Supporting Information

Oxidative Dehydrogenation of Propane over Transition Metal Sulfides Using Sulfur as an Alternative Oxidant

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Table S1. BET surface areas of the indicated metal oxide catalyst precursors, fresh metal sulfides, and spent catalysts after SODHP.

Catalyst	Oxide Precursor or Fresh Sulfide (m^2/g)	Spent Catalyst (m^2/g)
S-ZrO_2	36	27
S-TiO_2	32	19
S-Cr_2O_3	10	7
S-Co_3O_4	22	-
MoS_2	15	15

Table S2. Apparent experimental activation energies (E_{app}) for the indicated SODHP catalysts, derived from the Arrhenius plots in Figure S12 over the temperature range of 470-550 °C.

Catalyst	E_{app} (kJ/mol)	Linear fit R^2
S-ZrO_2	95.9±3.6	0.9958
S-TiO_2	97.3±6.3	0.9875
S-Cr_2O_3	85.9±7.9	0.9754
S-Co_3O_4	134±5.7	0.9945
MoS_2	85.5±6.1	0.9897
PdS	71.6±6.0	0.9795

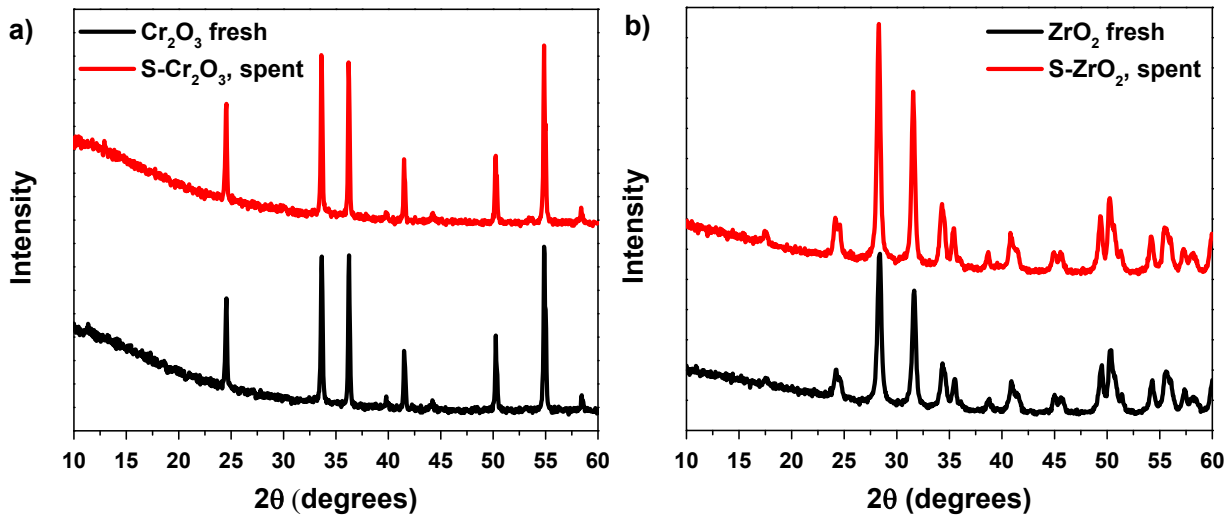

Figure S1. PXRD patterns of the catalyst oxide precursor (black) and spent S-M_xO_y catalyst after SODHP catalysis at 550 °C (red) for a) Cr_2O_3 and b) ZrO_2. The spent catalysts produce essentially identical diffraction patterns to the oxide precursors, indicating that bulk sulfidation does not occur for these

catalysts under the present conditions, and that any sulfide phase formed is amorphous and/or present as very thin films.

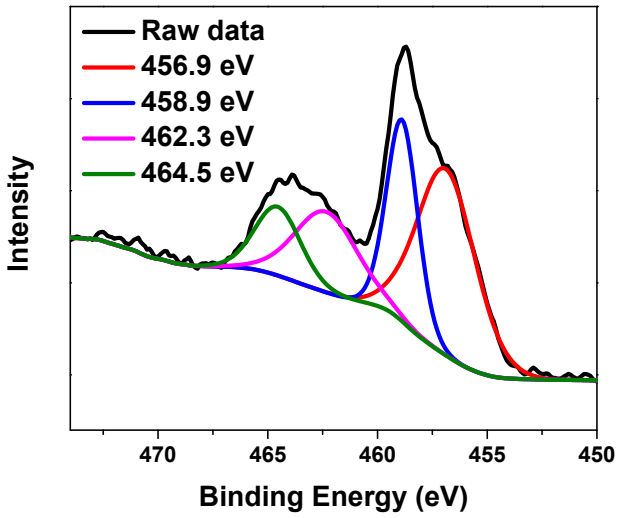

Figure S2. XPS of the Ti2p region for S-TiO_2. Deconvolution of this region yields a doublet for the $2p_{3/2}$ and $2p_{1/2}$ of TiS_2 (red and pink traces, respectively) and a second $2p_{2/3}$ and $2p_{1/2}$ doublet for TiO_2 (blue and green traces, respectively).

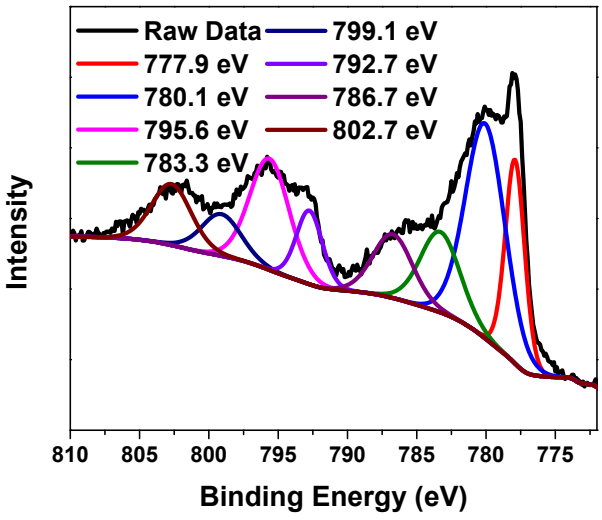

Figure S3. XPS of the Co2p region for S-Co_3O_4. Deconvolution of this region yields doublets corresponding to the $2p_{3/2}$ and $2p_{1/2}$ of Co^0, Co^{II}, and Co^{III}, as well as Co^{II} satellite features at 786.7 and 802.7 eV.

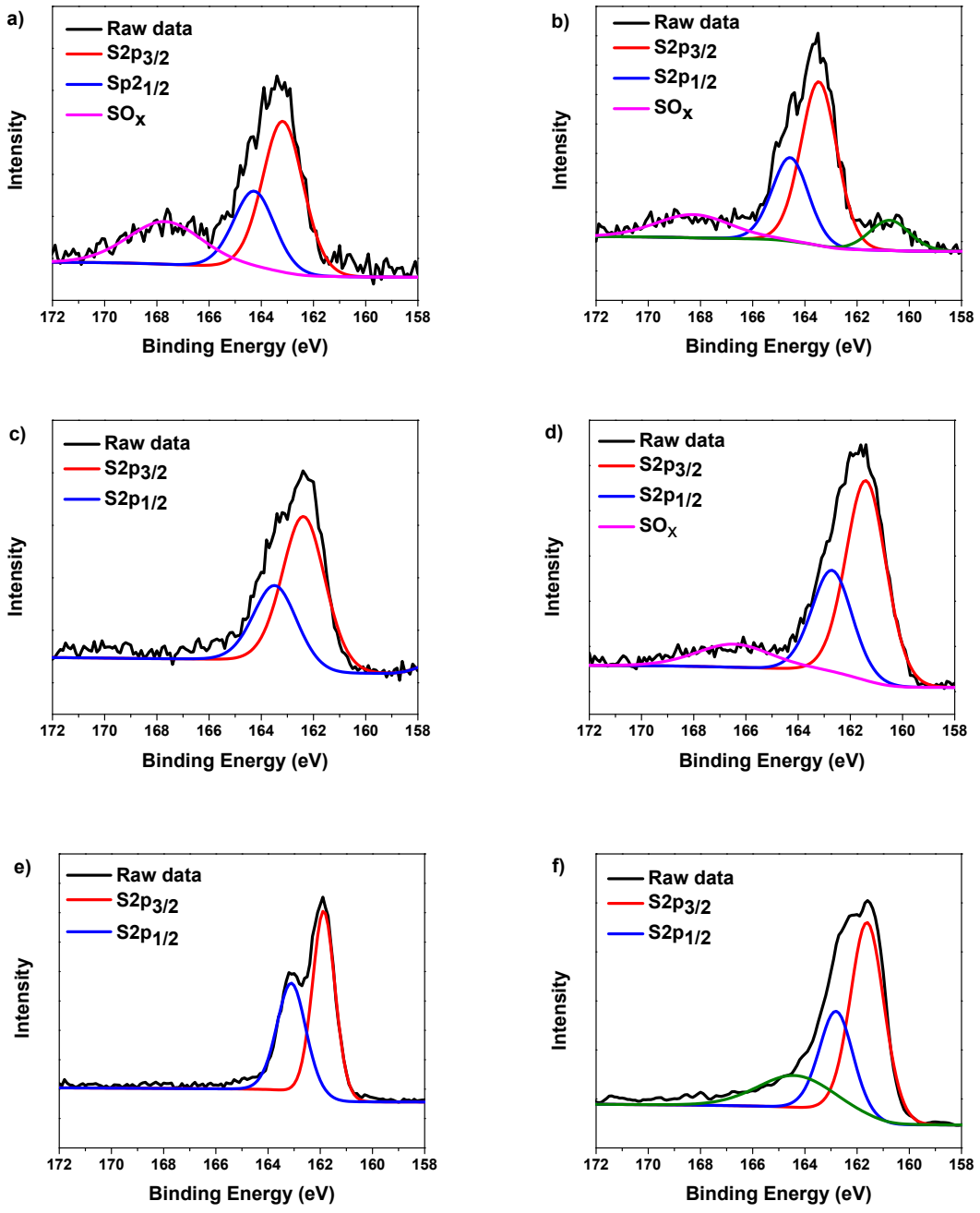

Figure S4. XPS of the S2p region for a) S-ZrO_2, b) S-TiO_2, c) S-Cr_2O_3, d) S-Co_3O_4, e) MoS_2, and f) PdS. This region contains a spin-orbit doublet corresponding to $S2p_{3/2}$ and $S2p_{1/2}$ (red and blue, respectively). Some catalysts also display a SO_x peak (pink).

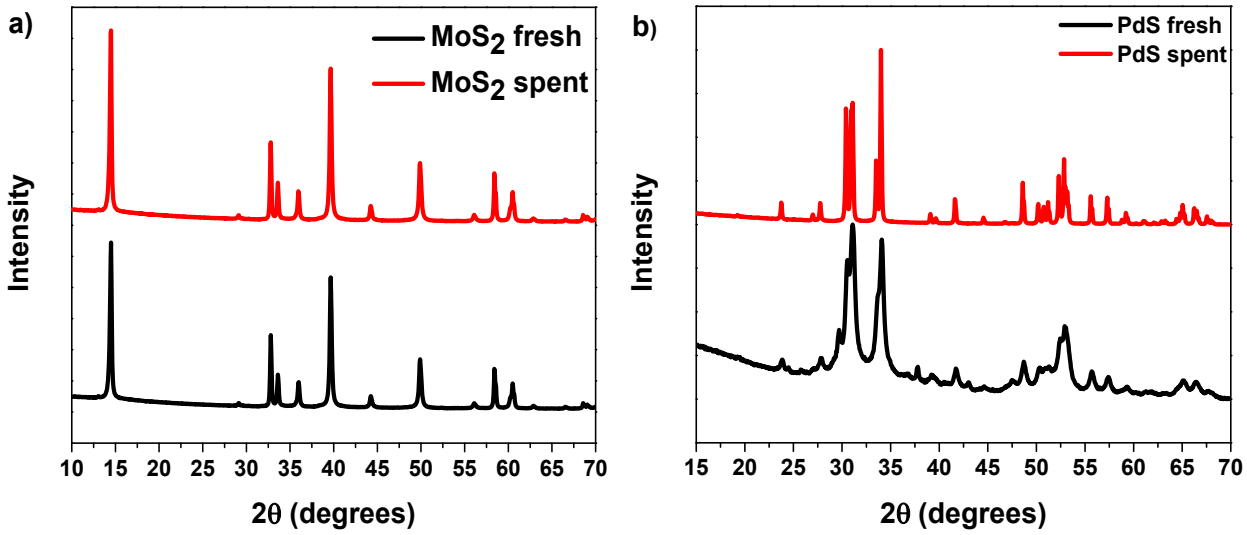

Figure S5. PXRD patterns of fresh (black) and spent sulfide catalysts after SODHP catalysis at 550 °C (red) for a) MoS_2 and b) PdS.

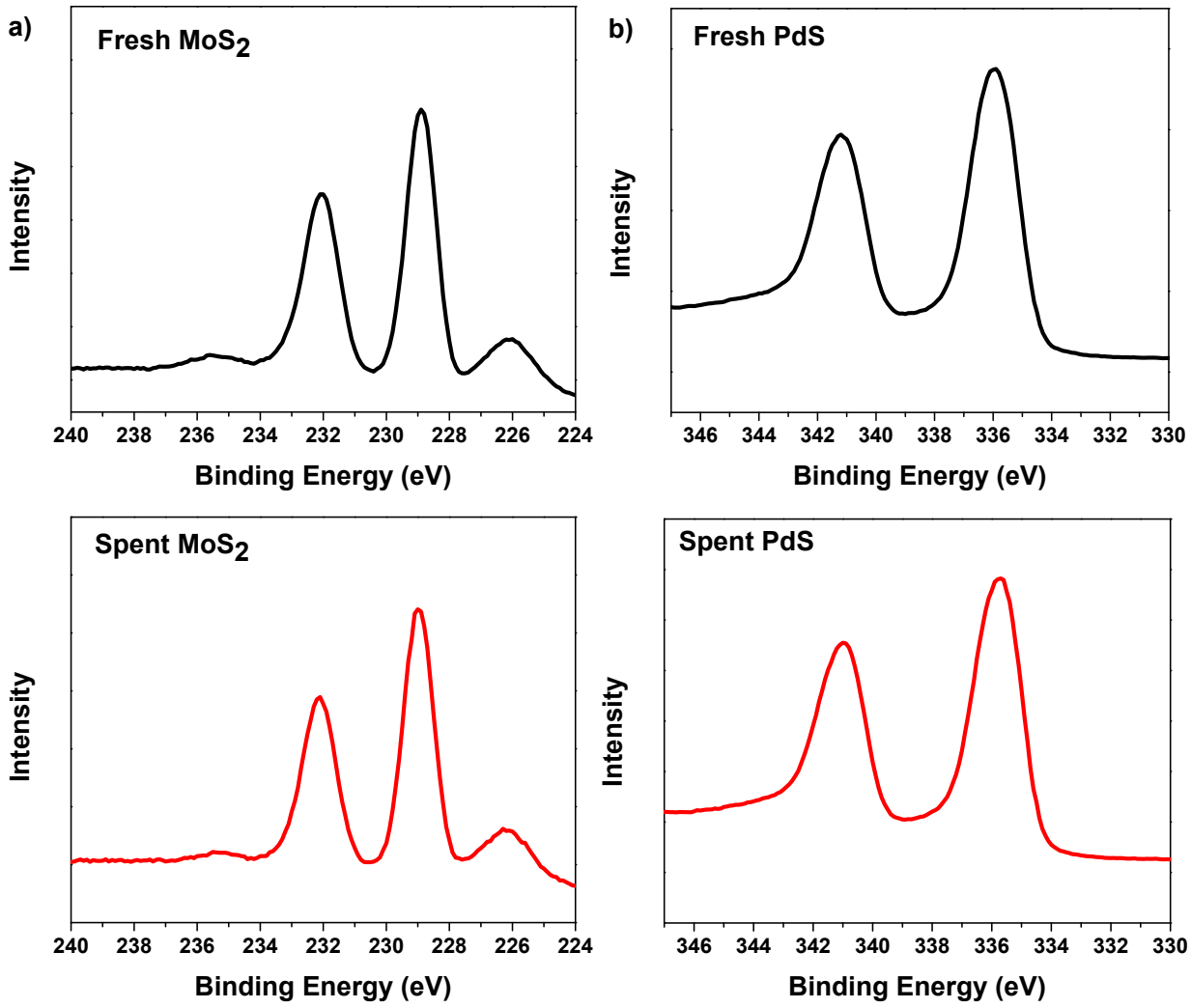

Figure S6. XPS spectra of a) the Mo3d region of MoS_2 and b) the Pd3d region of PdS before (top, black) and after (bottom, red) SODHP catalytic reactions. No significant change in oxidation state is observed between the fresh and spent materials.

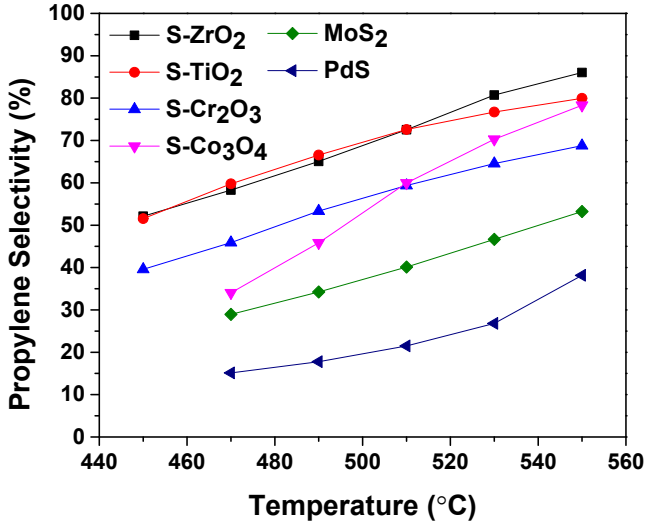

Figure S7. SODHP propylene selectivity as a function of temperature. The propylene selectivity increases with increasing temperature for all catalysts, indicating that the activation energy for propylene → CS_2 is lower than that for propane → propylene. Conditions: WHSV = 8.3 min^{-1}, propane/S_2 = 3.7.

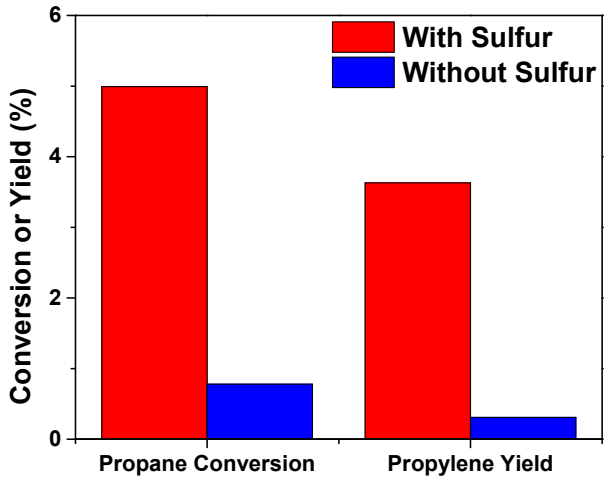

Figure S8. Propane conversion and propylene yield at 510 °C over S-ZrO_2 in the presence (red) and absence (blue) of sulfur in the reactant stream. In the absence of sulfur, the conversion and propylene yield are significantly decreased. Conditions: WHSV = 8.3 min^{-1}, propane/S_2 = 3.7 for the reaction with sulfur.

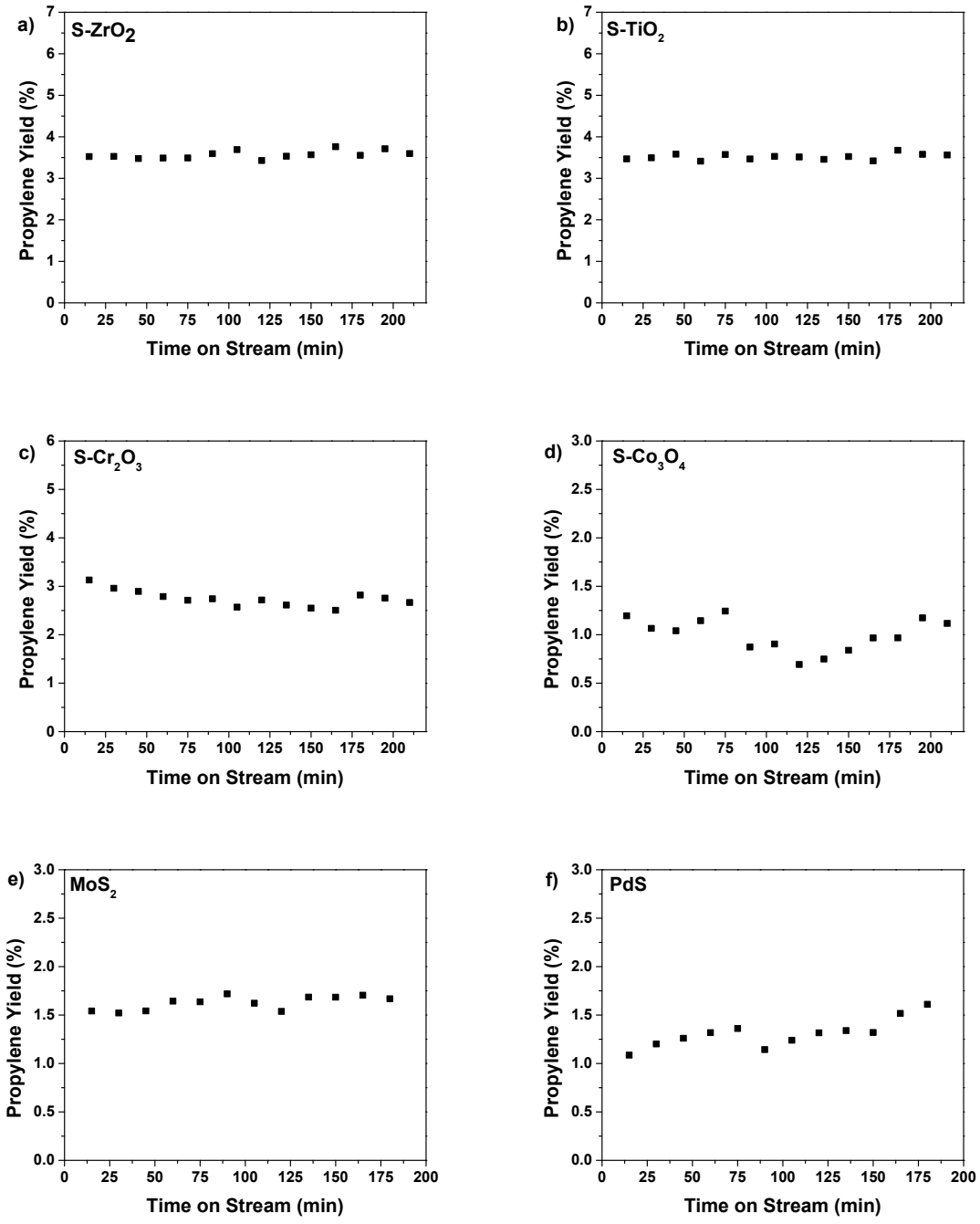

Figure S9. Stability of the SODHP propylene yield as a function of time on stream over a) S-ZrO_2, b) S-TiO_2, c) S-Cr_2O_3, d) S-Co_3O_4, e) MoS_2, and f) PdS at 510 °C. Conditions: WHSV = 8.3 min^{-1}, propane/S_2 = 3.7.

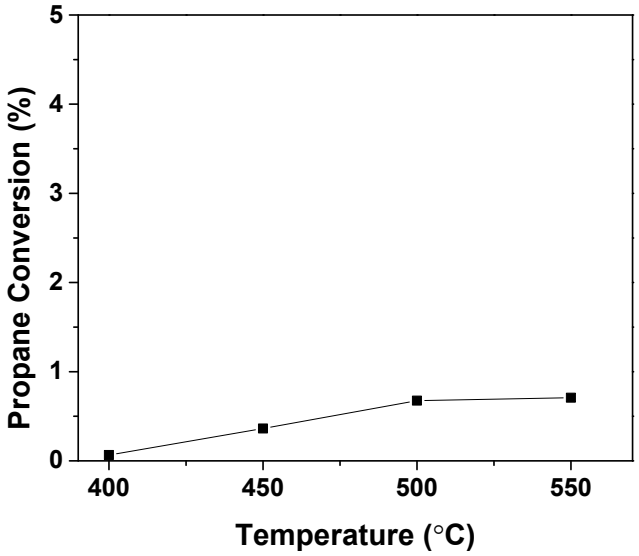

Figure S10. Propane conversion as a function of SODHP temperature without catalyst. The reactor was filled with low surface area quartz sand to act as a blank. The propane conversion remains below 1% within the 400 – 550 °C temperature range, indicating that homogenous gas phase reactions are not significant under SODHP conditions. Conditions: WHSV = 8.3 min^{-1}, propane/S_2 = 3.7.

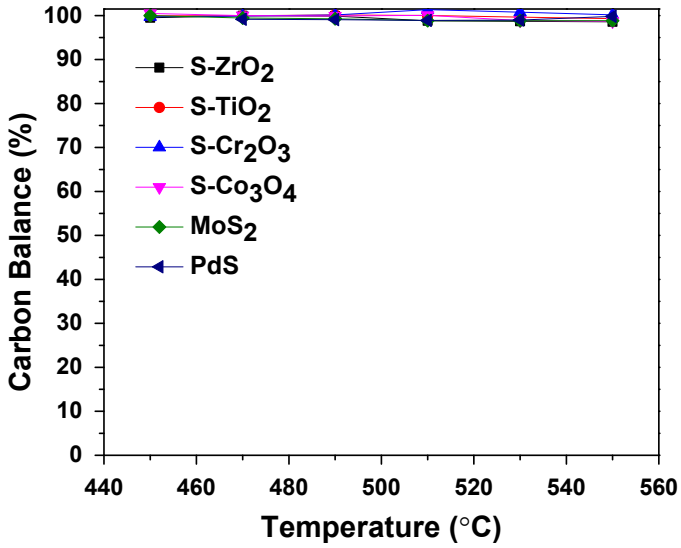

Figure S11. Carbon balance for the six SODHP catalysts as a function of reaction temperature for 3.5 h on stream at each temperature. Carbon balance was calculated based on the total moles of carbon in and out of the reactor. Conditions: WHSV = 8.3 min^{-1}, propane/S_2 = 3.7.

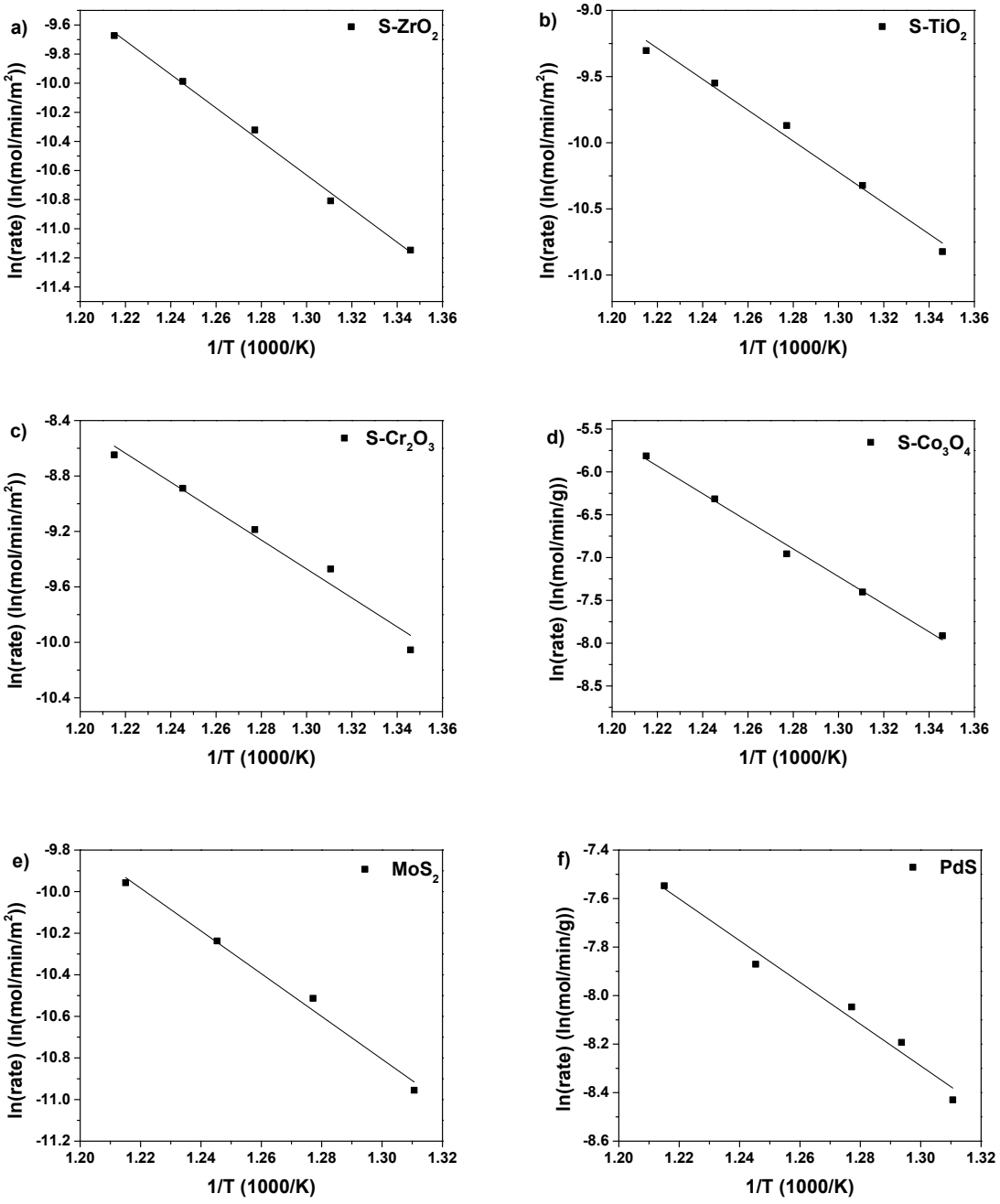

Figure S12. SODHP Arrhenius plots for a) $S\text{-}ZrO_2$, b) $S\text{-}TiO_2$, c) $S\text{-}Cr_2O_3$, d) $S\text{-}Co_3O_4$, e) MoS_2, and f) PdS, based on the rate of propylene formation. The temperature range is 470 – 550 °C.

Table S3. H_2S yields over the indicated SODHP catalysts at 550 °C, calculated on a sulfur basis. Conditions: WHSV = 8.3 min^{-1}, T = 510°C.

Catalyst	H_2S Yield (%)
S-ZrO_2	11.2
S-TiO_2	12.8
S-Cr_2O_3	11.1
S-Co_3O_4	4.7
MoS_2	8.7
PdS	58.2

Table S4. Propane conversion and propylene selectivity over S-ZrO_2 versus the propane/S_2 ratio in the feed gas. Conditions: WHSV = 8.3 min^{-1}, T = 510°C.

Propane/S_2 ratio	Propane Conversion (%)	Propylene Selectivity (%)
3.7	5.1	80.0
3.0	4.8	80.8
2.5	5.3	79.5
2.1	4.7	81.0