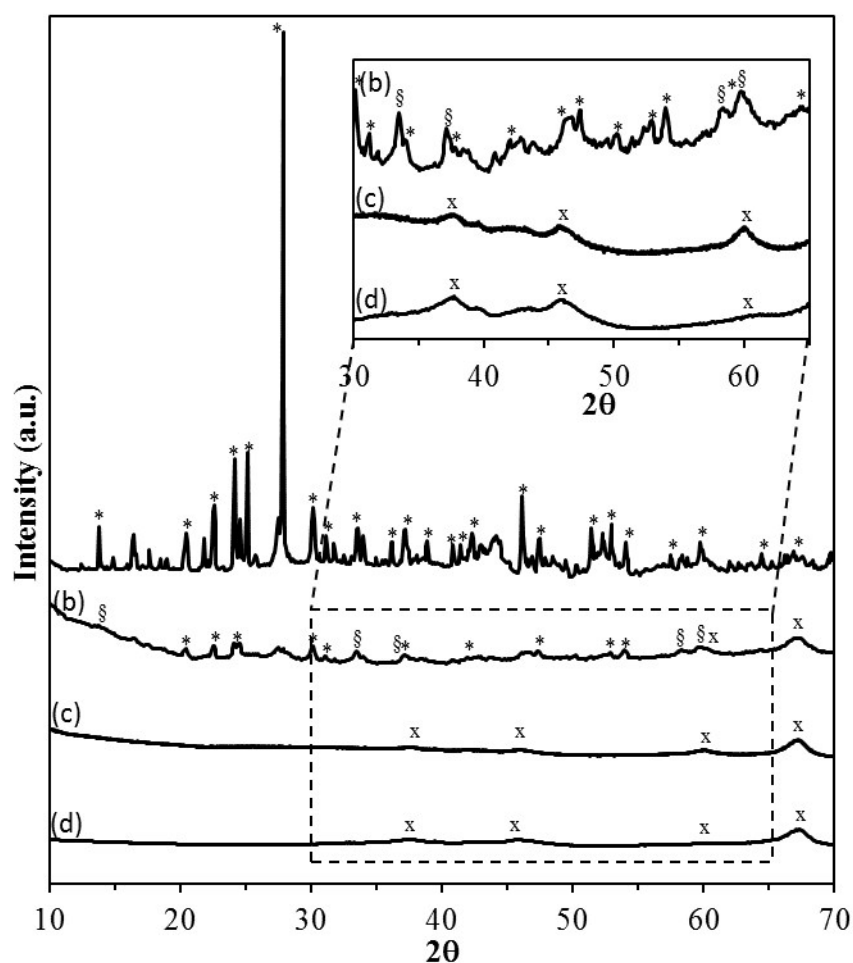


Figure S1 X-ray diffraction after sulfidation of a) $\text{Cs}_2\text{WS}_4/\text{Al}_2\text{O}_3$, b) $\text{CsW}/\text{Al}_2\text{O}_3$, c) $\text{Cs}/\text{Al}_2\text{O}_3$ and d) $\gamma\text{-Al}_2\text{O}_3$. The symbols are represented as: * as Cs_2WS_4 , § as WS_2 and x as $\gamma\text{-Al}_2\text{O}_3$.

Table S1 Raman shifts and assignments from the different sulfur anions.

Anion	Raman Shift (cm^{-1})	Assignment
Sulfite (SO_3^{-2})	496	(E) Antisymmetric SO_3 deformation
Sulfite (SO_3^{-2})	647	(A_1) Symmetric SO_3 deformation
Sulfite (SO_3^{-2})	986	(E) Antisymmetric SO_3 stretching
Thiosulfate ($\text{S}_2\text{O}_3^{-2}$)	323	(E) Symmetric S-S-O deformation
Thiosulfate ($\text{S}_2\text{O}_3^{-2}$)	452	(A_1) Symmetric SO_3 deformation
Thiosulfate ($\text{S}_2\text{O}_3^{-2}$)	656	(A_1) Symmetric S- SO_3 stretching
Thiosulfate ($\text{S}_2\text{O}_3^{-2}$)	1016	(A_1) Symmetric SO_3 stretching
Dithionate ($\text{S}_2\text{O}_6^{-2}$)	204	(E_u) Symmetric SO_3 deformation
Dithionate ($\text{S}_2\text{O}_6^{-2}$)	1000	(A_{2u}) Symmetric stretching
Pyrosulfite ($\text{S}_2\text{O}_5^{-2}$)	660	(A_1) Symmetric SO_3 deformation
Pyrosulfite ($\text{S}_2\text{O}_5^{-2}$)	1050	(A_1) Symmetric SO_3 stretching
Dithionite ($\text{S}_2\text{O}_4^{-2}$)	508	---

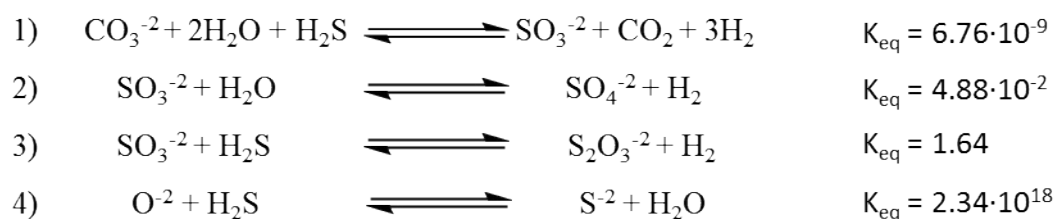


Figure S2. Plausible reactions yielding sulfur oxyanions and the corresponding equilibrium constants at 400 °C and 1 atm. The equilibrium constants were calculated with the HSC-chemistry software. The decomposition of CO_3^{-2} into SO_3^{-2} and CO_2 would be driven, under flow conditions, by the continuous removal of CO_2 and H_2 from the system pushing the equilibrium towards the product side.

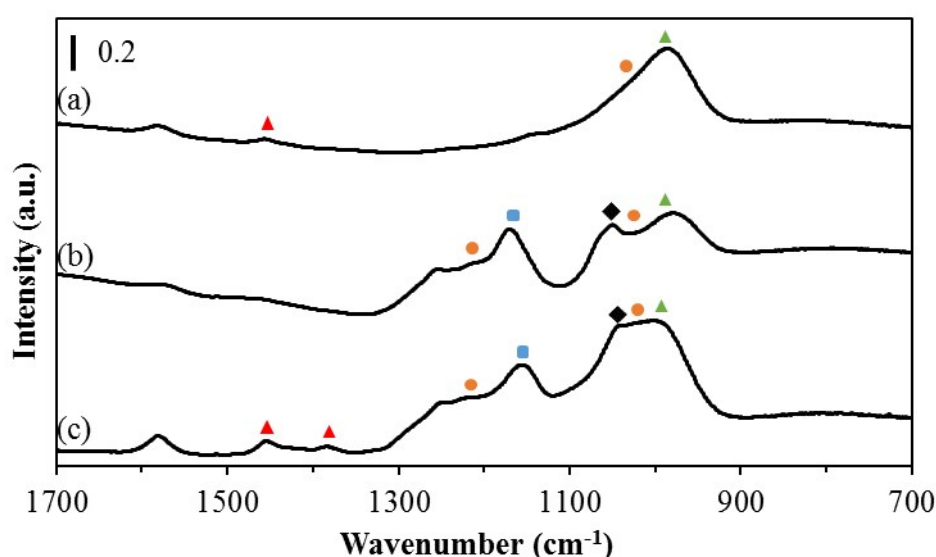


Figure S3. Infrared spectroscopy after sulfidation of a) $\text{Cs}_2\text{WS}_4/\text{Al}_2\text{O}_3$, b) $\text{CsW}/\text{Al}_2\text{O}_3$ and c) $\text{Cs}/\text{Al}_2\text{O}_3$. The symbols are represented by anions: thiosulfate (blue square), dithionate (black diamond), pyrosulfite (orange dot), pyrosulfate (red triangle) and sulfite (green triangle).

Table S2 Infrared bands and assignments from the different sulfur anions.

Anion	IR band (cm^{-1})	Assignment
Sulfite (SO_3^{-2})	968	(A_1) Symmetric SO_3 stretching
Thiosulfate ($\text{S}_2\text{O}_3^{-2}$)	1146	(E) Antisymmetric SO_3 stretching
Dithionate ($\text{S}_2\text{O}_6^{-2}$)	1000	(A_{2u}) Symmetric stretching
Pyrosulfite ($\text{S}_2\text{O}_5^{-2}$)	970	(A_2) Symmetric SO_2 stretching
Pyrosulfite ($\text{S}_2\text{O}_5^{-2}$)	1196	(A_2) Symmetric SO_3 stretching
Pyrosulfate ($\text{S}_2\text{O}_7^{-2}$)	1380	--
Pyrosulfate ($\text{S}_2\text{O}_7^{-2}$)	1450	--

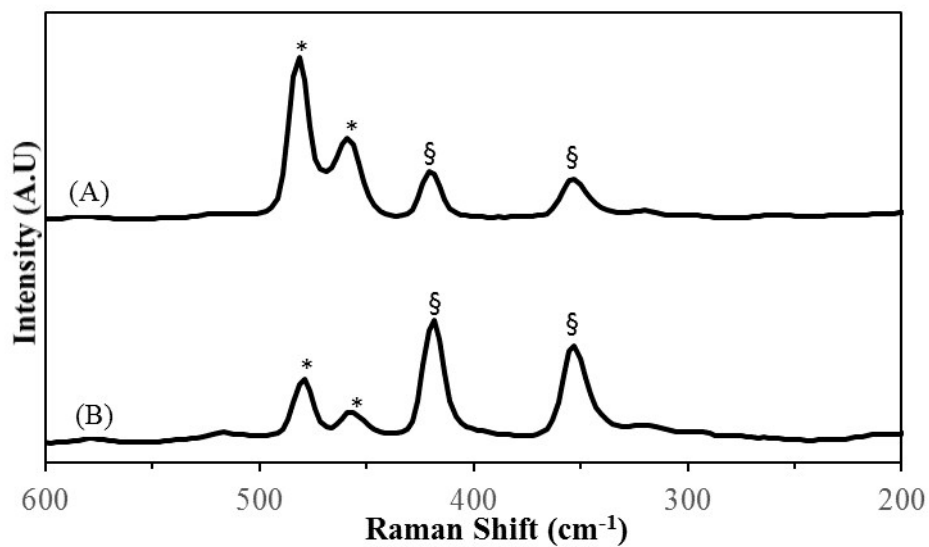


Figure S4 Raman spectra of the same $\text{Cs}_2\text{WS}_4/\text{Al}_2\text{O}_3$ sample after (A) and before reaction (B). The symbols (*) and (§) are assigned to the WS_4^{-2} and WS_2 phases.

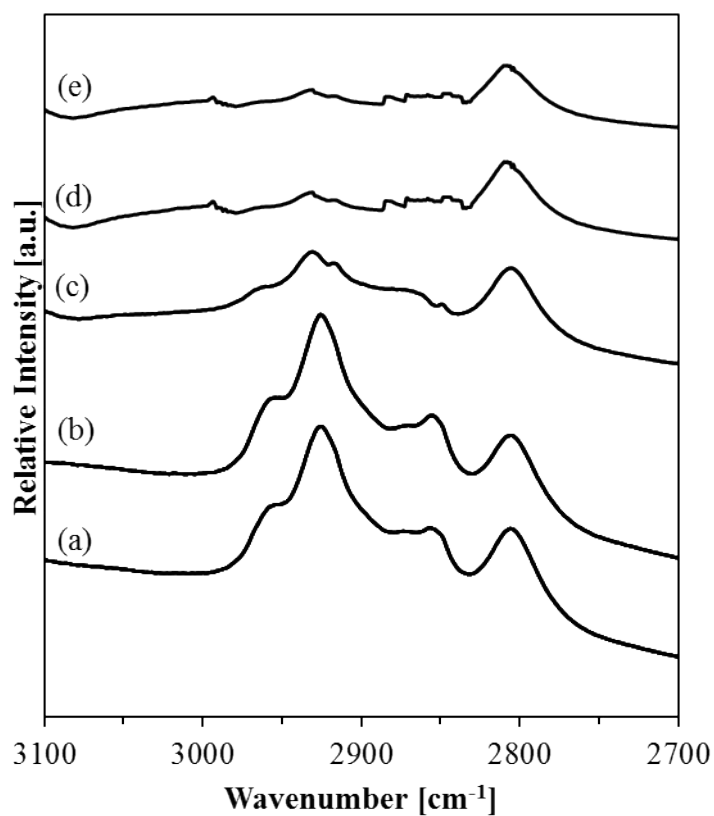


Figure S5 IR Spectra of methanol adsorbed on $\text{CsW}/\text{Al}_2\text{O}_3$ (previously sulfided) at a) 0.1 mbar and 50 °C, b) 1 mbar and 50 °C, c) 1 mbar and 100 °C, d) 1 mbar and 150 °C, e) 10⁻⁵ mbar and 300 °C.

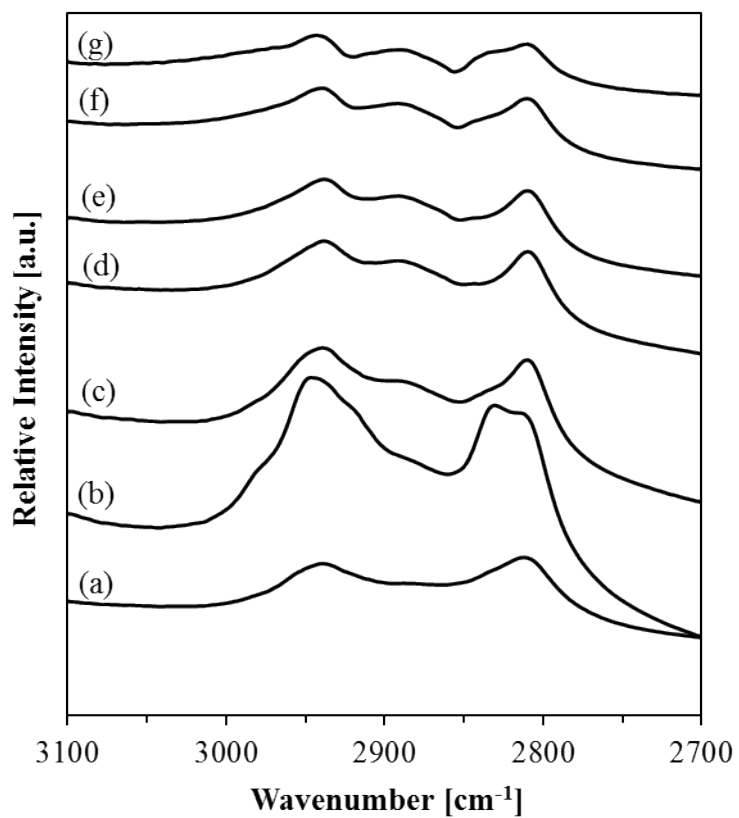


Figure S6 IR Spectra of methanol adsorbed on Cs/Al₂O₃ (previously sulfide) at a) 0.1 mbar and 50 °C, b) 1 mbar and 50 °C, c) 1 mbar and 100 °C, d) 1 mbar and 150 °C, e) 1 mbar and 200 °C, e) 1 mbar and 250 °C and e) 1 mbar and 300 °C.

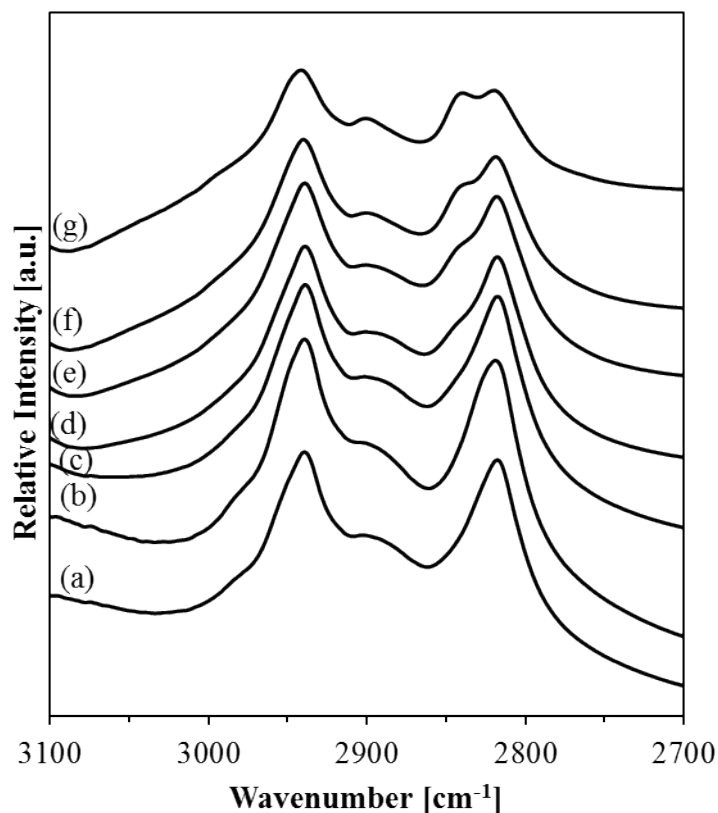


Figure S7 IR Spectra of methanol adsorbed on γ - Al_2O_3 (previously sulfided) at a) 0.1 mbar and 50 °C, b) 1 mbar and 50 °C, c) 1 mbar and 100 °C, d) 1 mbar and 150 °C, e) 1 mbar and 200 °C, e) 1 mbar and 250 °C and e) 1 mbar and 300 °C.

S.2 Catalytic Testing and Kinetic Data

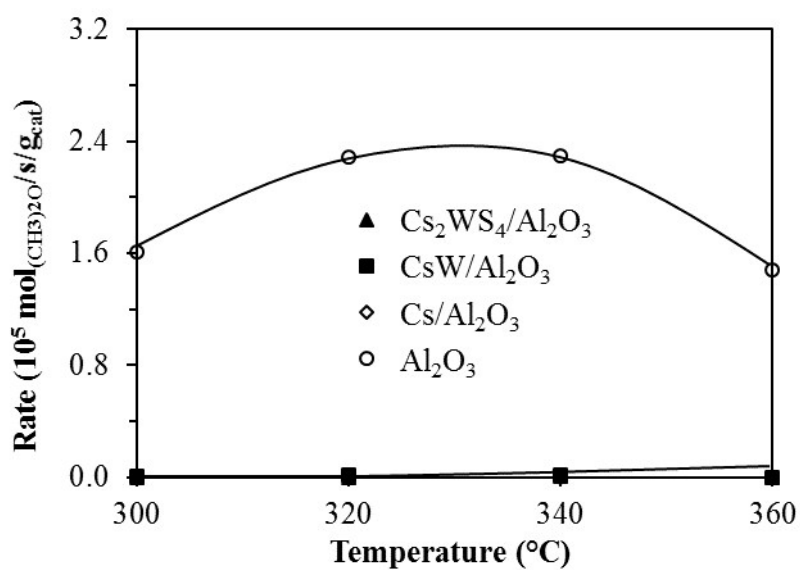


Figure S8 Dimethyl ether rate formation for $\text{Cs}_2\text{WS}_4/\text{Al}_2\text{O}_3$, $\text{CsW}/\text{Al}_2\text{O}_3$, $\text{Cs}/\text{Al}_2\text{O}_3$ and γ - Al_2O_3 , in between 300-360 °C.

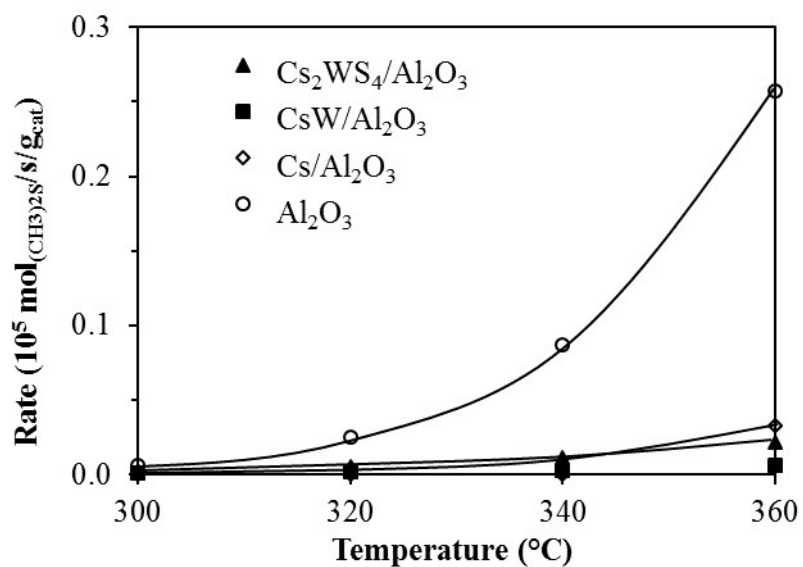


Figure S9 Dimethyl sulfide rate formation for Cs₂WS₄/Al₂O₃, CsW/Al₂O₃, Cs/Al₂O₃ and γ -Al₂O₃, in between 300-360 °C.

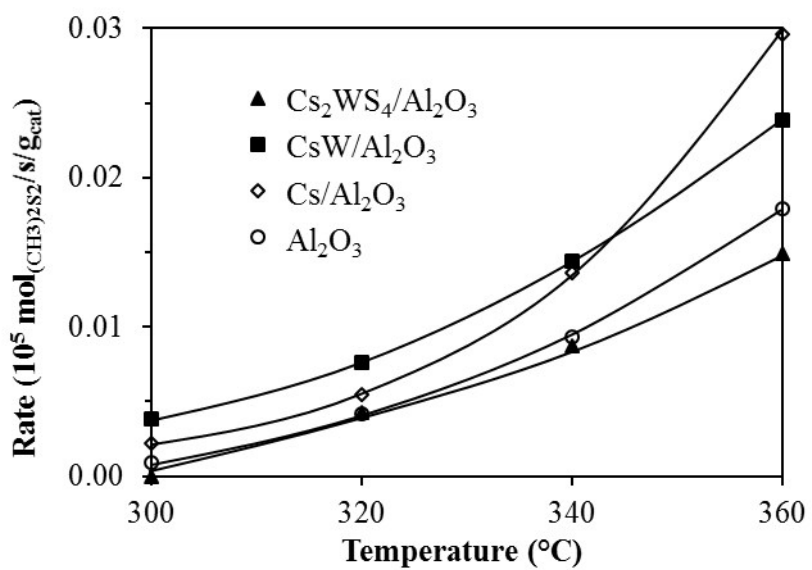


Figure S10 Dimethyl disulfide rate formation for Cs₂WS₄/Al₂O₃, CsW/Al₂O₃, Cs/Al₂O₃ and γ -Al₂O₃, in between 300-360 °C.

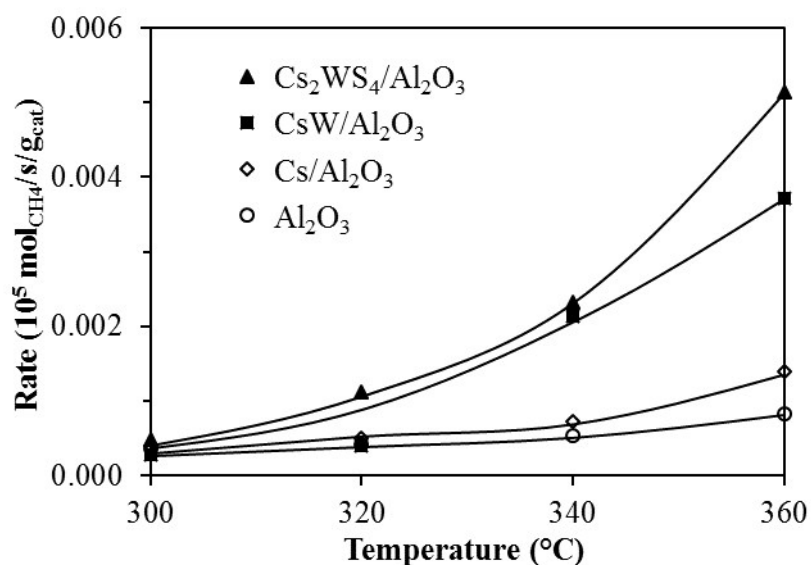


Figure S11 Methane rate formation for Cs₂WS₄/Al₂O₃, CsW/Al₂O₃, Cs/Al₂O₃ and γ -Al₂O₃, in between 300-360 °C.

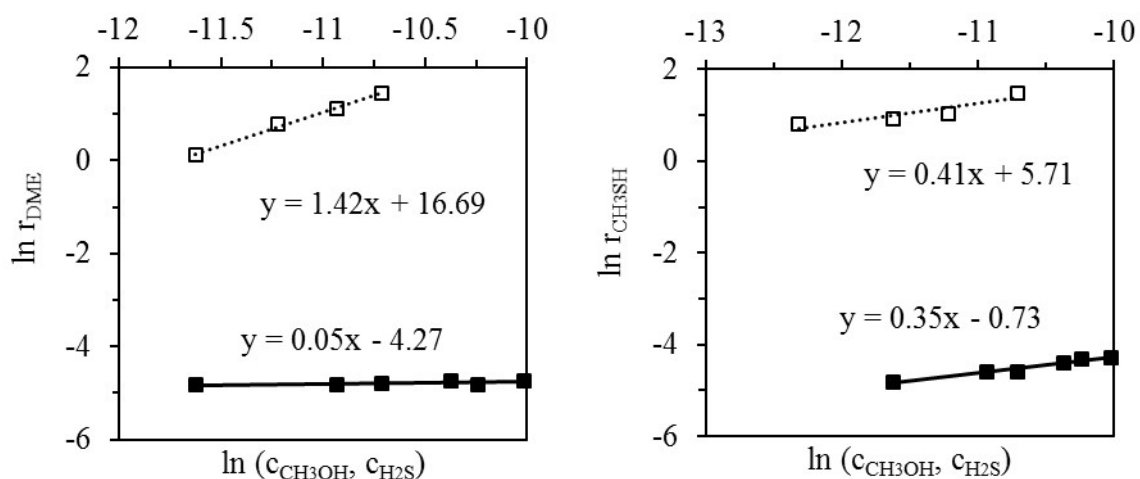


Figure S12 Left: Plot of ln rates of dimethyl ether production (Ln r_{DME}) along with ln of partial pressure of methanol (C_{CH₃OH}, empty squares) or H₂S (P_{H₂S}, filled squares) with Al₂O₃ catalyst at 300°C and 9 bar. Right: Plot of ln rates of methanethiol production (Ln r_{CH₃SH}) along with ln of partial pressure of methanol (C_{CH₃OH}, empty squares) or H₂S (P_{H₂S}, filled squares) with Al₂O₃ catalyst at 300°C and 9 bar.

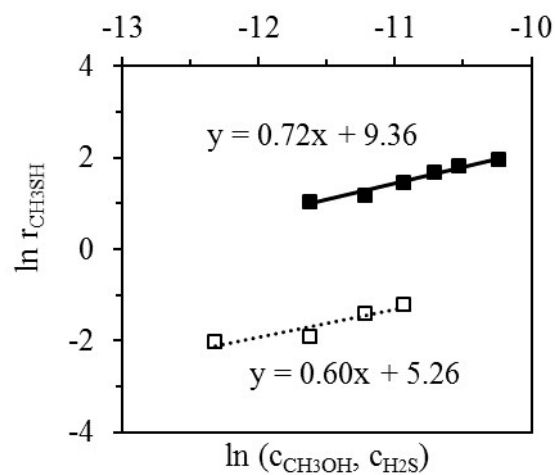


Figure S13 Plot of \ln rates of methanethiol production ($\ln r_{\text{CH}_3\text{SH}}$) along with \ln of partial pressure of methanol ($C_{\text{CH}_3\text{OH}}$, empty squares) or H_2S ($P_{\text{H}_2\text{S}}$, filled squares) with $\text{Cs}/\text{Al}_2\text{O}_3$ catalyst at 300°C and 9 bar.

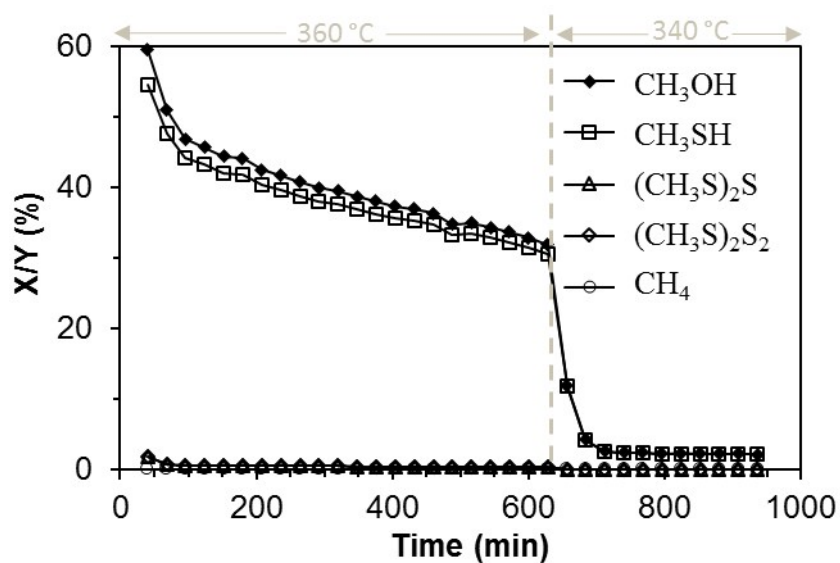
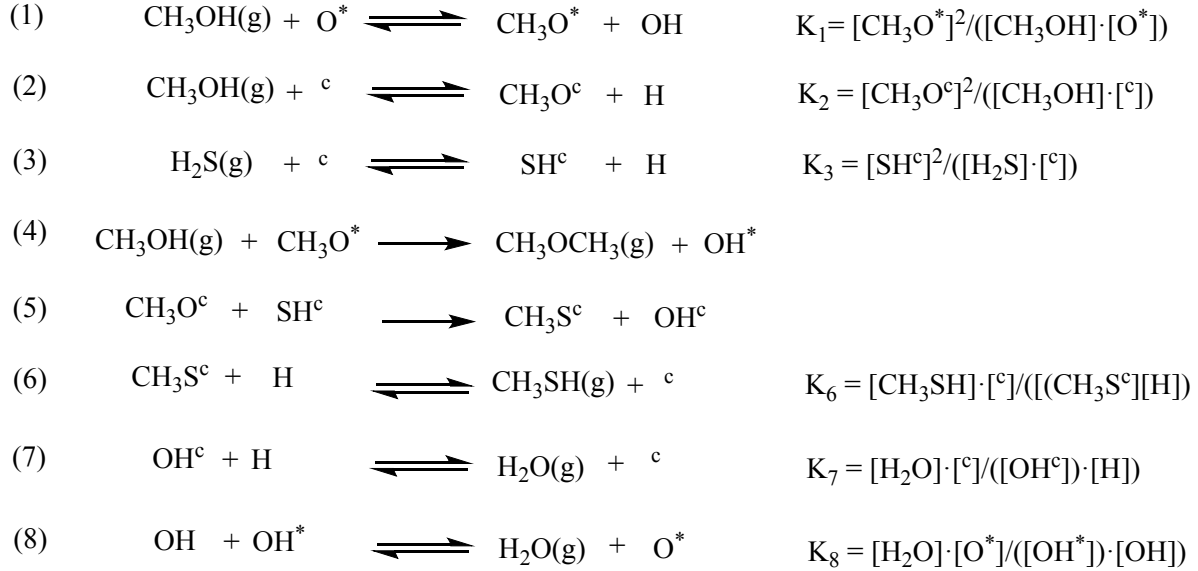


Figure S14 Methanol conversion and product yields during reaction of methanol and H_2S over Cs/SiO_2 at 360 and 340°C under same conditions as catalytic tests.

S.3 Derivation of bimolecular rate equations for the formation of dimethyl ether and methanethiol

The following reaction steps describe the formation of dimethyl ether (CH₃OCH₃) and methanethiol (CH₃SH):



Scheme S1 Reaction kinetic steps for the formation dimethyl ether (DME) and CH₃SH, being (O^{*}) the strong Lewis acid site and (c) the strong basic site of the Lewis acid-base pairs. The synthesis of DME follows an Eley-Rideal bimolecular reaction while the synthesis of CH₃SH follows a Langmuir-Hinshelwood bimolecular reaction.

The Lewis acid-base pair (LABS) sites are taking part in the formation of the methoxy on a strong Lewis acid site and the alcoholate on a strong basic site. In both cases there is a dissociation of the methanol having both respective equal number on acid a base sites ([^c] or [^{*}]). Assuming the Most Abundant Reaction Intermediates (MARI) and vacant sites ([^c] for strong Lewis acid sites:

$$[\text{LABS}^{\text{c}}] = [\text{c}] + [\text{CH}_3\text{O}^{\text{c}}] + [\text{SH}^{\text{c}}] + [\text{OH}^{\text{c}}] + [\text{CH}_3\text{S}^{\text{c}}]$$

$$[\text{LABS}^{\text{c}}] = [\text{c}] \cdot (1 + K_2^{0.5} \cdot [\text{CH}_3\text{OH}]^{0.5} + K_3^{0.5} \cdot [\text{H}_2\text{S}]^{0.5} + K_6^{-0.5} \cdot [\text{CH}_3\text{SH}]^{0.5} + K_7^{-0.5} \cdot [\text{H}_2\text{O}]^{0.5})$$

Following the same rationale for the formation of dimethyl ether with strong Lewis acid sites:

$$[\text{LABS}^*] = [*] \cdot (1 + K_1^{0.5} \cdot [\text{CH}_3\text{OH}]^{0.5} + K_8^{-0.5} \cdot [\text{H}_2\text{O}]^{0.5})$$

Assuming reaction 3 and 4 (Scheme S1) are the rate determining steps in the formation of dimethyl ether and methanethiol, respectively, the rate expressions for these two products are the following:

$$r_{CH_3SH} = k_5 \cdot [CH_3O^c] \cdot [SH^c] = k_5 \cdot K_2^{0.5} \cdot K_3^{0.5} \cdot [CH_3OH]^{0.5} \cdot [H_2S]^{0.5} \cdot [c]^2$$

$$r_{CH_3OCH_3} = k_4 \cdot [CH_3OH] \cdot [CH_3O^*] = k_4 \cdot K_1^{0.5} \cdot [CH_3OH]^{1.5} \cdot [^*]$$

Substituting the site balance gives:

$$r_{CH_3OCH_3} = \frac{k_4 K_1^{0.5} [CH_3OH]^{1.5}}{1 + K_1^{0.5} [CH_3OH]^{0.5} + \frac{[H_2O]^{0.5}}{K_8^{0.5}}} [LABS^*]$$

$$r_{CH_3SH} = \frac{k_5 K_2^{0.5} K_3^{0.5} [CH_3OH]^{0.5} [H_2S]^{0.5}}{(1 + K_2^{0.5} [CH_3OH]^{0.5} + K_3^{0.5} [H_2S]^{0.5} + \frac{[CH_3SH]^{0.5}}{K_6^{0.5}} + \frac{[H_2O]^{0.5}}{K_7^{0.5}})^2} [LABS^c]$$