

## Supplementary Information

### Mn-promoted MoS<sub>2</sub> catalysts for CO<sub>2</sub> hydrogenation: enhanced methanol selectivity due to MoS<sub>2</sub>/MnO<sub>x</sub> interfaces

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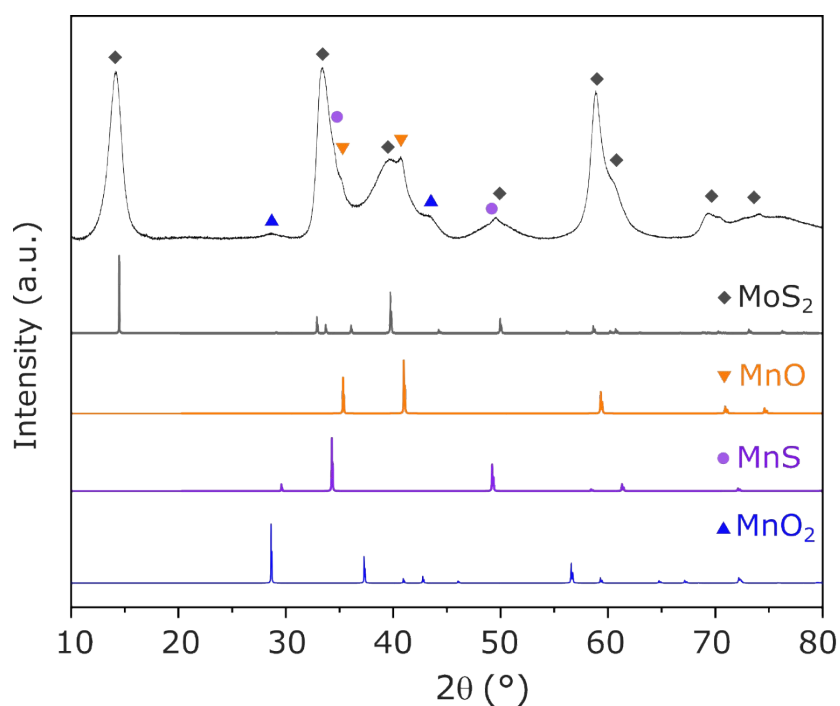


Figure S1 - XRD pattern of as-synthesized Mn(0.5)-MoS<sub>2</sub>, compared with the references MoS<sub>2</sub> (COD-ID 1010993), MnCO<sub>3</sub> (COD-ID 1011228), MnO (COD-ID 1514099) and MnS (COD-ID 1011351)

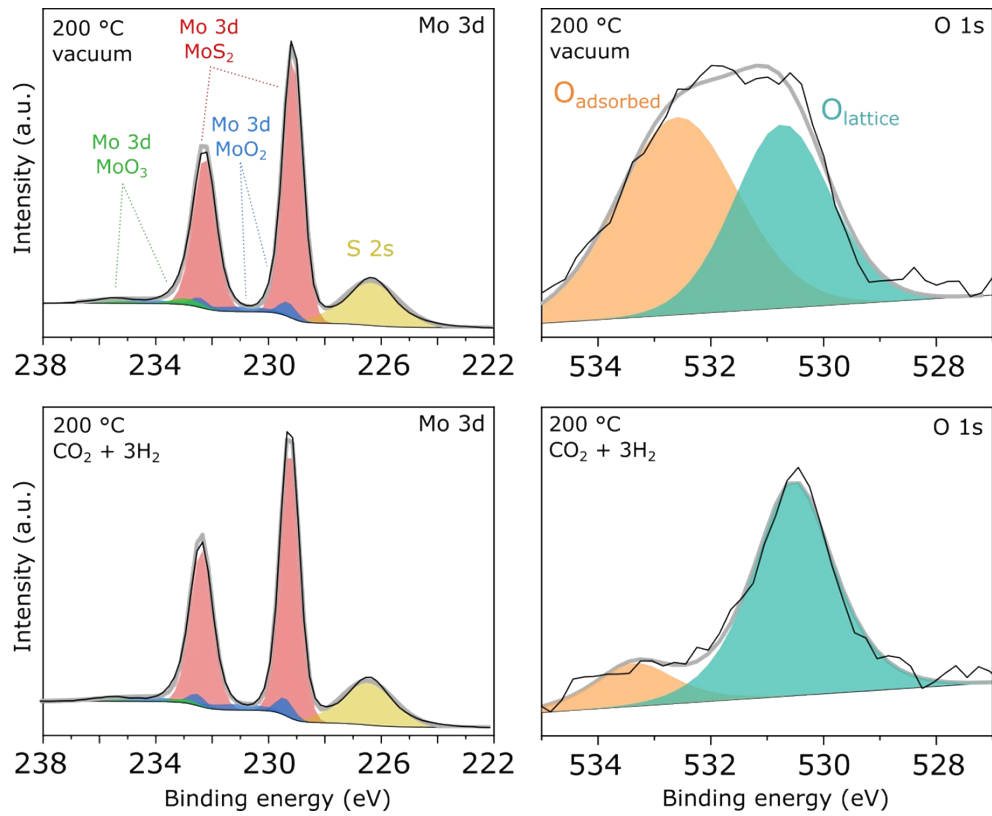


Figure S2 - NAP-XPS spectra of pure MoS<sub>2</sub> produced by hydrothermal synthesis, showing the regions Mo 3d and O 1s under vacuum at 200 °C, H<sub>2</sub> at 400 °C and CO<sub>2</sub>+3H<sub>2</sub> at 200 °C

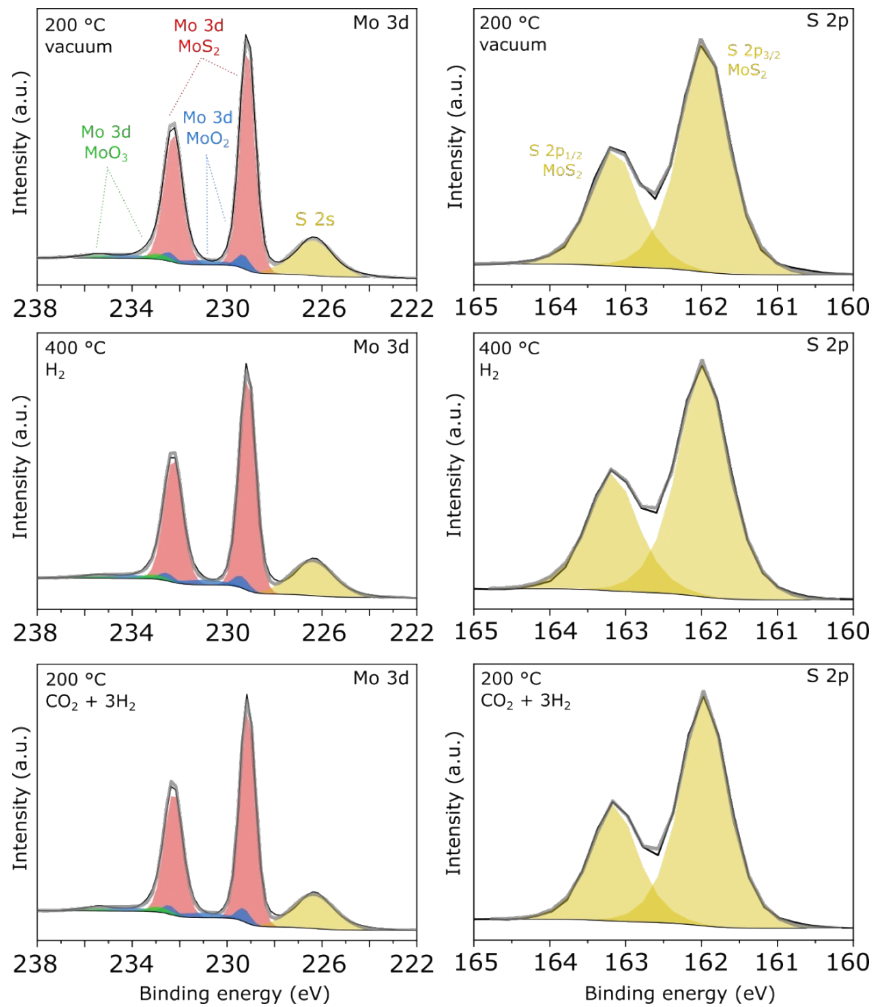


Figure S3 - NAP-XPS spectra of Mn(0.5)MoS<sub>2</sub> showing the regions Mo 3d and S 2p under vacuum at 200 °C, H<sub>2</sub> at 400 °C and CO<sub>2</sub>+3H<sub>2</sub> at 200 °C

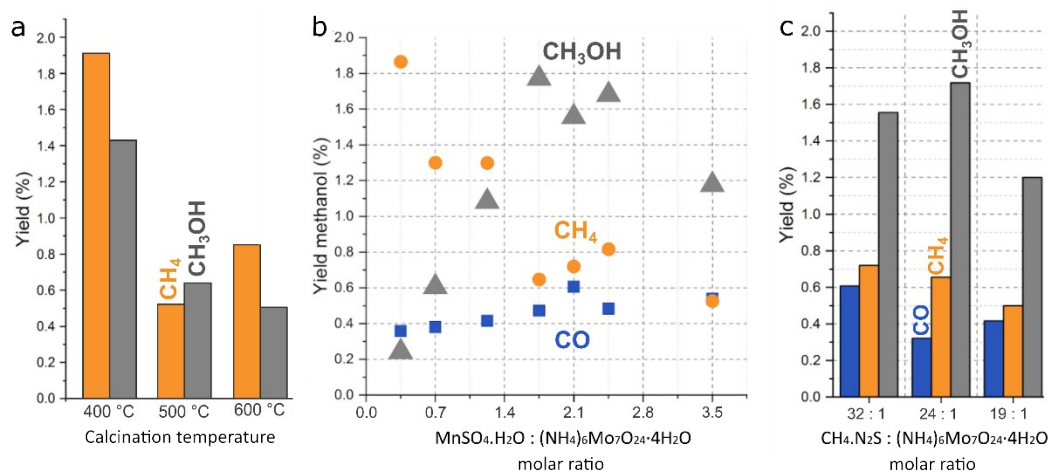


Figure S4 - Catalyst optimization, showing the product yields at 180 °C for the material synthesized using a) CH<sub>4</sub>N<sub>2</sub>S : MnSO<sub>4</sub>.H<sub>2</sub>O : (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O molar ratio of 32 : 3.5 : 1, while varying the calcination temperature (CO yields were not recorded), b) CH<sub>4</sub>N<sub>2</sub>S : (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O molar ratio of 4:1 with N<sub>2</sub> calcination at 400 °C, while varying the MnSO<sub>4</sub>.H<sub>2</sub>O : (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O molar ratio and c) MnSO<sub>4</sub>.H<sub>2</sub>O : (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O molar ratio of 2.1 with N<sub>2</sub> calcination at 400 °C, while varying the CH<sub>4</sub>N<sub>2</sub>S : (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O molar ratio

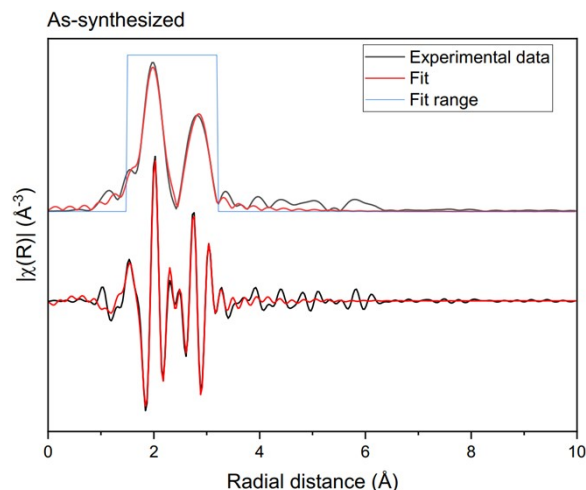


Figure S5 – EXAFS data (Mo K-edge) and fit of as-synthesized  $\text{Mn}(0.3)\text{MoS}_2$  and the Mo foil. Fitting was performed with a K-range from  $3.00$  to  $14 \text{ \AA}^{-1}$ . The amplitude reduction factor was determined by fitting of a metal foil with BCC structure<sup>2</sup>. The first two coordination shells were used with fixed coordination numbers (Mo-Mo1: 8, Mo-Mo2: 6). S02 was found to be 1. The experimental data was fitted in R-space in the coordination distance from  $1.5$  to  $3.2 \text{ \AA}$ . The model was derived from a  $\text{MoS}_2$ <sup>3</sup> crystal structure. Two paths (Mo-S and Mo-Mo) were used for the fit.

Mo-S			Mo-Mo			$E_0$ (eV)	R-factor
R (Å)	N	$\sigma^2$ (Å <sup>2</sup> )	R (Å)	N	$\sigma^2$ (Å <sup>2</sup> )		
$2.41 \pm 0.02$	4.8	0.003	$3.17 \pm 0.01$	4.3	0.004	$1.4 \pm 1.4$	0.013

Table S1 – EXAFS (Mo K-edge) fitting results of as-synthesized  $\text{Mn}(0.3)\text{MoS}_2$

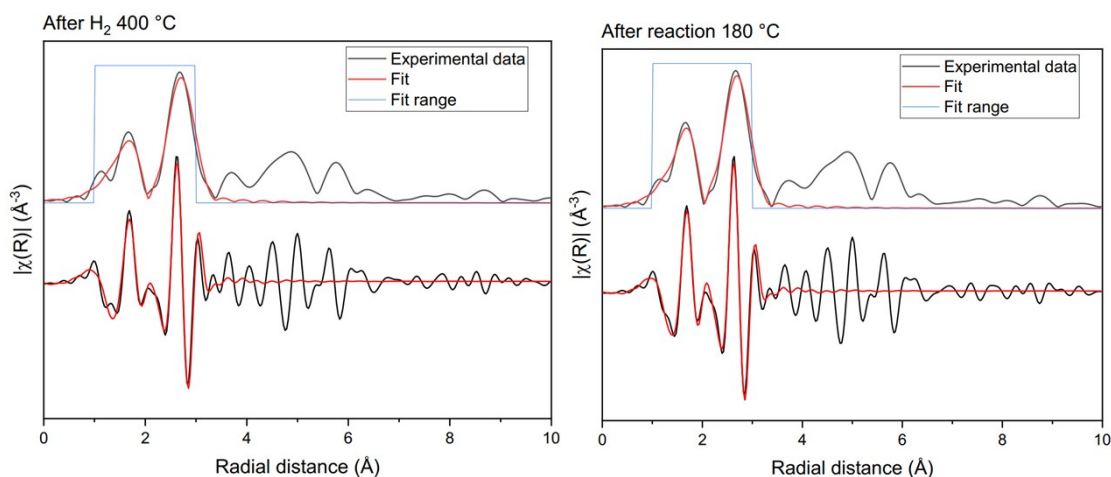


Figure S6 – EXAFS data (Mn K-edge) and fit of  $\text{Mn}(0.3)\text{MoS}_2$  after  $\text{H}_2$  pretreatment at  $400 \text{ }^\circ\text{C}$  and after reaction at  $180 \text{ }^\circ\text{C}$ . Fitting was performed with a K-range from  $2.5$  to  $10.9 \text{ \AA}^{-1}$  in the R-range of  $1.00$  to  $3.00 \text{ \AA}$ . The reference foil was used for energy calibration but due to its excessive thickness, the amplitude reduction factor could not be obtained. The fitting of the samples was performed with the crystal structure of  $\text{MnO}$ <sup>1</sup> and two paths (Mn-O, Mn-Mn) with fixed coordination numbers according to the crystal structure (Mn-O: 6, Mn-Mn: 12). After fitting the sample “After  $\text{H}_2$   $400 \text{ }^\circ\text{C}$ ” the amplitude reduction factor was fixed additionally to  $0.72$  for the fitting of “After reaction  $180 \text{ }^\circ\text{C}$ ”.

Sample	Mn-O			Mn-Mn			$E_0$ (eV)	R-factor
	R (Å)	N	$\sigma^2$ (Å <sup>2</sup> )	R (Å)	N	$\sigma^2$ (Å <sup>2</sup> )		
After H <sub>2</sub> 400°C	2.19 ± 0.03	6	0.015	3.16 ± 0.02	12	0.014	-0.7 ± 0.9	0.013
After Reaction 180°C	2.18 ± 0.04	6	0.011	3.15 ± 0.01	12	0.013	-2.0 ± 0.8	0.009

Table S2 – EXAFS (Mn K-edge) fitting results of Mn(0.3)MoS<sub>2</sub> after H<sub>2</sub> pretreatment at 400 °C and after reaction at 180 °C

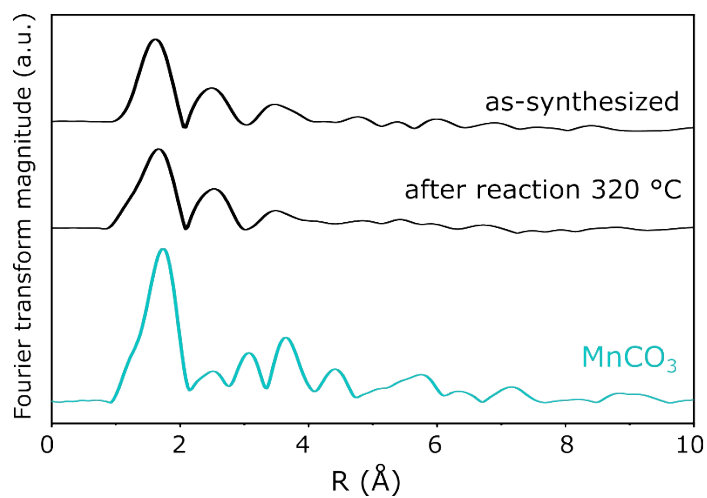


Figure S7 - EXAFS spectra of the Mn K-edge from Mn(0.3)-MoS<sub>2</sub> after synthesis and catalytic reaction at 320 °C, compared to a MnCO<sub>3</sub> reference samples.

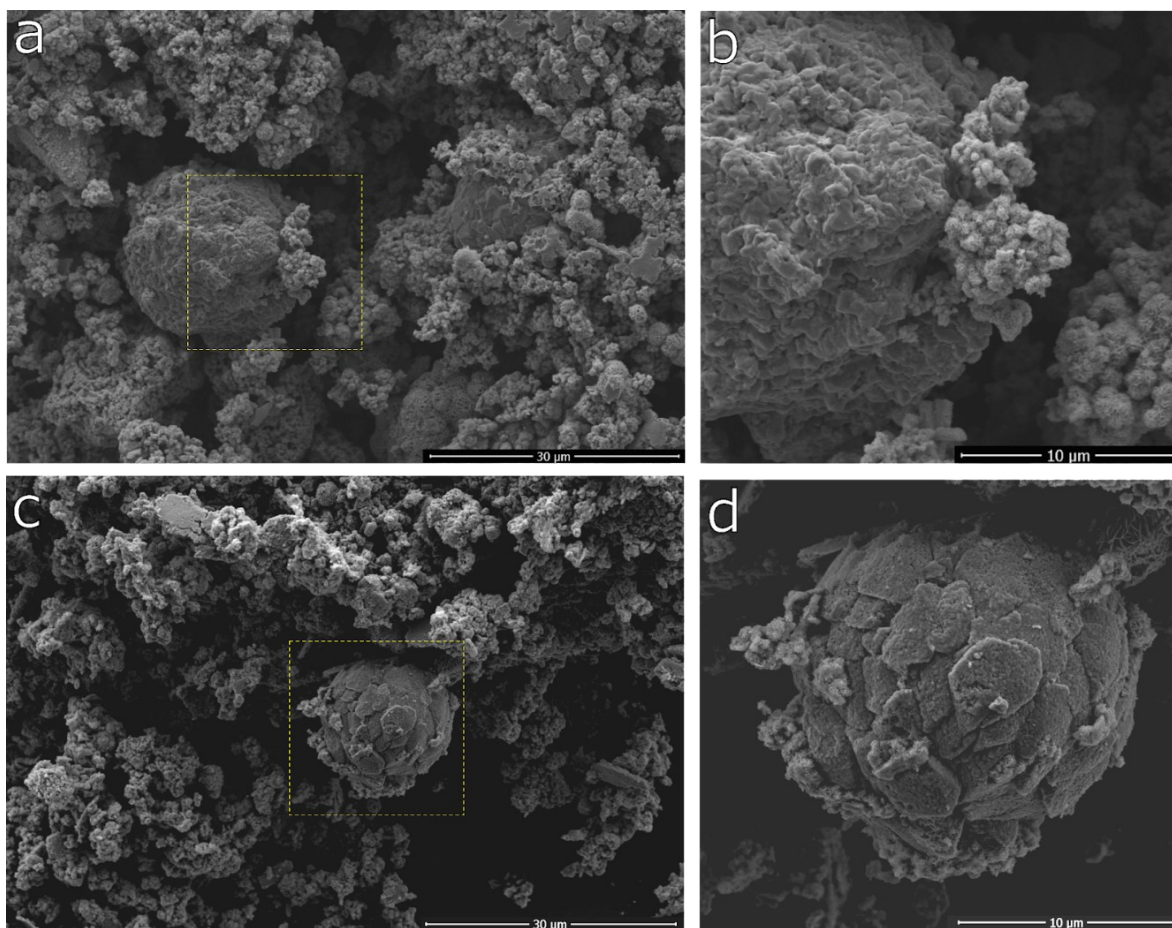


Figure S8 - Additional SEM micrographs of a,b) as-synthesized Mn(0.3)-MoS<sub>2</sub> and c,d) Mn(0.3)-MoS<sub>2</sub> after H<sub>2</sub> treatment and catalytic reaction at 180 °C

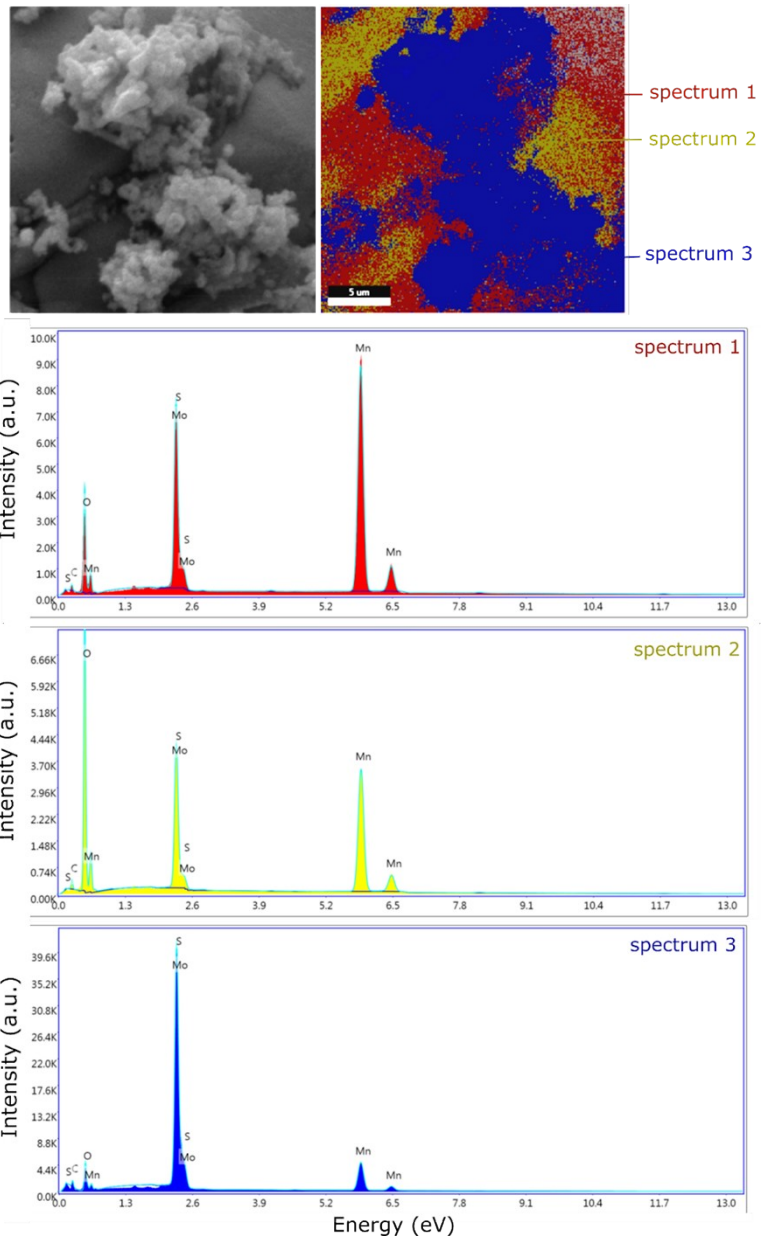


Figure S9 - SEM micrograph of the region analyzed by EDX, alongside the EDX mapping and the related spectra

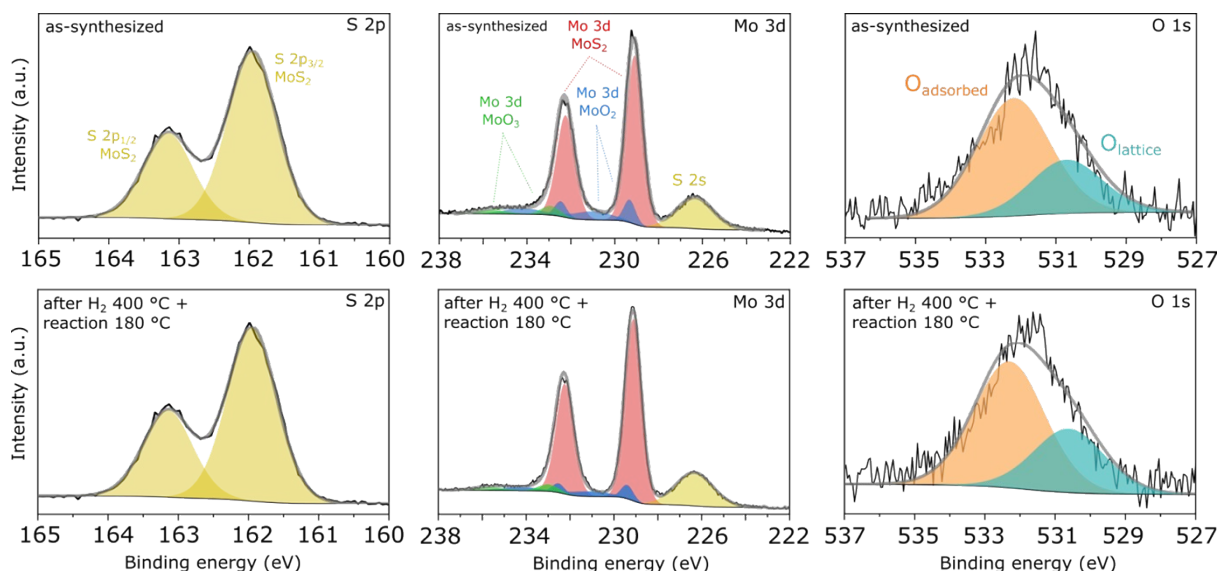


Figure S10 - NAP-XPS spectra of as-synthesized and spent Mn(0.3)-MoS<sub>2</sub> catalysts showing the regions S 2p, Mo 3d and O 1s

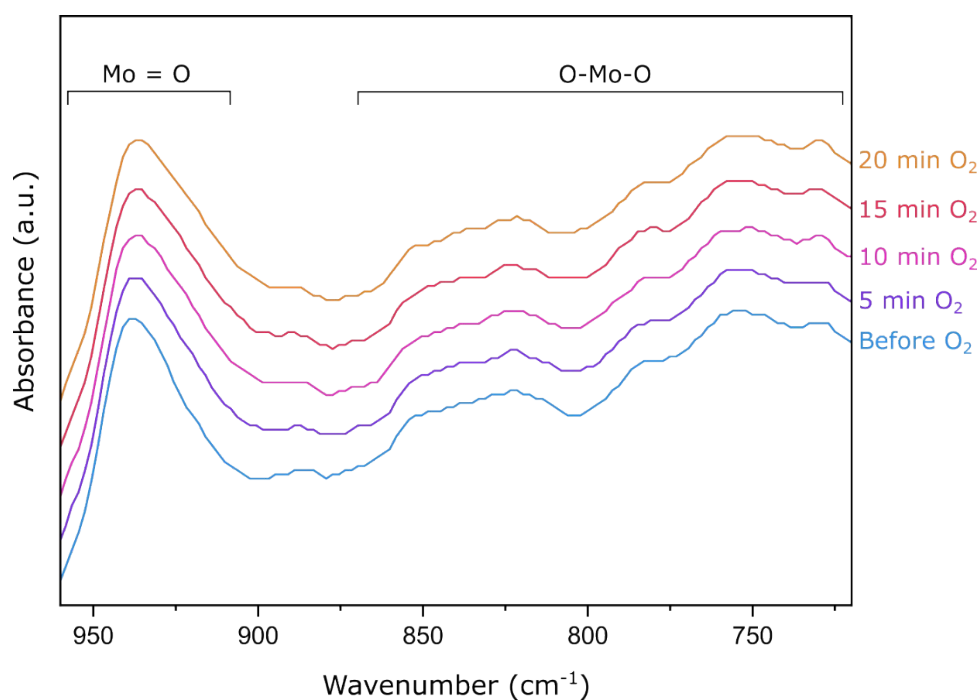


Figure S11 - DRIFTS spectra of Mn(0.3)-MoS<sub>2</sub> during O<sub>2</sub> chemisorption. The experiment was carried out using a BrukerVertex 70 spectrometer (liquid N<sub>2</sub>-cooled MCT detector). The cell inlet was connected to mass flow controllers for O<sub>2</sub>, H<sub>2</sub> and Ar. The powder sample was placed in a crucible located inside the cell. After purging with Ar, the cell was heated up to 400 °C and kept for 3h under H<sub>2</sub> flow. Finally, the cell was cooled to room temperature under Ar flow and O<sub>2</sub> flow was introduced while IR spectra were periodically recorded.



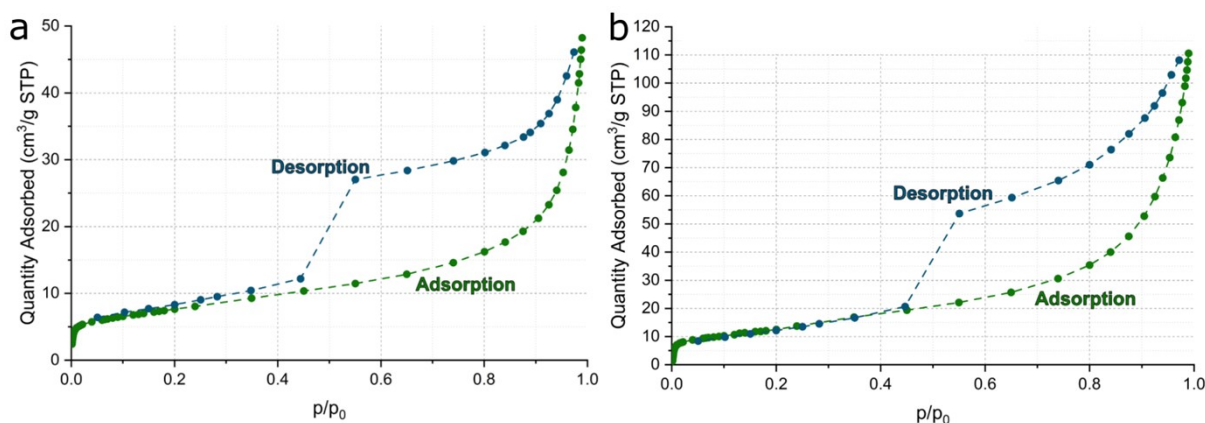


Figure S12 - N<sub>2</sub> adsorption-desorption isotherms at -196 °C of a) pure MoS<sub>2</sub> and b) Mn(0.3)-MoS<sub>2</sub>. Analysis was conducted with a Micromeritics ASAP 2020, after degassed at 350 °C for 8 h under vacuum. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method, with the respective values shown in Table S3.

Catalyst	CH <sub>3</sub> OH sel. (mol%)	CO <sub>2</sub> conv. (mol%)	T (°C)	P (bar)	GHSV (mL g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )	Cat. mass (g)	SA (m <sup>2</sup> g <sup>-1</sup> )	H <sub>2</sub> :CO <sub>2</sub> ratio	Ref.
MoS <sub>2</sub>	0	2.0	180	20	300	1.00	25	3:1	This work
Mn(0.3)-MoS <sub>2</sub>	64	2.8	180	20	300	1.00	41	3:1	This work
FL-MoS <sub>2</sub>	94	12.5	180	50	3000	0.20	130	3:1	[4]
Cu/MoS <sub>2</sub> @SiO <sub>2</sub>	93	3.0	180	50	8000	0.15	98	4:1	[5]
MoS <sub>2</sub> /ZnS	88	2.1	180	50	6000	0.20	86	4:1	[6]
MoS <sub>2</sub> /Ni <sub>0.2</sub>	84	1.0	260	50	12000	0.20	41	3:1	[7]
MoS <sub>2</sub> /Co <sub>0.2</sub>	74	0.7	260	50	12000	0.20	n.a.	3:1	[7]

Table S3 – Comparison of catalytic performance of materials presented in this work with previously reported MoS<sub>2</sub>-based catalysts, in terms of CH<sub>3</sub>OH selectivity, CO<sub>2</sub> conversion, reaction temperature, pressure, gas hourly space velocity, catalyst mass, surface area and H<sub>2</sub>:CO<sub>2</sub> ratio

## References

- 1 R.E.G. Pacalo, E.K. Graham. Pressure and temperature dependence of the elastic properties of synthetic MnO, *Physics and Chemistry of Minerals* 18, 69-80 (1991)
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- 4 J. Hu, *et al.* Sulfur vacancy-rich MoS<sub>2</sub> as a catalyst for the hydrogenation of CO<sub>2</sub> to methanol. *Nature Catalysis* 4, 242-250 (2021)
- 5 S. Zhou *et al.* Strained few-layer MoS<sub>2</sub> with atomic copper and selectively exposed in-plane sulfur vacancies for CO<sub>2</sub> hydrogenation to methanol. *Nature Communications* 14, 5872 (2023)
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