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In situ XPS studies of MoS₂-based CO₂ hydrogenation catalysts

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Abstract

Various formulations of Co, Ni and K modified MoS₂-based catalysts were synthesized hydrothermally and compared in their catalytic performance in CO₂ hydrogenation at 21 bar and 220 °C–330 °C. The products were CO, CH₄ and methanol. The addition of K reduced the selectivity to CH₄ and moved the maximum of the methanol formation rate to a higher temperature. The materials were characterized by N₂ physisorption, temperature programmed oxidation, temperature programmed reduction, and x-ray diffraction spectra (XRD). Under reducing conditions the catalysts were stable until 700 °C and under oxidizing conditions until 300 °C. XRD had shown mainly a MoS₂ phase, as well as metal sulfide in the cobalt and nickel promoted catalysts. Different species of Mo and O were observed under reaction conditions by *in situ* x-ray photoelectron spectroscopy (XPS). When switching from H₂ to CO₂ + H₂ an increase in the amount of oxygen, both lattice oxygen and surface adsorbates, was observed as a consequence of CO₂ addition and H₂O formation in the reaction. The amount of lattice oxygen correlates with the minor amount of Mo(VI) detected. Increasing reaction temperature and thus conversion led to an increase of the O 1s signals at 533 eV assigned to surface OH, formate and adsorbed H₂O. XPS measurements in CO₂ + H₂ feed showed an effect of K addition on the adsorbate-related O 1s peak, which appeared at lower binding energy (532 eV) and was assigned to carbonates. This may indicate a different reaction mechanism in the presence of the promoter.

Supplementary material for this article is available [online](#)

Keywords: molybdenum sulfide, CO₂ hydrogenation, promoter, methanol, CO, NAP-XPS

(Some figures may appear in color only in the online journal)

1. Introduction

CO₂ is a well-known greenhouse gas and the amount in the atmosphere is still rising. Carbon capture and utilization, which includes heterogeneous catalytic hydrogenation, is an approach to reduce CO₂ emissions [1]. In this work, MoS₂

based catalysts were tested in their activity to produce valuable compounds like CO and methanol out of CO₂ and H₂. The aim was to test catalysts that are tolerant to possible sulfur contaminants in the reaction gas. This is of interest for using flue gas directly without additional purification steps. MoS₂ based catalysts promise to fulfill this criterium [2]. Both CO and methanol are valuable base chemicals for the chemical industry [3].

Reactions occurring on these catalysts are the reverse water–gas shift RWGS (CO₂ + H₂ ⇌ CO + H₂O), methane formation (CO₂ + 4H₂ ⇌ CH₄ + 2H₂O) and methanol synthesis (CO₂ + 3H₂ ⇌ CH₃OH + H₂O) [4–7].

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MoS₂ catalysts are known for their activity in hydrodesulfurization, CO hydrogenation and in more recent publications also for CO₂ hydrogenation [8–12]. The conversion of CO to higher alcohols has been described over MoS₂ in literature. A recent publication of Zeng *et al* described the formation of C3+ alcohols over K-promoted MoS₂. While the unpromoted catalyst showed a low selectivity to liquid oxygenates, K-promoted catalysts enabled a higher selectivity to higher alcohols [13].

Liu and Liu performed mechanistic studies of methanol formation from CO₂ and H₂ over a modified Mo₆S₈ cluster by density-functional theory (DFT) calculation. They found that the Mo₆S₈ cluster is able to change its catalytic properties by metal modification via two effects. First, electron transfer from M to Mo₆S₈ takes place and reduces the Mo cation. Second, the metal directly participates in the reaction. Depending on the type of metal, different reaction mechanisms take place [14].

Several reaction pathways have been suggested for methanol formation. Methanol can be produced by the reverse water–gas shift and subsequent CO hydrogenation, or directly via the formate pathway. Co and Ni promoted Mo₆S₈ clusters follow a modified formate pathway. In this process, the *HCOOH species is directly hydrogenated to *H₂CO, *H₃CO and CH₃OH. In the two-step reaction, CO is formed via carboxyl intermediates (*HOCO) in the first step, which is then converted to CH₃OH via *HCO, *H₂CO and *H₃CO intermediates. Liu and Liu predicted the two-step pathway for K-promoted MoS₂ [14, 15].

Nieskens *et al* used CoMoS catalysts to produce higher alcohols from CO₂ and H₂. A pressure of about 100 bar and temperatures of 310 °C and 340 °C were used. The products were mainly CO, alcohols and CH₄ [4]. Liu *et al* studied Mo–Co–K sulfide catalysts for CO₂ hydrogenation. Under optimal conditions higher alcohol formation was observed. Different products were obtained depending on the promoter. K-promoted catalysts produced alcohols, whereas catalysts without K formed mainly hydrocarbons and CO [5].

In this work, several promoted MoS₂ based catalysts were tested for their activity in CO₂ hydrogenation and studied by *in situ* XPS. The materials were also characterized by XRD, N₂ physisorption, temperature programmed oxidation (TPO) and temperature programmed reduction (TPR).

2. Experimental

2.1. Catalyst synthesis

The catalysts were synthesized by a hydrothermal synthesis route. Ammonium molybdate, thiourea and the metal nitrate were dissolved in water and heated for 16 h at 200 °C. After that, the product was cooled to room temperature, separated by centrifugation and washed three times with water. After drying for 2 h at 125 °C, potassium carbonate was added by impregnation of a saturated potassium carbonate solution. The powder was dried overnight. The catalysts were calcined at 500 °C for 2 h under helium.

2.2. Materials characterization

2.2.1. N₂ physisorption. Adsorption-desorption isotherms were recorded with a Micromeritics ASAP 2020 at 77 K. Brunauer–Emmet–Teller method was used to calculate the specific surface area and the Barrett–Joyner–Halenda model was used to determine the average pore diameter and volume from the desorption branch. For pretreatment the samples were heated for 3 h to 300 °C in vacuum.

2.2.2. TPO/TPR. TPO was performed in a gas mixture of 20% oxygen in argon with a flow of 25 ml min⁻¹. Temperature programmed reduction was done in 60% hydrogen in argon. 100 mg of the pure sample was used and heated with a ramp of 5 °C min⁻¹. The produced gas was analyzed by mass spectrometry (Pfeiffer Vacuum QMA 200 with tungsten filament and SEM detector).

2.2.3. XRD. The XRD spectra were recorded with a PANalytical Empyrean in Bragg–Brentano geometry. A Cu-K α x-ray tube (Cu-K α $\lambda_1 = 1.5406$ Å, $\lambda_2 = 1.5444$ Å) was used as an x-ray source and operated at 45 kV and 40 mA. The scan range 2Θ was 10°–90° and a GaliPIX detector was used.

2.3. Catalytic measurements

The measurements were carried out in a fixed bed plug flow steel reactor using a ‘micro effi’ (PID Eng&Tech) system. 1 g of pure catalyst was used. Before the catalytic measurement, the catalyst was treated at 21 bar with pure hydrogen at 400 °C for 4 h. For performing the catalytic reaction, the gas mixture was 20% CO₂, 60% H₂ and 20% He at 21 bar with a total flow of 5 mlN min⁻¹.

The products were detected by an Inficon Micro GC 3000 with a Plot Q column.

2.4. *In situ* XPS

For *in situ* XPS measurements a lab-based near ambient-pressure XPS (NAP-XPS) system from SPECS (Berlin, Germany) with a custom built sample stage (optimized for catalytic measurements) was used [16]. A XR 50 microfocus x-ray source provided monochromatic Al K α (1486.6 eV) radiation. Photoelectrons were detected by a Phoibos 150 NAP hemispherical analyzer. The recorded data was analyzed using the CasaXPS software (Casa Software Ltd, Teignmouth, UK). A linear or Shirley background was added and peaks were fitted with Gauss–Lorentz (GL) sum functions. Mo(IV) 3d_{5/2} was used for calibration at a binding energy of 229.14 eV [17].

About 75 mg of the sample was pressed into a pellet (diameter ~7 mm). The pellet was mounted on a steel backplate on a quartz sample holder. Mo 3d, O 1s, S 2p and C 1s spectra were recorded. The pretreatment was done at 400 °C in 0.75 mbar H₂. Reaction conditions were 1 mbar reaction mixture (CO₂:H₂ = 1:3) at 200 °C and 300 °C.

Table 1. Catalysts overview.

	K/Mo (molar ratio)	Co/Mo (molar ratio)	Ni/Mo (molar ratio)
MoS ₂	0	0	0
MoS ₂ + K	0.5	0	0
Co(0.50)MoS _x	0	0.5	0
Co(0.25)MoS _x + K	0.5	0.25	0
Co(0.50)MoS _x + K	0.5	0.5	0
Ni(0.25)MoS _x + K	0.5	0	0.25
Ni(0.50)MoS _x + K	0.5	0	0.5
Co(0.25)Ni(0.25) MoS _x + K	0.5	0.25	0.25

3. Results and discussion

We compared the catalytic activity and selectivity for CO₂ hydrogenation on pure MoS₂ to Co, Ni and K promoted MoS₂ catalysts. Different variations of the promoted catalysts were synthesized, listed in table 1. K was added in a molar ratio of K/Mo = 0.50. For Co and Ni, the molar ratio was 0.25 and 0.50 for K-promoted catalysts and 0.50 for MoS₂ without K.

3.1. Materials characterization

3.1.1. N₂ physisorption. Figure 1(a) illustrates the Brunauer–Emmett–Teller (BET) surface area of pure and promoted MoS₂ catalysts. Pure MoS₂ exhibited a much higher specific surface area compared to K-promoted catalysts. While unpromoted MoS₂ showed a BET surface area of about 25 m² g⁻¹, surface areas of K-promoted MoS₂ were in the range of approximately 5–10 m² g⁻¹. A lower pore volume was measured for K-promoted catalysts, indicating a lower surface area due to blocked pores. This agrees with results from the literature [13]. There was no correlation between surface area and Co and Ni content. Rietveld refinement showed that the content of Co and Ni sulfide phases was very low. The presence of additional sulfide phases hardly affects the total surface area.

3.1.2. TPR/TPO. Here, we investigate the stability of these materials in oxidizing and reducing the atmosphere. Figure 1(b) illustrates the recorded mass m/z of 64 during heating in O₂/Ar, which is assigned to SO₂. Oxidation of the sample started at about 280 °C, the peak maximum occurred at 355 °C.

To investigate how very stable the sample is under reducing atmosphere, it was heated in 60% H₂/Ar at 5 °C min⁻¹ while recording the mass 34 (H₂S). No reduction was detected up to 700 °C.

3.1.3. XRD. Fresh and used catalysts were analyzed by XRD. The diffractograms are shown in figure 2. The MoS₂ catalyst was phase pure (PDF 04-006-0605). Some catalysts contain small amounts of MoO₂ (PDF 04-008-4309), which may have been formed by residual oxygen during calcination. K₂SO₄ (PDF 04-006-8317) was found in the K-promoted

material, although K₂CO₃ was added as a precursor. The used MoS₂ + K catalyst hardly differed from the fresh one. CoS (PDF 04-003-2150) was found in the fresh Co-promoted catalyst. In contrast, Co₉S₈ (PDF 00-056-0002) was found in the used CoMoS_x + K catalyst. This reveals a slight loss of sulfur during the reaction. The situation was similar for the Ni-promoted catalysts. While NiS (PDF 04-006-6018) was found in the fresh catalysts, Ni₃S₂ (PDF 04-008-8458) was detected in the used catalyst [17–20].

3.2. Catalytic activity and selectivity

Pure MoS₂ (K/Mo = 0) mainly produced CH₄ and CO. CH₄ was the main product (at 280 °C CO:CH₄ = 1:8.2), and the production increased strongly with temperature.

Figure 3(a) compares the CO yield for several MoS₂ based catalysts at different temperatures. Pure MoS₂ showed the lowest CO formation activity. More CO was obtained by adding K. The Co-promoted catalyst with Co/Mo = 0.50 turned out to be even more active towards CO formation (+127% at 280 °C) than the K-promoted MoS₂ catalyst. The highest CO yield up to ~15% was obtained when both K and Co or Ni were added. There was hardly any difference in catalysis between Co and Ni promoted MoS₂ + K. Also, the promoter content (M/Mo = 0.25 or 0.50) showed no effect on performance. In addition, the CO yield has shown differing temperature dependence. For Co/Ni promoted MoS₂ + K catalysts, the yield increased almost linearly with temperature, whereas for MoS₂ + K, it exhibited an exponential dependence.

The production of methane is almost completely prevented by adding K (figure 3(b)). At 320 °C, a methane yield of about 20% was determined over MoS₂, whereas MoS₂ + K showed hardly any formation of CH₄. Only trace amounts of methane were detected over all K-promoted catalysts. In contrast, addition of Co did not completely prevent methane production, but reduced it to about 1/6 for MoS₂ compared to Co(0.50)MoS_x.

Formation of small amounts of methanol occurred only over promoted catalysts. Figure 3(c) summarizes the methanol yields. MoS₂ showed no detectable methanol formation. CoMoS_x produced some methanol at 180 °C. MoS₂ + K showed the highest yield. The addition of Co and Ni to MoS₂ + K was not beneficial for methanol formation, in contrast, CoMoS_x + K and NiMoS_x + K produced less methanol than MoS₂ + K. The highest yield was found in a temperature range of 280 °C–300 °C.

Table 2 lists the product formation rates and table 3 reaction orders at 280 °C. CO formation showed little dependence on CO₂ concentration, while for H₂ the reaction order of CO formation was about 1. CO₂ concentration also had only small effects on CH₄ and methanol production. The formation of CH₄ is, however, strongly dependent on hydrogen concentration with a reaction order above 1. Also, methanol formation showed a strong dependence on H₂. While the H₂ reaction order was 1.5 on MoS₂ + K, it was even higher with 2.6 and 2.7 for Co(0.50)MoS_x + K and Ni(0.25)MoS_x + K, respectively. The differences in H₂ and CO₂ orders for catalysts with

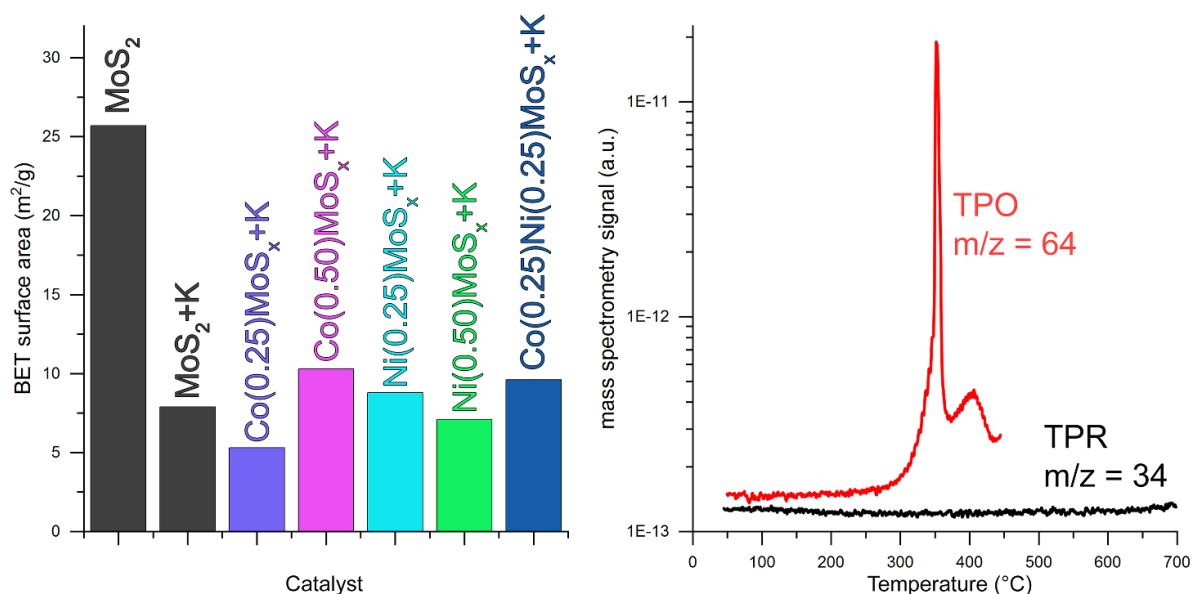


Figure 1. (a) BET surface areas of MoS₂ catalysts (b) TPO of MoS₂ in 20% O₂/Ar and TPR of MoS₂ in 60% H₂/Ar with a heating ramp of 5 °C min⁻¹.

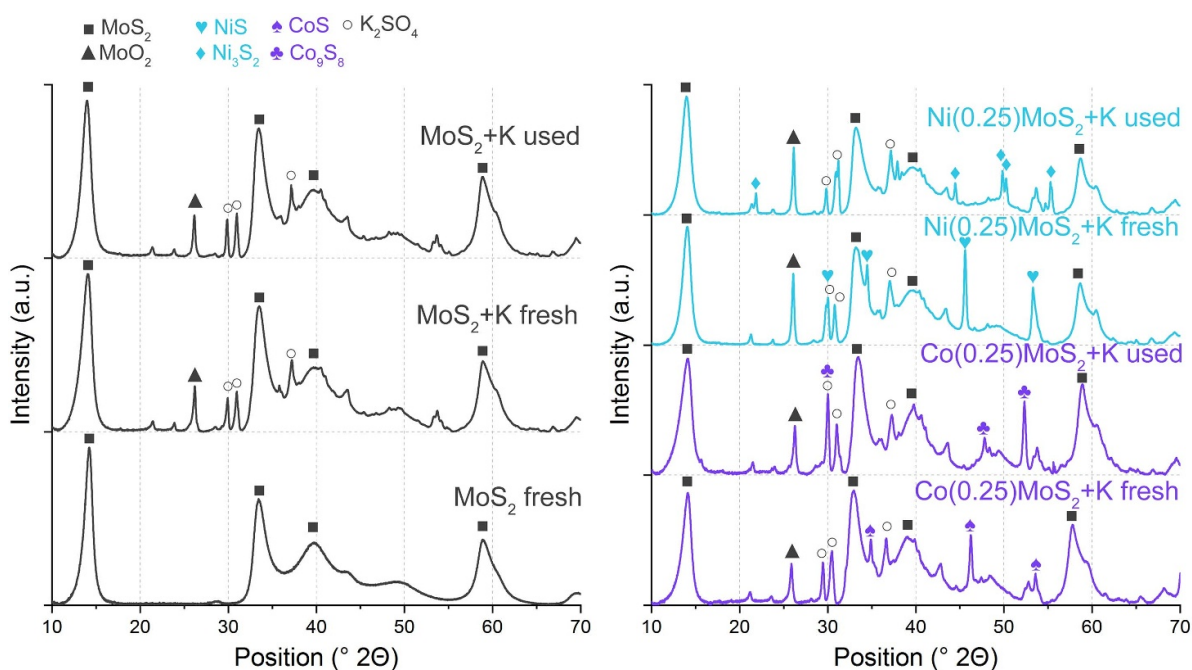


Figure 2. XRD spectra of fresh and used MoS₂ based catalysts.

and without Co and Ni promotion might be due to a different reaction mechanism.

Based on DFT calculations, Liu and Liu proposed different reaction mechanisms for Mo₆S₈ clusters with and without modification by various metals [14], including K and Ni. Methanol can be produced by the reverse water-gas shift and subsequent CO hydrogenation, or directly via the formate pathway. In our work, MoS₂ showed significantly different catalytic properties than MoS₂ + K and the materials promoted with Ni or Co. Pure MoS₂ produced mainly CH₄, and no methanol was observed under the conditions

applied. MoS₂ + K exhibited higher CO formation rate. This may be consistent with the proposed two-step reaction for the K-Mo₆S₈ cluster.

Our results are also in agreement with Liu *et al* [5]. The addition of K decreased hydrocarbon formation and increased alcohol formation.

3.3. NAP-XPS of MoS₂

To obtain more information on the surface composition of the unpromoted MoS₂ material under different conditions,

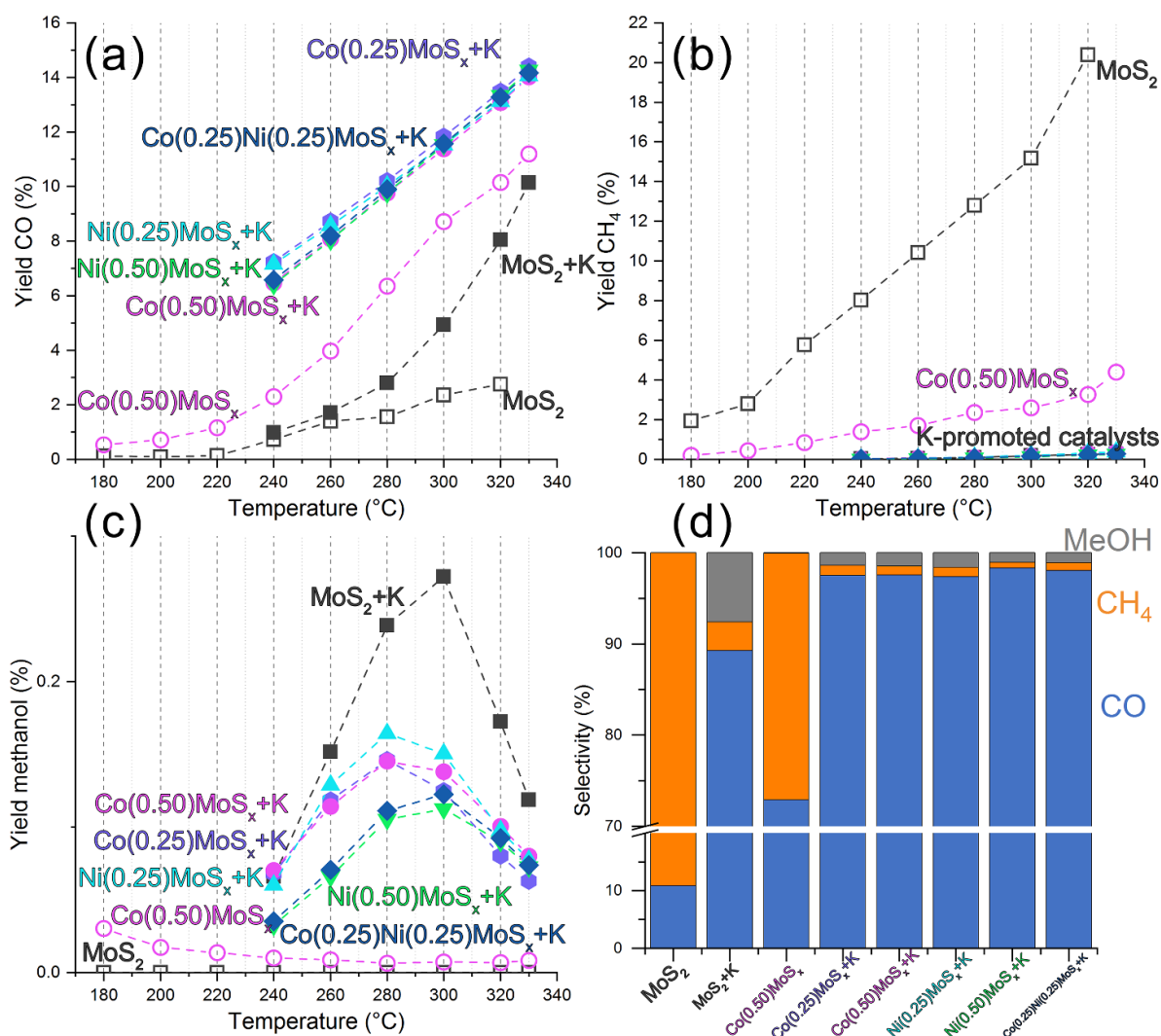


Figure 3. Catalytic activity of several MoS₂ based catalysts at 21 bar, 300 mlN/(g_{catalyst}*h), 20% CO₂, 60% H₂ and 20% He. (a) Yield of CO, (b) yield of CH₄, (c) yield of methanol, (d) selectivities at 280 °C.

Table 2. Formation rate of products orders at 280 °C, 300 mlN/(g_{catalyst}*h), 21 bar, 20% CO₂, 60% H₂, 20% He.

	formation rate (μmol g ⁻¹ h ⁻¹)		
	CO	CH ₄	MeOH
MoS ₂	205	1691	0
MoS ₂ + K	370	13	32
Co050MoS	839	312	1
Co025MoS + K	1348	15	19
Co050MoS + K	1289	13	19
Ni025MoS + K	1324	14	22
Ni050MoS + K	1289	8	14
CoNiMoS + K	1309	11	15

NAP-XPS measurements were performed during reduction and in reaction atmosphere. At first, spectra were collected at 200 °C in ultra-high vacuum, followed by pretreatment in 0.75 mbar H₂ at 400 °C and further collection of spectra. The sample was cooled to 200 °C in H₂ atmosphere. Then,

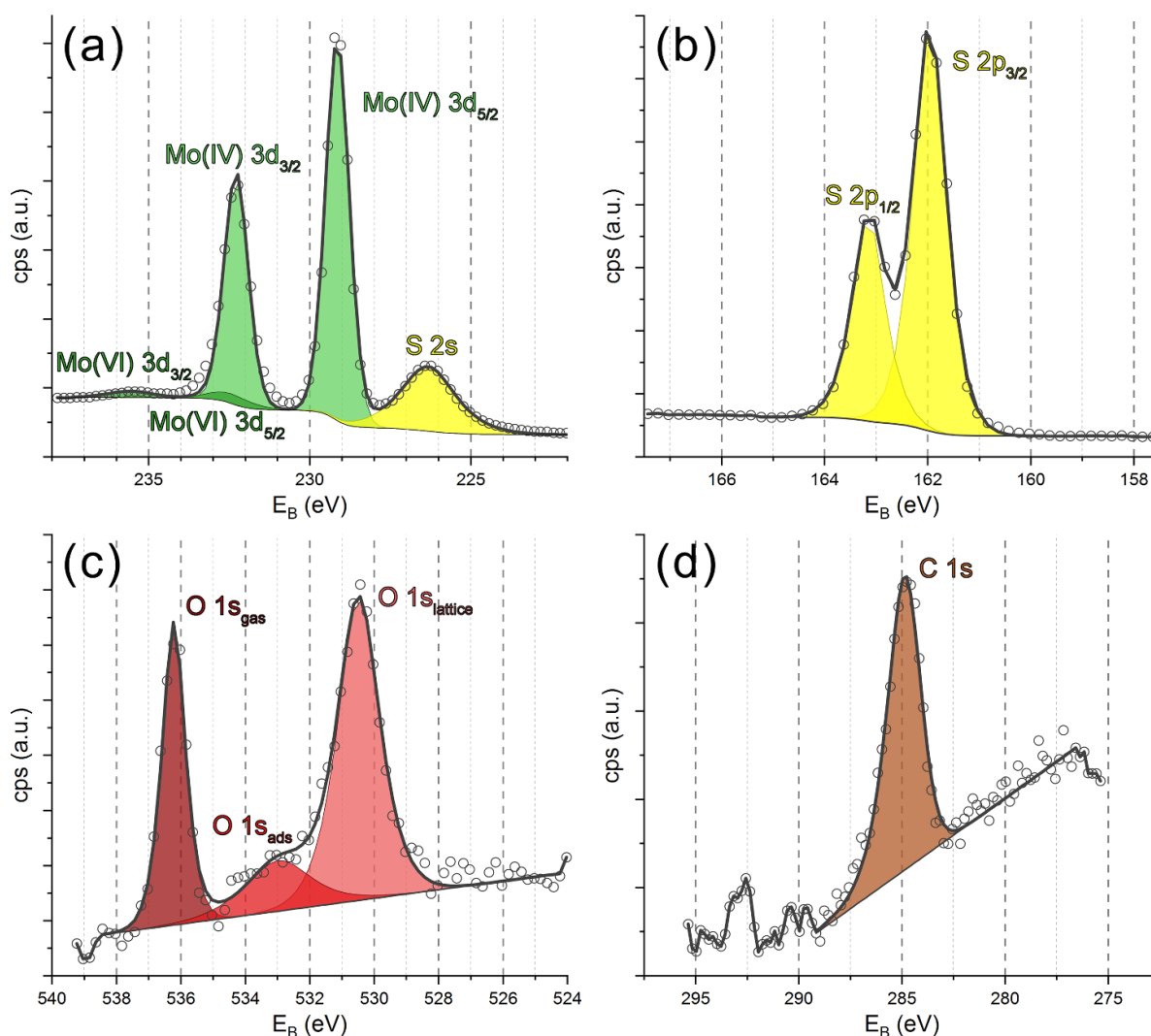
a reaction mixture of 1 mbar CO₂:H₂ = 1:3 was dosed into the NAP-XPS chamber, and the sample was analyzed at 200 °C and 300 °C during catalytic reaction.

An exemplary fit of the Mo 3d spectral range is visualized in figure 4(a). The Mo peaks were fitted with an GL(30) function, the S 2s with GL(70). Doublet separation from Mo 3d_{5/2} and Mo 3d_{3/2} of 3.14 eV was taken from the literature [21]. The main oxidation state of Mo was IV, minor amounts of Mo(VI) were found [22]. The amount of Mo(VI) at the surface varied with the conditions applied, as discussed below. In addition, also the S 2s signal is visible in this range. The S 2p spectral range is shown in figure 4(b). For both signals, only one S species was observed.

Several oxygen species were found in the O 1s spectra. The O 1s spectrum of the MoS₂ sample under CO₂ + H₂ at 200 °C is shown in figure 4(c). The peak at about 530.5 eV is attributed to lattice oxygen [23], likely from MoO₃. O 1s with a binding energy of about 533 eV originates from adsorbed species like surface hydroxyls and water [4, 24]. CO should appear at lower binding energy (531.5 eV). The existence of molecularly

Table 3. Reaction orders at 280 °C, 300 mlN/(g_{catalyst} * h), 21 bar, 20% CO₂, 60% H₂, 20% He.

	CO formation		CH ₄ formation		MeOH formation	
	CO ₂ order	H ₂ order	CO ₂ order	H ₂ order	CO ₂ order	H ₂ order
MoS ₂ + K	0.48 ± 0.00	1.07 ± 0.12	-0.18 ± 0.00	1.48 ± 0.19	-0.21 ± 0.02	1.52 ± 0.03
Co(0.50)MoS _x + K	0.17 ± 0.24	0.86 ± 0.20	-0.54 ± 0.60	1.63 ± 0.73	0.45 ± 0.10	2.63 ± 0.06
Ni(0.25)MoS _x + K	0.52 ± 0.01	0.73 ± 0.00	-0.08 ± 0.13	1.24 ± 0.09	0.24 ± 0.02	2.67 ± 0.14

**Figure 4.** (a) Mo 3d, (b) S 2p, (c) O 1s and (d) C 1s in situ XPS spectra of MoS₂ at 200 °C in H₂ + CO₂ atmosphere.

adsorbed CO₂ on the surface is not feasible at reaction temperatures. Adsorbed formate species may also contribute to the adsorbate species at 533 eV, as it is a possible intermediate in the reaction; however, corresponding C 1s peaks are absent (figure 4(d)) [25]. Thus, we assign these species to mostly OH and H₂O at the surface. Under CO₂ + H₂ additional peaks from gas phase species are visible and absent in H₂. The peak at 536 eV present under the reaction atmosphere originates from the gas phase CO₂ [26]. The distribution of all oxygen species in MoS₂ is visualized in figure 5. The peak of adsorbed species at about 533 eV was particularly large before the pretreatment. In addition, a signal at 534 eV was

only visible prior to pretreatment. The amount of oxygen rapidly decreased at 400 °C under hydrogen and then increased again upon adding CO₂. This indicates that the oxygen originates from CO₂ from the gas phase and/or H₂O formed as a reaction product. When comparing reaction at 200 °C and 300 °C, the adsorbate-related signal increases with temperature and thus conversion. At 300 °C during reaction, this peak showed a much higher area and full width half maximum.

The C 1s range shows mainly the presence of adventitious carbon, which was fitted by an asymmetric GL(30) function (figure 4(d)). No significant amounts of C–O adsorbates were visible. The energy range around the Fermi level is shown in

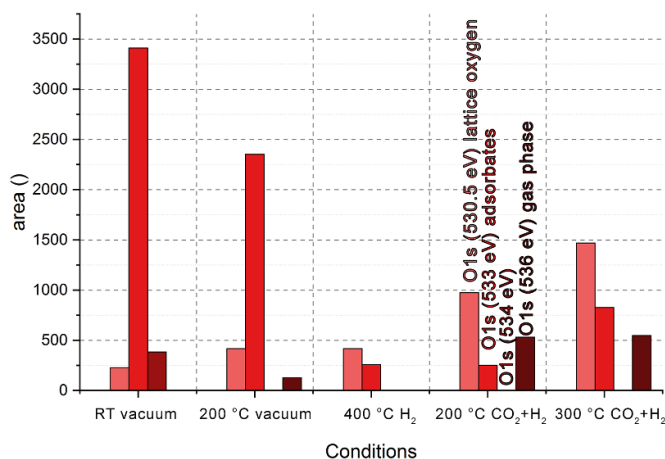


Figure 5. Amount of oxygen species on MoS₂ at different conditions. The peak at about 530.5 eV is attributed to lattice oxygen. The peak at 533 eV originates from adsorbed species. The signal at 534 eV was only found prior to pretreatment. The peak at 536 eV originates from the gas phase CO₂.

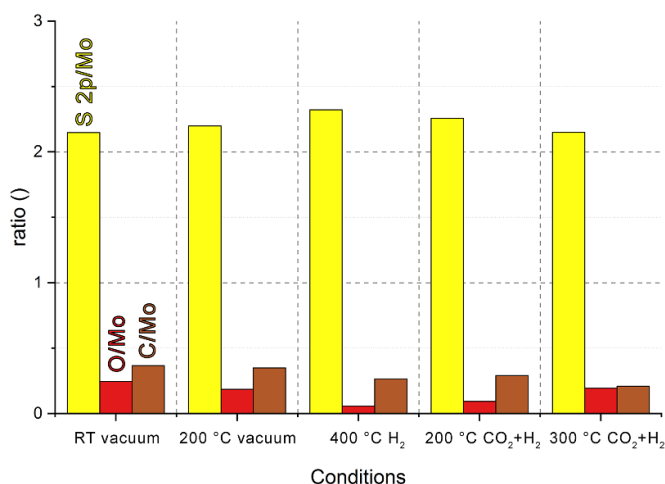


Figure 6. Relative surface concentrations of S, O (without gas phase) and C (without gas phase) of MoS₂ during the experiment.

the supplementary information (figure SI 1 (available online at stacks.iop.org/JPD/54/324002/mmedia)).

Surface concentrations of S, O and C changed during the experiment, as displayed in figure 6. The area of Mo 3d was corrected with a cross section of 0.1303 Mbarn [27] and taken for concentration calculations. The S/Mo ratio was calculated from S 2p and Mo 3d peak areas corrected by the element-specific cross sections [27], and were slightly above two throughout the experiment. The surface concentration of oxygen depended on the conditions. The lowest amount of total oxygen at the surface was found at 400 °C under hydrogen atmosphere, under the most reducing conditions we applied. When switching to the reaction mixture an increase in the amount of oxygen was observed as a consequence of the addition of CO₂ and the formation of H₂O during the reaction.

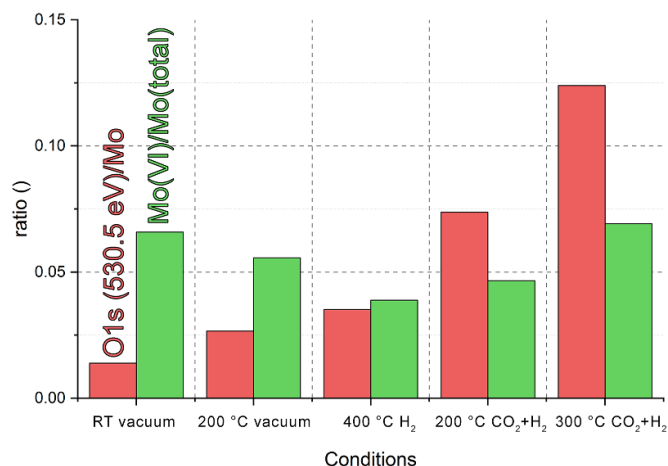


Figure 7. Relative amount of lattice oxygen and fraction of Mo(VI).

The ratio of Mo(VI) to Mo(IV) changed at different temperatures and conditions, as represented in figure 7. The lowest fraction of Mo(VI) was measured after the pretreatment in H₂, whereas under reaction atmosphere the fraction of oxidized species increased, in parallel to the amount of lattice oxygen. The increase of Mo(VI) and lattice oxygen concentrations in the reaction atmosphere as compared to pure hydrogen indicates the formation of small amounts of MoO₃ at the surface during reaction.

Furthermore, the MoS₂ + K catalyst was analyzed by *in situ* XPS in order to obtain information on the effect of K on the Mo and potential intermediates. After pretreatment under 0.75 mbar H₂ at 400 °C, spectra were measured under reaction atmosphere (H₂:CO₂ = 3:1) at 1 mbar and 200 °C. The Mo 3d, S 2p, O 1s, K 2p and C 1s regions are illustrated in figure 8.

No difference in the Mo 3d and S 2p regions was seen compared to pure MoS₂ under reaction conditions. In the O 1s region, the broad adsorbate-related peak observed at 533 eV on the MoS₂ was not detected on MoS₂ + K. We have assigned this peak to the surface OH or formates. Instead, a signal at 532 eV occurred, which was already visible prior to reaction in the absence of CO₂. The peak may originate from carbonate species [28], or from sulfate [29]. Potassium is added as a carbonate in the synthesis and may take up CO₂ upon exposure to the ambient atmosphere. The 532 eV peak is the only adsorbate-related species present under reaction conditions in the O 1s range and changed its intensity with varying conditions indicating its potential involvement in the reaction. No peak characteristic for sulfate was observed in the S 2p region during the reaction.

The interaction between K and CO₂ can be extraordinarily strong, which may lead to the activation of CO₂ (formation of CO₂⁻) and finally its dissociation into carbonate and CO, as proposed by Kiss *et al* [28]. In this case, CO₂ hydrogenation may occur via successive CO hydrogenation. This supports our assumption of different reaction mechanisms occurring in the presence of different promoters.

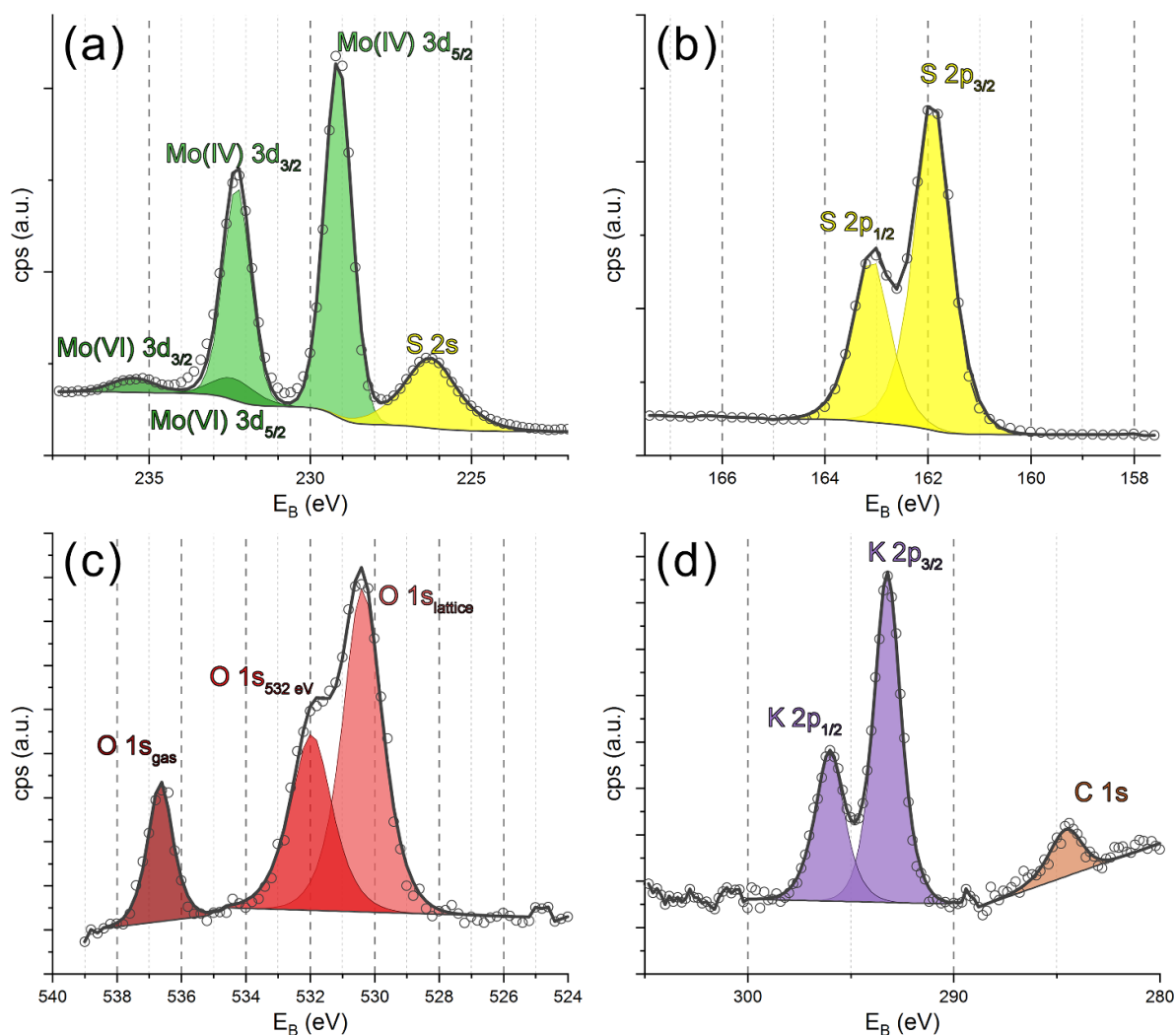


Figure 8. (a) Mo 3d, (b) S 2p, (c) O 1s and (d) K 2p and C 1s in situ XPS spectra of MoS₂ + K at 200 °C in H₂ + CO₂ atmosphere.

4. Conclusion

Promotion of MoS₂ catalysts with different metals changes their catalytic properties. While the main product over pure MoS₂ is CH₄ under the conditions applied, K addition leads to a higher CO and methanol formation.

XRD proved the existence of a MoS₂ phase in all catalysts. K was present as K₂SO₄, Co and Ni as sulfide. In the fresh catalysts, CoS and NiS was found. In comparison, Co₉S₈ and Ni₃S₂ were present in the used catalysts. N₂ physisorption showed a reduction of the BET surface area when K was added. No significant difference was found between CoMoS_x + K, NiMoS_x + K and MoS₂ + K catalysts. Under oxidizing atmosphere, the catalyst is stable below 280 °C. TPR experiments showed no reduction until 700 °C.

In situ XPS showed the formation of small amounts of Mo(VI) species under reaction atmosphere and adsorbed oxygen compounds, most likely surface hydroxyls and formate, in particular, with increasing temperature and thus conversion.

In situ XPS measurements did not show an effect of the K addition on the Mo binding energy. However, the O 1s peak related to adsorbates was found at lower binding energy and was assigned to carbonates, which may indicate a different reaction mechanism as compared to the unpromoted MoS₂.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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