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Exploring novel catalysts for the production of green methanol from CO_2

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CO_2 hydrogenation to methanol

H_2 from electrolysis powered by PV/solar

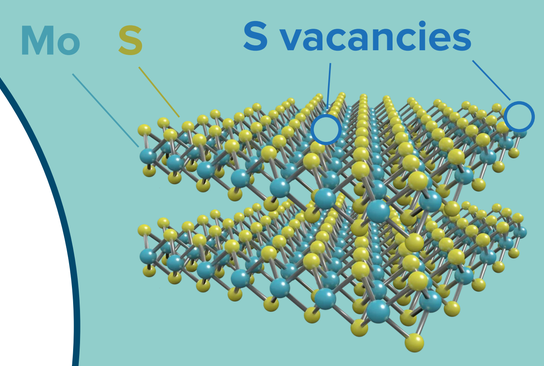
Captured CO_2 (biomass, steel, cement industry, etc)

Typically ~250 °C, 50 bar, with Cu/ZnO catalysts:

$$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O$$

Sustainable alternative to the conventional fossil fuel-based methanol synthesis

Molybdenum sulfide (MoS_2) catalysts

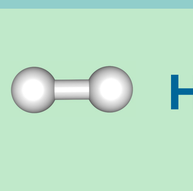


H_2
T > 300° C

in-plane vacancies: CO_2 hydrogenation to CH_3OH [1]

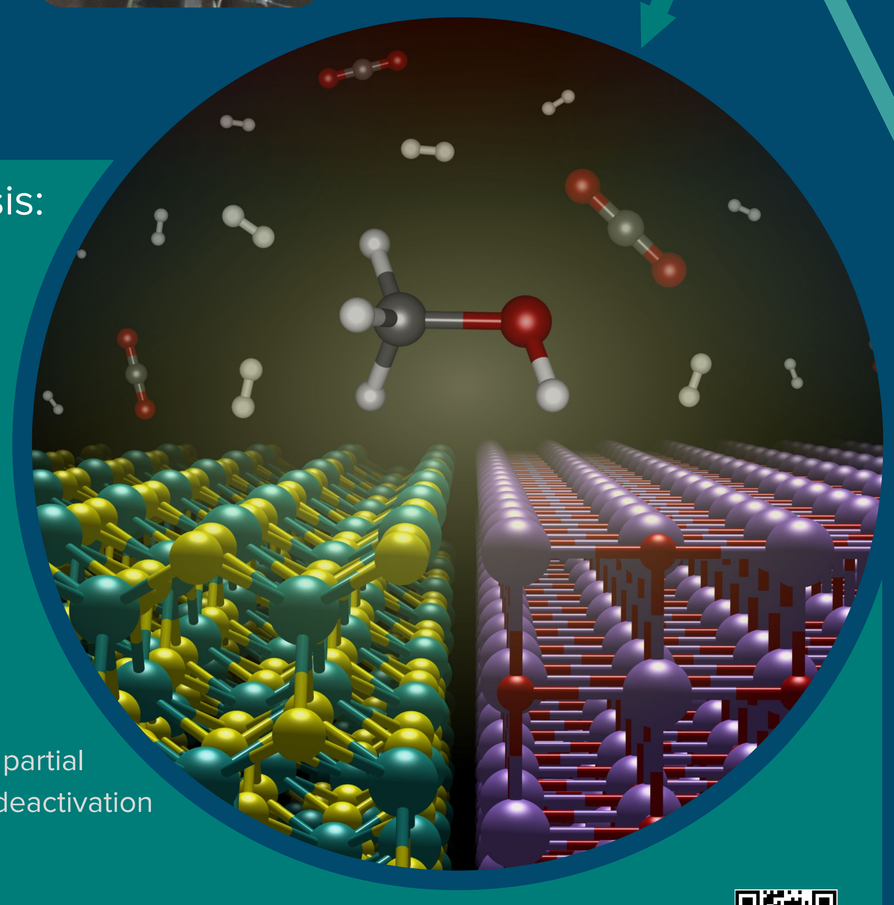
edge vacancies: CO_2 hydrogenation to CH_4

Advantages of MoS_2:
- Stability
- Tolerance to sulfur impurities
- Operation under mild conditions [1]



Mild reaction conditions

- H_2 pretreatment at 300-400°C
- 20 bar, 180 °C
- 1 gram catalyst



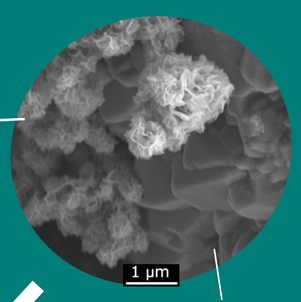
Material characterization

Structure:
- X-ray diffraction (XRD)
- X-ray absorption spectroscopy (XAS)
- Transmission Electron Microscopy (TEM)
- Electron Paramagnetic Resonance (EPR)

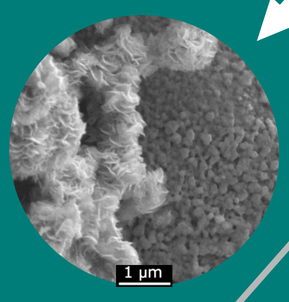
Surface:
- X-ray photoelectron spectroscopy (XPS)
- Scanning Electron Microscopy (SEM)

Mn-promoted MoS_2

- Made by hydrothermal synthesis:



H_2
400 °C



$MnCO_3$

reaction above 250 °C causes partial carbonation + deactivation

MoS_2/MnO_x active phase, retained during reaction at 180 °C

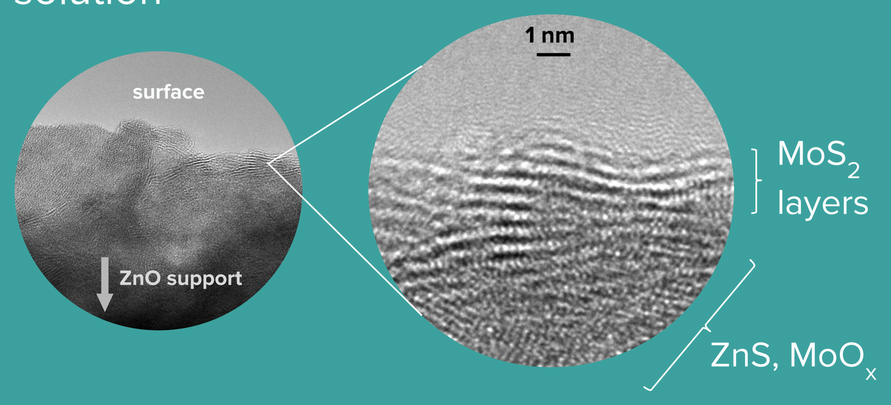
Mn-promoted MoS_2: CH_3OH + CH_4 + CO — 64% selectivity — 2.8% total CO_2 conversion

pure MoS_2 (hydrothermal synthesis): CH_4 — 2.1% total CO_2 conversion

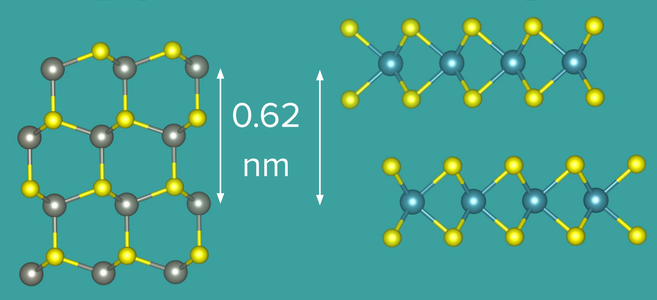
RSC Catalysis Science and Technology, vol. 14, no. 5, 2024 [2]

ZnO-supported MoS_2

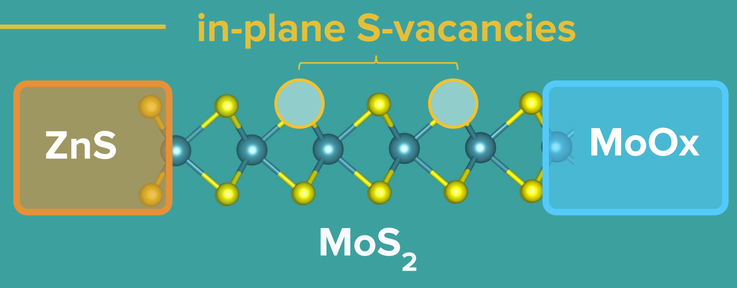
- ZnO support impregnated with a Mo, S solution



Lattice matching might promote MoS_2/ZnS dispersion



Hypothesis under investigation - growth of sulfides / oxides near MoS_2 may block edge S-vacancies: [3]



ZnO-supported MoS_2: CH_3OH + CH_4 — 2.3% total CO_2 conversion — 95% selectivity

Selective CO_2 hydrogenation to methanol

SiOx-supported MoS_2: CH_3OH + CH_4 — 2.2% total CO_2 conversion — 41% selectivity

Cu/ZnO catalyst (Alfa Aesar): CH_3OH + CO — 7.7% total CO_2 conversion — 61% selectivity

Reference catalysts

CoZol catalyst

Spin-off targeting upscaling studies, experiments with industrial CO_2 sources:

References:
[1] Hu, J. *et al*. Sulfur vacancy-rich MoS_2 as a catalyst for the hydrogenation of CO_2 to methanol. *Nature Catalysis* (2021), 4, 242-250
[2] Alves, G.A.S. *et al*. Mn-promoted MoS_2 catalysts for CO_2 hydrogenation: enhanced methanol selectivity due to MoS_2/MnO_x interfaces. *Catalysis Science & Technology* (2024), 14, 5, 1138
[3] Zhou, S., Zeng, H. C. Boxlike Assemblages of Few-Layer MoS_2 Nanosheets with Edge Blockage for High-Efficiency Hydrogenation of CO_2 to Methanol. *ACS Catalysis* (2022), 12, 16, 9872–9886