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Published in:
ACS Catalysis

Link to article, DOI:
10.1021/acscatal.1c04767

Publication date:
2022

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Using Transient XAS to Detect Minute Levels of Reversible S-O Exchange at the Active Sites of MoS₂-Based Hydrotreating Catalysts: Effect of Metal Loading, Promotion, Temperature, and Oxygenate Reactant

Abhijeet Gaur,* Matthias Stehle, Marc-André Serrer, Magnus Zingler Stummann, Camille La Fontaine, Valérie Briois, Jan-Dierk Grunwaldt, and Martin Høj*

Cite This: ACS Catal. 2022, 12, 633–647

ABSTRACT: Modulation excitation spectroscopy (MES) coupled with time-resolved X-ray absorption spectroscopy (XAS) was applied to unpromoted and Co-promoted Mo-based hydrotreating catalysts (i.e., Mo and CoMo catalysts) for investigating the minute as well as instantaneous differences in active site composition under the influence of H₂S and H₂O.Transient experiments during alternating sulfur- and water-rich conditions were performed at temperatures between 400 and 500 °C using catalysts with varying Co/Mo metal loadings to study the correlative effect of these factors on the stability of the active sites. For both types of catalysts, the features of the demodulated Mo K-edge spectrum matching the difference spectra of the MoS₂ and MoO₃ references indicate a reversible oxidation–sulfidation process during H₂O/H₂S cycling.In the case of CoMo catalysts with increasing metal loadings, transient XAS at the Mo K- as well as Co K-edge revealed minute levels of S-O exchange at both sulfided Mo and Co sites, although 26 to 47% of the Co was bound as stable CoAl₂O₄, which does not form a bulk sulfide. Thus, even in the presence of multiple Co phases (oxide and sulfide) and a low number of active sites relative to the total number of Mo atoms, transient XAS can successfully detect the changes occurring over both the active Co and Mo sites. Furthermore, the comparison of the amplitude of the demodulated spectra showed that Mo atoms are more prone to S-O exchange with increasing temperature, while Co promotion stabilized the molybdenum sulfide. MES-coupled XAS experiments with 1-propanol performed to evaluate the degree of S-O exchange in the presence of another oxygenate reactant revealed the higher affinity of water toward these sulfided Mo sites as compared to 1-propanol.

KEYWORDS: hydrodeoxygenation, Mo sulfide catalyst, CoMo catalyst, transient XAS, EXAFS, modulation excitation spectroscopy, surface sensitivity

1. INTRODUCTION

Sulfided CoMo, NiMo, and Mo catalysts are industrially used for hydrotreating crude oil due to their moderate costs and inherent sulfur tolerant nature as compared to most reduced metal catalysts.1,2 The catalysts are also active for hydrodeoxygenation (HDO) of bio-oil and oxygenate model compounds, showing promising activity and stability.3-8 Recently, it has been reported that these catalysts are also used industrially for HDO of renewable feeds such as used cooking oil and animal fat.9 Addition of a promoter (Co or Ni) to MoS₂ leads to enhanced deoxygenation activity due to increased formation of coordinatively unsaturated sites.9,10 Furthermore, the state of the active sites is strongly influenced by the H₂O/H₂S ratio. By maintaining the optimal H₂O/H₂S ratio, S-O exchanges that lead to deactivation of active sulfided Mo sites can be avoided. In order to optimize sulfided catalysts for HDO, the influence of H₂S and H₂O were thoroughly investigated experimentally in a previous study, both in terms of HDO activity and catalyst structure.10 The active sites of CoMoS₂ and Ni-MoS₂ catalysts are located at the edges and corners of MoS₂ nanoparticles and, thus, only constitute a small fraction of all Mo atoms in the catalyst.12,13 However, further characterization is needed to unravel the actual structure and composition of the catalytically active sites.

Received: October 15, 2021
Revised: December 5, 2021
Published: December 23, 2021
relevant for HDO, especially under realistic reaction conditions. This requires the use of techniques that are sensitive enough to detect minute changes relative to the bulk MoS₂.¹⁴

Recently, Stummann et al.¹⁵ have investigated these HDO catalysts to study the effect of CoMo loading and support acidity on the product distribution and deoxygenation activity in catalytic hydropyrolysis of biomass. Detailed understanding of the effect of catalyst properties on product selectivity has been obtained by characterizing the calcined oxide precursors with Raman spectroscopy, temperature-programmed desorption of ammonia (NH₃-TPD), and N₂ physiosorption (BET method). Further, the spent catalysts were characterized with electron microscopy (SEM and STEM). It has been shown that by increasing the CoMo loading and/or changing the support acidity, it was possible to decrease the oxygen content in the organic phase while maintaining a high yield.

In another study, Plais et al.¹⁶ have used Co K-edge quick-X-ray absorption spectroscopy (quick-XAS) combined with multivariate analysis to study the sulfidation pathways under a 10% H₂S/H₂ atmosphere for oxidic cobalt species supported on alumina and silica. A transformation of oxidic cobalt species into nanometer-sized CoS₂ particles was observed before the final conversion into nanometer-sized Co₉S₈ particles. It has been concluded that the smaller the size of the Co₉S₈ nanoparticles, the higher the amount of formed CoS₂ after cooling under a sulfiding atmosphere. Further, the quantification of the CoMoS active species has been performed in situ during the sulfidation of a calcined Co-promoted MoS₂-based HDS catalyst by using the column-wise augmented strategy in multivariate curve regression with alternating least square (MCR-ALS) analysis.

For unpromoted and Co/Ni-promoted MoS₂-based HDO catalysts, Dabros et al.⁷ have reported DFT studies, catalytic activity tests, and in situ XAS to provide detailed information on the activity and stability of these catalysts upon variation of the partial pressures of H₂O and H₂S. DFT calculations showed that the active edge of MoS₂ could be stabilized against S-O exchanges by increasing the partial pressure of H₂S or by promotion with either Ni or Co. The evolution of the active sulfide phase of the catalysts and the influence of varying H₂O/H₂S ratios on the catalyst structure have been studied in situ with XAS showing that the catalysts were tolerant toward water and that the active phases were present as small and highly dispersed particles.

Dynamic conditions of temperature, pressure, gas atmosphere, etc., can cause chemical transformation of the catalysts, specifically changes to the surface composition while the bulk structure remains the same. Thus, complementary techniques are required for detailed studies of the structural, electronic, and chemical properties of catalysts under dynamic reaction conditions. X-ray absorption spectroscopy (XAS) is an element-specific technique, and due to the high penetration of hard X-rays through the reactor and the catalyst bed, it can probe the state of a catalyst under working conditions.¹⁷,¹⁸

However, the sensitivity of XAS toward minority species is usually very low, as it is probing the bulk. In such cases, the combination of XAS with modulation excitation spectroscopy (MES) under transient experimental conditions (e.g., type and concentration of reactants or temperature) can be used to separate the spectroscopic signals from active species undergoing transformation from the spectator species.¹⁹ MES is used in combination with a variety of time-resolved spectroscopic techniques such as XAS, X-ray diffraction (XRD), infrared (IR), and Raman spectroscopy,¹⁹–²⁴ MES analysis exclusively provides signals from species responding to the external stimulation, which makes it possible to extract signals from these minority species that are otherwise difficult to observe.¹⁴,²⁴–²⁶ Thus, the combination of XAS with MES²⁷ has been helpful to understand the catalytic process by providing chemical, structural, and electronic insights into the catalysts and other involved species.

In a recent study, Serrer et al.²⁸ have used XAS-coupled MES to study the role of iron in bimetallic Ni–Fe catalysts during CO₂ methanation. By enhancing the surface sensitivity of XAS with MES, it was observed that Fe shows a highly dynamic behavior during CO₂ activation. It was proposed that an Fe⁰ ⇄ Fe²⁺ ⇄ Fe³⁺ redox cycle, highly likely located at the interface between FeOₓ clusters and the surface of the metal particles, promotes CO₂ dissociation during the methanation reaction. Lately, Czioska et al.²⁹ have studied the IrO₂-catalyzed oxygen evolution reaction (OER) at various potentials by employing conventional operando and MES-XAS measurements for understanding the different mechanisms that occur during OER. By using difference spectra and FEFF9 calculations, two different OER modes were assigned that took place in the uncalcined as well as in the calcined samples. MES-XAS unraveled that these modes could be assigned to a modification in the role of oxygen vacancies in the mechanism when switching from low to high OER potentials.

In an earlier work,¹⁴ we have studied a MoS₂-based HDO catalyst by employing XAS-coupled MES where the catalytic system was modulated by periodically alternating between H₂O/H₂ and H₂S/H₂ conditions while the spectra were acquired continuously. By employing MES-XAS for unpromoted as well as Co- and Ni-promoted MoS₂ catalysts, it was concluded that O atoms replace S atoms at the edges of MoS₂ during H₂O exposure. The extent of S-O exchange was reduced for promoted catalysts, indicating the positive effect of promotion on catalytic activity.

In the present work, in order to examine the effect of various factors on the stability and activity of the HDO catalysts, we report a detailed MES coupled time-resolved XAS study on Co promoted and unpromoted MoS₂ catalysts. This study provides an experimental environment for measuring dynamic changes to the active site composition under the influence of H₂S and H₂O or 1-propanol. Co-promoted MoS₂ catalysts having varying metal loadings were investigated at the Co K- and Mo K-edges, and experiments were performed at different temperatures (400, 450, and 500 °C) under H₂O/H₂S or 1-propanol/H₂S cycling to study the effect of temperature, oxygenate reactant, metal loading, and promotion on the stability of the active sites. The obtained results were discussed to explain the changes taking place on catalyst surfaces and also to compare the degree of these changes due to the variation in reaction conditions.

2. EXPERIMENTAL SECTION

2.1. Catalysts Preparation. The catalysts were prepared by incipient wetness impregnation using MgAl₂O₄ (supplied by Haldor Topse) as the support material. The precursors used for the preparation were (NH₄)₀.₅MoO₄·4H₂O (Fluka ≥99.0%) for Mo and Co(NO₃)₂·6H₂O (Fluka ≥98%) for Co. After impregnation with Mo, the catalyst was dried overnight at 110 °C before it was impregnated with Co. The
catalysts were then calcined under an air flow of 1.24–1.30 NL/min technical air (20% O2 in N2) at 500 °C (ramp: 5 °C/min) and holding for 3 h. The calcined catalysts were sieved to 180–355 μm to remove any agglomerates or dust formed during the catalyst preparation. The elemental composition and the specific surface area (BET method) of the calcined CoMo catalysts after impregnation are given in Table 1.

### Table 1. Metal Loading, Co/Mo-Ratio, and Specific Surface Area of the CoMo Catalysts after Calcination

<table>
<thead>
<tr>
<th>Sample</th>
<th>Co loading (wt %)</th>
<th>Mo loading (wt %)</th>
<th>Co/Mo ratio (molar)</th>
<th>Specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoMo 1</td>
<td>0.64</td>
<td>3.4</td>
<td>0.30</td>
<td>60</td>
</tr>
<tr>
<td>CoMo 2</td>
<td>1.49</td>
<td>7.7</td>
<td>0.31</td>
<td>136</td>
</tr>
<tr>
<td>CoMo 3</td>
<td>1.86</td>
<td>10.1</td>
<td>0.31</td>
<td>148</td>
</tr>
</tbody>
</table>

#### 2.2. X-Ray Absorption Spectroscopy (XAS) Data Acquisition

Time-resolved quick-XAS\textsuperscript{30} data were recorded at the ROCK beamline,\textsuperscript{31} SOLEIL synchrotron. For this purpose, the quick-EXAFS (QEXAFS) method with recording XAS data “on the fly”\textsuperscript{30,32} was used based on a cam-driven tilt table on which the channel-cut is installed.\textsuperscript{33} The beamline is equipped with two independent channel-cut monochromators (Si(111) and Si(220)) and a remotely controlled automation for exchanging optics and detectors (Okken ionization chambers).\textsuperscript{34} By this, fast switches between the edge positions of the different metals were facilitated to monitor quasi-simultaneous structural changes in the reactor, i.e., changes at the Mo K-edge and Co K-edge. The oscillation frequency of the monochromators was fixed at 2 Hz, leading to a spectrum acquisition with increasing Bragg angles every 250 ms. Taking advantage of the small beam size of X-rays (typically 0.5 mm (H) × 0.3 mm (V)) at the focusing position at the ROCK beamline, for the MES experiments involving 1-propanol, the spectra were measured alternately at the inlet as well as at the outlet position of the quartz microreactor to compare the state of the catalyst along the fixed bed. For MES experiments involving H2O, spectra were measured at the middle of the catalyst along the outlet position of the quartz microreactor to compare the state of the catalyst during each period are added up, making them detectable. Thereby, periodic changes occurring at identical phase shifts during each period are added up, making them detectable.

$$\mu(E, \Delta \varphi) = \frac{2}{T} \int_{0}^{T} \mu(E, t) \sin\left(\frac{360° \cdot t + \Delta \varphi}{T}\right) dt$$  \hspace{1cm} (1)$$

The phase-resolved spectra were analyzed qualitatively and quantitatively by comparing them to difference spectra of pairs of compounds expected to result from the two alternating reaction conditions.

Extended X-ray absorption fine structure (EXAFS) spectra of the reference compounds MoO3, MoO2, MoS2, CoS2, Co3S4, CoO, CoAl2O4, CoO2, CoAl-LDH, and CoMoO4, were recorded for calibration and analysis purposes. Fourier transformation (FT) of the resulting spectrum from k-space to R-space and theoretical model fitting was performed using the software package IFEFFIT interfaces Athena and Artemis.\textsuperscript{38} Model structures obtained from references, i.e., sulfides and oxides of the corresponding metals, have been used to fit the experimental data in R-space for determining the structural parameters. These parameters include energy shift of the path (ΔE0), change in the half path length (ΔR), amplitude reduction factor (S0²), number of identical paths (N), and relative mean-square displacement of the atoms included in path (Debye–Waller factor, σ²). At the Mo K-edge, EXAFS spectra were fitted in the range of R = 1.0–4.0 Å and k = 2.1–12.4 Å⁻¹. The amplitude reduction factor (S0²), as determined from Mo foil, was fixed at 0.97, and one energy precursor was first dehydrated and then converted to the active sulﬁde form by treating it under a slow rate of 10% H2S/H2 (25–35 NmL/min) and heating to 400 °C with a holding time of 30 min at the target temperature. In the next step, a pneumatic four-way valve was used to perform the MES experiments by cycling between 3% H2O/H2 (1st cycle, 180 s) and 500 ppm H2S/H2 (2nd cycle, 180 s) with a total period of 360 s. XAS spectra for CoMo samples have been recorded in transmission mode using the alternate measurement of Co and Mo K-edges during the in situ sulfidation step. Single edge acquisition was performed during the MES step. For collection and initial processing of the spectra, a graphical user interface (GUI, developed at SOLEIL) dedicated to the data obtained at the ROCK beamline was employed:35 By using the GUI, the data were merged to improve the signal to noise ratio after energy interpolation according to an energy grid specific to each edge. Normalization was performed by defining an absolute energy scale of the maximum of the first derivative of the metal reference foil to the tabulated one, i.e., 20003.9 eV for Mo K- and 7709 eV for Co K-edge.

#### 2.3. Modulation Excitation Spectroscopy (MES) and X-ray Absorption Spectroscopy (XAS) Data Analysis

One MES experiment consisted of 10–15 periods of 6 min each while recording XAS spectra with a frequency of 2 Hz, making a total of 7200 spectra during one run of 60/90 min. To deal with the large amount of data, MES analysis was performed using MatLab scripts where these normalized spectra were first averaged in 10 s intervals to obtain a set of 36 time-resolved spectra. This averaging enhanced the signal-to-noise ratio for detection of small changes during a 360 s period. These time-resolved spectra were transformed into phase-resolved spectra using eq 1, which demodulates the averaged time-resolved series of spectra $\mu(E, t)$\textsuperscript{36,37} into a phase-resolved set $\mu(E, \Delta \varphi)$ by probing with a sine function of period $T = 360$ s and phase shift $\Delta \varphi$, 0° ≤ $\Delta \varphi$ < 360°. Thereby, periodic changes occurring at identical phase shifts during each period are added up, making them detectable.

Figure 1 shows an overview of the different steps performed during MES experiments. The oxide catalyst was dehydrated and then converted to the active sulfide form by treating it under a slow rate of 10% H2S/H2 (25–35 NmL/min) and heating to 400 °C with a holding time of 30 min at the target temperature. In the next step, a pneumatic four-way valve was used to perform the MES experiments by cycling between 3% H2O/H2 (1st cycle, 180 s) and 500 ppm H2S/H2 (2nd cycle, 180 s) with a total period of 360 s. XAS spectra for CoMo samples have been recorded in transmission mode using the alternate measurement of Co and Mo K-edges during the in situ sulfidation step. Single edge acquisition was performed during the MES step. For collection and initial processing of the spectra, a graphical user interface (GUI, developed at SOLEIL) dedicated to the data obtained at the ROCK beamline was employed:35 By using the GUI, the data were merged to improve the signal to noise ratio after energy interpolation according to an energy grid specific to each edge. Normalization was performed by defining an absolute energy scale of the maximum of the first derivative of the metal reference foil to the tabulated one, i.e., 20003.9 eV for Mo K- and 7709 eV for Co K-edge.

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The phase-resolved spectra were analyzed qualitatively and quantitatively by comparing them to difference spectra of pairs of compounds expected to result from the two alternating reaction conditions.

Extended X-ray absorption fine structure (EXAFS) spectra of the reference compounds MoO3, MoO2, MoS2, CoS2, Co3S4, CoO, CoAl2O4, CoO2, CoAl-LDH, and CoMoO4, were recorded for calibration and analysis purposes. Fourier transformation (FT) of the resulting spectrum from k-space to R-space and theoretical model fitting was performed using the software package IFEFFIT interfaces Athena and Artemis.\textsuperscript{38} Model structures obtained from references, i.e., sulfides and oxides of the corresponding metals, have been used to fit the experimental data in R-space for determining the structural parameters. These parameters include energy shift of the path (ΔE0), change in the half path length (ΔR), amplitude reduction factor (S0²), number of identical paths (N), and relative mean-square displacement of the atoms included in path (Debye–Waller factor, σ²). At the Mo K-edge, EXAFS spectra were fitted in the range of R = 1.0–4.0 Å and k = 2.1–12.4 Å⁻¹. The amplitude reduction factor (S0²), as determined from Mo foil, was fixed at 0.97, and one energy
shift parameter \( E_0 \) was defined for all scattering paths. Scattering paths Mo-O, Mo-S, and Mo-Mo obtained from reference models were used and parameters \( N \), \( \Delta R \), and \( \sigma^2 \) were fitted. \( \sigma^2 \) for the Mo-O bond has been fixed to the value as determined from the pre-calcined sample, and \( \sigma^2 \) for the Mo-Mo path has been fixed to the value as determined from \( \text{MoS}_2 \). At the Co K-edge, EXAFS spectra were fitted in the range of \( R = 1.0 - 4.0 \) Å and \( k = 2.8 - 11.5 \) Å\(^{-1} \). The amplitude reduction factor \( S_0^2 \), as determined from Co foil, was fixed at 0.83 and one energy shift parameter \( E_0 \) was defined for all scattering paths. Scattering paths Co-S, Co-Co1, Co-Co2, Co-Al and Co-Mo obtained from reference models were used and parameters \( N \), \( \Delta R \), and \( \sigma^2 \) were fitted.

### Table 2. Structural Parameters Obtained from EXAFS Analysis at the Mo K-Edge for the CoMo Catalysts with Different Metal Loadings

<table>
<thead>
<tr>
<th>sample</th>
<th>scattering paths and obtained fitting parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo-O1</td>
</tr>
<tr>
<td>400 °C H(_2)S</td>
<td>( R ) (Å)</td>
</tr>
<tr>
<td>CoMo 1</td>
<td>1.63 ± 0.09</td>
</tr>
<tr>
<td>CoMo 2</td>
<td>1.60 ± 0.08</td>
</tr>
<tr>
<td>CoMo 3</td>
<td>1.60 ± 0.08</td>
</tr>
</tbody>
</table>

\(^a\)\( S_0^2 \) is fixed to 0.97 as determined by Mo metal foil. \(^b\)Fixed during the fitting.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of Metal Loading and Temperature on the Active Sites of CoMo Catalysts

3.1.1. Active Phase of Mo after In Situ Sulphidation. **Figure 2a** shows the Mo K-edge X-ray absorption near edge structure (XANES) spectra of the CoMo 1 catalyst at room temperature under He (black curve) and after in situ sulphidation at 400 °C under H\(_2\)S (red curve) along with the reference spectra of MoO\(_3\) (blue dashed curve) and MoS\(_2\) (green dashed curve). The formation of the Mo(IV)S\(_2\) phase was confirmed by the complete depletion of the pre-edge peak P, shifting of the edge toward lower energy, and appearance of the feature S at 20,012 eV, *i.e.*, characteristic features observed in the MoS\(_2\) reference spectrum. In the corresponding Fourier transformed (FT) EXAFS spectra shown in **Figure 2b**, the first peak around 2 Å (not phase corrected) shows the presence of Mo-S backscattering similar
to the reference MoS$_2$. The amplitude of this peak is almost half compared to that for bulk MoS$_2$, indicating a decrease in Mo-S coordination, i.e., the presence of vacancies. The second peak, which corresponds to Mo-Mo backscattering, is observed with very low amplitude, indicating a smaller particle size than bulk MoS$_2$. However, the decrease in amplitude of the backscattering contributions in the FT EXAFS spectra is not only correlated to the coordination numbers but also to the structural as well as the thermal disorder. Hence, these changes need to be substantiated by EXAFS fitting. Figure 2c,d shows the Mo K-XANES and FT EXAFS spectra of the in situ-sulfided CoMo samples with different metal loadings, respectively. The XANES features indicate that the degree of sulfidation of the Mo sites in these samples was similar. In the FT EXAFS, comparatively high amplitude of the backscattering peaks is observed for CoMo 1 with the lowest metal loading. The structural parameters determined from fitting the EXAFS for these sulfide samples are given in Table 2, and corresponding fitting curves are given in the Supporting Information, Figure S1.

Mo-S backscattering was observed at $\sim$2.42 Å with CNs of 4.9, 4.8, and 4.7 for CoMo 1, CoMo 2, and CoMo 3, respectively. The Mo-S CN is 6 in the bulk phase, which indicates the presence of a MoS$_2$ phase with sulfur-deficient Mo sites in these catalysts as also reported by earlier studies. A Mo-O contribution at $\sim$1.62 Å with a very low CN of $\sim$0.24 has been explained as interaction with the support with no actual bonding between Mo and O. The Mo-Mo coordination at 3.18–3.19 Å is also in agreement with earlier reported values. However, the CN of Mo-Mo was found to be slightly higher, i.e., 1.3 for CoMo 1 with the lowest metal loading. Thus, it can be concluded that the Mo sulfide phase obtained after in situ sulfidation at 400 °C was similar for the CoMo samples with different metal loadings and complete sulfidation of the Mo oxide phase was achieved in each case, i.e., the bulk phase for MES was MoS$_2$ with sulfur-deficient Mo sites.

3.1.2. Dynamic Changes over Mo Sites during H$_2$O vs H$_2$S Cycling by MES-Coupled XAS. Figure 3a shows 36 time-resolved XANES spectra at Mo K-edge (covering 10 s each) obtained during 3% H$_2$O/H$_2$ (0–180 s) vs 500 ppm H$_2$S/H$_2$ (180–360 s) cycling from averaging 10 periods for the sample CoMo 1. In these spectra, no changes were observed in the intensity and shape of features, which indicates that during H$_2$O/H$_2$S cycling, the bulk sulfide phase of Mo remained intact, as expected. However, the small atomic changes occurring at the edges during cycling conditions could be probed by demodulating the time-resolved spectra into phase-resolved spectra, as given in Figure 3b. For clarity, the demodulated spectra are shown only at selected values of phase shift ($\Delta \phi$). During the demodulation process, the contribution from static species was removed and averaging over 10 periods provided a high signal-to-noise ratio.

As shown in Figure 3c, the features of the demodulated spectrum with the highest amplitude (phase shift $\Delta \phi = 150^\circ$) matched remarkably well to the difference between the spectra of the MoS$_2$ and MoO$_3$ references. This agreement shows that S-O exchange took place on Mo sites during H$_2$O/H$_2$ and H$_2$S/H$_2$ cycling. However, the amplitude of the demodulated spectrum was more than two orders of magnitude (a factor of

Figure 3. (a) Normalized, time-resolved Mo K-edge XANES consisting of a total of 36 spectra covering 10 s each for the CoMo 1 catalyst during 3% H$_2$O/H$_2$ (0–180 s) vs 500 ppm H$_2$S/H$_2$ (180–360 s) cycling and 10 period average. (b) Corresponding demodulated spectra at selected values of phase angle ($\Delta \phi$). (c) Comparison of the (MoS$_2$ – MoO$_3$) difference spectrum (blue dashed line) with the maximum amplitude signal obtained at $\Delta \phi = 150^\circ$ after demodulation (red line) for the CoMo 1 catalyst.
smaller than the difference of the reference spectra, corresponding to a reversible oxidation—sulfidation process for approximately 2–3 Mo atoms for every thousand Mo atoms. Hence, minuscule changes occurring over the Mo sites, which were not possible to detect by conventional XAS, were successfully detected by coupling XAS with MES. Similar cycling experiments were performed for the other two CoMo samples. The time-resolved spectra and corresponding demodulated spectra for CoMo 2 and CoMo 3 are given in the Supporting Information, Figure S2. Figure 4a compares the maximum amplitude obtained for the demodulated spectra at the Mo K-edge, where CoMo1 shows higher amplitude compared to CoMo 2 and CoMo 3, i.e., lower CoMo loading resulted in a higher fraction of Mo sites undergoing S-O exchange. For CoMo 2 and CoMo 3, an almost equal amplitude of the demodulated spectra is obtained, which means a further increase in the metal loading will not affect the fraction of Mo sites prone to S-O exchange. As shown in Figure S2, the maximum amplitude of the demodulated spectra for CoMo 2 was observed at $\Delta \phi = 150^\circ$, similar to that of CoMo1. In contrast, for CoMo 3, it was observed at $\Delta \phi = 120^\circ$. This indicates that with higher metal loading, the changes occurred faster. In another set of MES experiments, the cycling experiments were performed at higher temperatures with CoMo 1, i.e., at 450 and 500 °C, to monitor the effect of temperature on the S-O exchange occurring at the Mo sites of the Co-promoted catalyst. The time-resolved spectra and corresponding
probably due to the lower metal loading. In CoMo 1, the
shown in Figure S4) where in CoMo 1, 65% CoAl2O4 was
CoAl-LDH. The initial oxidized phase of Co is found to be
indicating higher contribution from this phase. This has been
Co3O4. On the other hand, CoMo 2 had 16% CoAl2O4 with
found to be present along with 17% CoAl-LDH and 18%
14% CoAl-LDH and 70% Co3O4, while CoMo 3 had 17%
Co3O4. The FT EXAFS spectra shown in the inset of
Figure 5a also
demonstrated spectra for CoMo 1 at 450 and 500 °C are given
in the Supporting Information, Figure S3. Figure 4b shows that
with increasing temperature, the maximum amplitude
increased. Thus, at higher temperature an increased fraction
of Mo sulfide sites was oxidized under the effect of H2O. This
likely reflects a change in equilibrium toward the oxides at
increasing temperature. The maximum amplitude of demodu-
lated spectra was observed at Δρ = 120° (Figure S3) when
performing MES experiments at 450 and 500 °C, showing that
at higher temperature, the S-O exchange takes place at a faster
rate than MES at 400 °C (Δρ = 150°). The Y-axis of both
Figure 4a,b are kept at same range in order to directly compare
the effect of loading and temperature on S-O exchange for the
Co-promoted MoS2 catalyst. Based on MES-XAS analysis in
the present study, the two factors were observed to act in the
opposite direction, i.e., an increase in metal loading stabilizes
the catalyst against the unwanted S-O exchange, whereas an
increase in temperature makes the catalyst more prone to such
a process.

3.1.3. Active Phase of Co Sites after In Situ Sulphidation.
Figure 5a shows the Co K-edge XANES spectra of the CoMo
catalysts at room temperature under He along with the spectra
of the corresponding LCF analysis performed on CoMo 1 and CoMo 3.
The initial oxidized phase of Co is found to be different in CoMo 1 compared to CoMo 2 and CoMo 3, probably due to the lower metal loading. In CoMo 1, the characteristic features of CoAl2O4 are prominent, thus indicating higher contribution from this phase. This has been confirmed by XANES linear combination fitting (LCF) (shown in Figure S4) where in CoMo 1, 65% CoAl2O4 was found to be present along with 17% Co-Al-LDH and 18% Co3O4. On the other hand, CoMo 2 had 16% CoAl2O4 with 14% Co-Al-LDH and 70% Co3O4, while CoMo 3 had 17% CoAl2O4 with 17% Co-Al-LDH and 66% Co3O4. Thus, CoMo 2 and CoMo 3 had almost the same phase compositions. The hydrotalcite-like phase evolving from Co and Al (Co-Al-LDH) must be present before calcination. During calcination, this Co-Al-LDH phase decomposed into nano Co3O4 and CoAl2O4, but when the catalyst is exposed to air moisture, a part of decomposed LDH can be reformed.

The FT EXAFS spectra shown in the inset of Figure 5a also
indicate a different coordination environment in CoMo 1 as
compared to CoMo 2 and CoMo 3. From EXAFS fitting
results, given in Table 3 and Supporting Information Figure S5,
Co-Al backscattering was observed at 3.45 Å in CoMo 1 in the
higher metal shells, along with Co–Co and Co–Mo. In the case of
CoMo 2 and CoMo 3, only Co-Co and Co-Mo backscattering were observed. However, for all CoMo samples Co-O backscattering was observed at ∼1.93 Å with a CN slightly higher than 4, as expected for a mixture of cobalt species. The large values of the DW factor for metal–metal shells represent the higher disorder in the calcined CoMo samples due to the presence of mixed phases of CoAl2O4, CoAl-LDH, and Co3O4.

Normalized Co K-XANES spectra for the CoMo 2 during in
situ sulphidation are given in Figure 5b. The intensity of pre-edge feature at ∼7710 eV increased, whereas the white line intensity decreased considerably, indicating sulphidation of Co oxide. For comparison, normalized XANES spectra for the CoMo catalysts after in situ sulphidation at 400 °C under H2S are shown in Figure 5c. As expected, differences between the sulphide phases can be observed for the catalysts due to the presence of different oxide phases initially and the incomplete sulphidation of these oxide phases. For confirming the contribution of different phases present in the sulphided catalysts, LCF analysis using probable standards were performed. Figure 5d shows the LCF performed on CoMo 2 using the different reference spectra (c.f., Table 4) where good agreement between the data and fit was observed. The corresponding LCF analysis performed on CoMo 1 and CoMo 3 is given in the Supporting Information, Figure S4.

### Table 3. Structural Parameters Obtained from EXAFS Analysis at the Co K-Edge for the CoMo Catalysts with Different Metal Loadings

<table>
<thead>
<tr>
<th>sample</th>
<th>Co-O1</th>
<th>Co-O1/Co2 (Co3O4)</th>
<th>Co-Al/Co3 (CoAl2O4)</th>
<th>Co-Mo (CoMoO4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT He</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R (Å)</td>
<td>CN</td>
<td>σ² (Å²)</td>
<td>R (Å)</td>
<td>σ² (Å²)</td>
</tr>
<tr>
<td>CoMo 1</td>
<td>1.97</td>
<td>4.2 ± 0.6</td>
<td>0.0055 ± 0.0016</td>
<td>3.01/3.45</td>
</tr>
<tr>
<td>CoMo 2</td>
<td>1.93</td>
<td>4.4 ± 0.4</td>
<td>0.0056 ± 0.0010</td>
<td>3.00/4'</td>
</tr>
<tr>
<td>CoMo 3</td>
<td>1.93</td>
<td>4.4 ± 0.4</td>
<td>0.0053 ± 0.0008</td>
<td>3.00/4'</td>
</tr>
</tbody>
</table>

RT He

<table>
<thead>
<tr>
<th>sample</th>
<th>Co-O1</th>
<th>Co-O1/Co2 (Co3O4)</th>
<th>Co-Al/Co3 (CoAl2O4)</th>
<th>Co-Mo (CoMoO4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R (Å)</td>
<td>CN</td>
<td>σ² (Å²)</td>
<td>R (Å)</td>
<td>σ² (Å²)</td>
</tr>
<tr>
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<td>3.00/4'</td>
</tr>
</tbody>
</table>

**a** S02 is fixed to 0.83 as determined by Co metal foil. *b*Paths taken from Co reference model. *c*Fixed during the fitting.

### Table 4. Linear Combination Fitting Results for the In Situ Sulphided CoMo Catalysts at 400 °C

<table>
<thead>
<tr>
<th>sample</th>
<th>Co3O4</th>
<th>CoAl2O4</th>
<th>CoAl-LDH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoMo 1</td>
<td>65%</td>
<td>17%</td>
<td>18%</td>
</tr>
<tr>
<td>CoMo 2</td>
<td>64%</td>
<td>16%</td>
<td>19%</td>
</tr>
<tr>
<td>CoMo 3</td>
<td>66%</td>
<td>17%</td>
<td>17%</td>
</tr>
</tbody>
</table>

LCF results given in Table 4 confirmed that CoMo 1 (with lowest loading) was least sulphided with 44.2% contribution from Co3O4, due to the relatively larger amount of CoAl2O4, which does not sulphide. CoMo 2 had ~70% contribution from Co sulfide species, whereas CoMo 3 had ~61% with major fraction coming from Co3O4 and minor fraction from CoAl2O4. For all three sulphided CoMo catalysts, contribution from the Co3O4 phase is almost similar (~44%). Thus, partial sulphidation of Co species was observed since cobalt aluminate does not
sulfi de. It is to be mentioned here that the active sulfi de phase for Co-promoted MoS$_2$ catalysts also consists of the CoMoS phase, whose quantification requires rigorous data analysis, which was not attempted here. The small contribution from CoAl-LDH shows the presence of this Co oxide species, which is in agreement with the results reported earlier.

The EXAFS fitting for the sulfi ded CoMo 2 catalysts is given in the Supporting Information, Figure S5, and the fitting results for CoMo 2 are given in Table 3. The first shell had a contribution from Co-O with a CN of 1 (fixed) and Co-S with a CN of 2.6, confirming the presence of mixed phases. In the higher shells, Co-Co backscattering was observed at 3.00 Å. Fitting the EXAFS spectra of the other two sulfi ded CoMo catalysts did not give reasonable parameters, probably due to the higher presence of mixed Co oxide phases. Thus, the bulk phase before MES was a mixture of sulfi de phases of Co and CoAlO$_2$. However, cobalt is expected to be stable as CoAlO$_2$ during the cycling and the advantage of MES is that this phase can be discriminated and only the active sulfi de phase of Co is studied.

3.1.4. Dynamic Changes over Co Sites during H$_2$O vs H$_2$S Cycling by MES-Coupled XAS. Figure 6a shows time-resolved XANES spectra of the sulfi ded CoMo 2 catalyst at the Co K-edge during H$_2$O vs H$_2$S cycling obtained from averaging 10 periods. Again, no changes can be observed in the characteristic features. This shows that Co species did not undergo any major phase transition during cycling conditions as compared with the state obtained after sulfi dation at 400 °C. The corresponding demodulated spectra of the CoMo 2 catalyst during H$_2$O vs H$_2$S cycling are shown in Figure 6b. Strong features can be observed here, which were undetectable in

Figure 6. (a) Normalized, time-resolved Co K-edge XANES consisting of a total of 36 spectra covering 10 s each for the CoMo 2 catalyst during 3% H$_2$O/H$_2$ (0–180 s) vs 500 ppm H$_2$S/H$_2$ (180–360 s) cycling and 10 period average. (b) Corresponding demodulated spectra at selected phase angles ($\Delta$\(\phi\)). (c) Comparison of the (Co$_3$S$_4$ − CoO) and (Co$_9$S$_8$ − CoO) difference spectra (red and blue dashed lines) with the maximum amplitude signal obtained after demodulation (black line) for the catalyst.

Figure 7. Comparison of the maximum amplitude signal obtained after demodulation at the Co K-edge for the (a) CoMo catalysts with different metal loadings and (b) the CoMo 1 catalyst with cycling experiments performed at different temperatures.

sulfi de. It is to be mentioned here that the active sulfi de phase for Co-promoted MoS$_2$ catalysts also consists of the CoMoS phase, whose quantification requires rigorous data analysis, which was not attempted here. The small contribution from CoAl-LDH shows the presence of this Co oxide species, which is in agreement with the results reported earlier.

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time-resolved spectra, indicating that minute changes do occur at Co sites. The maximum amplitude was observed at phase shift \( \Delta \phi = 150^\circ \), which was also the case for MES-XAS at the Mo K-edge, indicating that the changes occur at a similar rate for both Co and Mo sites. These features can be resolved by comparing the demodulated spectrum with the maximum amplitude to the difference spectra of the references, i.e., \((\text{Co}_3\text{S}_4 \text{− CoO})\) and \((\text{Co}_9\text{S}_8 \text{− CoO})\) as shown in Figure 6c.

A good agreement is observed between the demodulated spectrum obtained experimentally and difference spectra from references. Though the shapes look almost same for the two difference spectra, the \((\text{Co}_9\text{S}_8 \text{− CoO})\) spectrum is a bit shifted to lower energy and the \((\text{Co}_3\text{S}_4 \text{− CoO})\) fits better in the white line region. This demonstrates that some Co sulfide sites were oxidized and resulted during H\(_2\)O/H\(_2\) and H\(_2\)S/H\(_2\) cycling, respectively. In addition, difference spectra of Co sulfide references with other Co oxide references, i.e., Co\(_2\)O\(_3\) and Co\(_3\)O\(_4\) were also compared with the demodulated spectrum, but a satisfactory match was not obtained. This indicates that during cycling, the Co sulfide species reversibly transformed into Co\(^{2+}\) oxide species only.

In order to study the effect of metal loading on the reversible oxidation–sulfidation of Co sites, similar transient XAS experiments were performed on the other two catalysts, i.e., CoMo 1 and CoMo 3. The time-resolved spectra and corresponding demodulated spectra at the Co K-edge for CoMo 1 and CoMo 3 are given in the Supporting Information, Figure S6. Figure 7a compares the maximum amplitude of the demodulated spectra obtained for CoMo 1, CoMo 2, and CoMo 3. A higher intensity of the feature at 7725 eV is observed in the case of CoMo 3, indicating an increase in the fraction of Co sites that underwent transformation during cycling with increasing metal loading. For CoMo 1, the maximum amplitude was observed at \( \Delta \phi = 150^\circ \) (Figure S6) similar to that of CoMo 2; however, for CoMo 3, it was observed at \( \Delta \phi = 120^\circ \). This indicates that with higher metal loading, the changes occurred faster also at Co sites, like at Mo sites.

As mentioned earlier, the cycling experiments were performed for CoMo 1 at higher temperatures, i.e., 450 and 500 °C, to monitor the effect of temperature on the transitions occurring at the Mo sites as well as Co sites. The time-resolved spectra and corresponding demodulated spectra at Co K-edge for CoMo 1 at 450 and 500 °C are given in the Supporting Information, Figure S7. Figure 7b shows the comparison of the demodulated spectra at different temperatures. A small increase in the amplitude is observed with increasing temperature; however, this variation in the amplitude was of the order of the spectral noise. At 450 °C, the maximum amplitude was observed at \( \Delta \phi = 120^\circ \) (Figure S7), whereas at 500 °C, this value was observed to be 150°, the same as at 400 °C.

Thus, there is no clear sign that the phase changes occurring at Co sites during cycling were affected by increasing temperature. Hence, the Co sites showed a different behavior compared to the Mo sites where an influence of the temperature was found (Figure 4). Thus, Mo sites were comparatively more affected by the increase in temperature and metal loading than the Co sites, indicating the stable nature of Co sites under these cycling conditions. In a previous study\(^{15}\) on these CoMo samples, by analyzing HAADF-STEM images of spent catalyst samples from 450 °C catalytic
hydrolysis experiments, the mean slab length was found to be between 2.65 and 3.07 nm and the frequency of monolayer slabs was between 94 and 99%, indicating a similar degree of stacking. It was shown that cobalt, molybdenum, and sulfur were well-distributed on the alumina, indicating successful incorporation of the Co into the MoS₂ structure (CoMoS phase). The similar slab lengths, degree of stacking, and formation of the CoMoS phase showed that the catalysts were representative for comparing the effect of the CoMo loading.

Assuming the MoS₂ particles formed upon sulfidation, which are typically 3–4 nm slabs of 1–2 layers, are the same for all CoMo catalysts and hence the ratio of surface to “bulk” Mo atoms should also be the same in this case. A similar size of these MoS₂ particles present in the CoMo catalysts can also be corroborated from the comparable CNs obtained from EXAFS fits (Table 2). Thus, a higher fraction of Mo sites undergoing S-O exchange for CoMo 1 (cf., Figure 4a) is related to the CoMo 1 catalyst having a larger fraction of CoAl₂O₄ than the other two catalysts. This Co will not be available for the promotion of the MoS₂, and hence protection from S-O exchange in the presence of H₂O.

3.2. Effect of Temperature and Promotion in the Demodulated Spectra of Unpromoted Mo Catalyst during H₂O/H₂–H₂S/H₂ Cycling. Figure 8a shows 36 time-resolved XANES spectra at the Mo K-edge (covering 10 s each) during 3% H₂O/H₂ (0−180 s) vs 500 ppm H₂S/H₂ (180−360 s) cycling at 400 °C obtained from averaging 10 periods for the sample Mo. No changes can be detected in these spectra, showing that the bulk phase for MES was MoS₂. This has been confirmed by comparison with the spectra of references and EXAFS fitting results given in the Supporting Information, Figure S8 and Table S1. Corresponding demodulated XANES spectra at 400 °C are shown in Figure 8b, where the expected features indicating minute changes occurring at Mo sites can be clearly observed. The features of the demodulated spectrum with the highest amplitude (phase shift Δϕ = 150°) matched the difference spectrum of the MoS₂ and MoO₃ references, as shown in Figure 8c. This agreement shows that S-O exchange took place on Mo sites during H₂O/H₂ and H₂S/H₂ cycling.

To monitor the effect of temperature on the S-O exchange occurring at the Mo sites of the unpromoted catalyst, MES experiments were also performed at higher temperatures, 450 and 500 °C. The time-resolved spectra and corresponding demodulated spectra at the Mo K-edge for Mo at 450 and 500 °C are given in the Supporting Information, Figure S9. Figure 8d gives a comparison of the maximum amplitude for demodulated spectra obtained at the different temperatures for the unpromoted Mo catalyst. It can be seen that with increasing temperature, the maximum amplitude increased, i.e., 0.0020 at 400 °C, 0.0029 at 450 °C, and 0.0038 at 500 °C. Thus, with an increase of 100 °C, the fraction of Mo sulfide sites undergoing S-O exchange almost doubled, indicating that the unpromoted catalyst will be more prone to such undesired changes at higher temperatures, probably due to the shift of the equilibrium toward the oxide. The maximum amplitude (Figure S9) was observed at Δϕ = 120° in the case of MES experiments at 450 and 500 °C, showing a faster rate at higher temperature, similar to the nature of Mo sites observed in the case of CoMo 1. In Figure 8d, the maximum amplitude demodulated spectrum for the CoMo 2 catalyst at 400 °C (0.0013) is also plotted (dashed curve), which is lower than that of the Mo catalyst at 400 °C, indicating a positive effect of Co promotion. This is in agreement with our previous study, where a decrease in S-O exchange upon promotion has been discussed in detail for Co/Ni-promoted Mo catalysts.

3.3. Comparing the Effect of the Oxygenate Reactant on Demodulated Spectra: H₂O/H₂–H₂S/H₂ vs 1-Propanol/H₂–H₂S/H₂ Cycling. As water is the product of HDO, it is also relevant to perform the MES experiments with an oxygenate reactant instead of water. In the present case, the experiments were limited to gas phase reactants and feeding by bubbling hydrogen through a reservoir of liquid at room temperature. Hence, 1-propanol was chosen as the reactant due to the similar vapor pressure and the same number of oxygen atoms per molecule as water. A primary alcohol is expected to react over the HDO catalysts, forming the corresponding alkene or alkane, here propene or propane, by dehydration and hydrogenation reactions, respectively. Hence, MS traces were measured during the cycling experiments with 1-propanol/H₂–H₂S/H₂.

The MS traces during 1-propanol/H₂–H₂S/H₂ cycling for the Mo catalyst at 400 and 450 °C and for the CoMo 2 catalyst at 400 °C are shown in Figure 9. Conversion of 1-propanol (m/z = 31) to propene (m/z = 41), corrected for the 1-propanol contribution to this mass) and water (m/z = 18) was observed, but propane (m/z = 44) was not detected. Hence, only dehydration and no hydrogenation took place. This is likely due to the low pressure of hydrogen, since the MES experiments were performed at close to atmospheric pressure.
From Figure 9, a deactivation of the catalyst was observed during the first cycles at each temperature as the propene and water signal decreased in maximum intensity (amplitude of the peaks in the 1-propanol/H₂ cycle) and the 1-propanol signal increased in maximum intensity with each period. After about 5−6 periods for the Mo catalyst and 7−8 periods for the CoMo 2, the peak intensity became more or less constant.

With the help of the focused beam (0.5 mm (H) × 0.3 mm (V)) at the ROCK beamline, the spectra were measured alternately at the inlet as well as at the outlet position of the quartz microreactor to compare the state of the catalyst as function of the reactant conversion over the catalyst bed. A higher concentration of the reactant 1-propanol was present at the inlet, while a higher concentration of the products propene and water was present at the outlet due to conversion of 1-propanol.

Demodulated XANES spectra of the unpromoted Mo catalyst at the Mo K-edge during 1-propanol/H₂ (0−180 s) vs 500 ppm H₂S/H₂ (180−360 s) cycling at the (a) inlet and (b) outlet of the quartz microreactor. Comparison of the (MoS₂−MoO₃) difference spectrum (blue dashed line) with the maximum amplitude signal obtained after demodulation (red line) for the catalyst at the (c) inlet and (d) outlet of the microreactor.

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Demodulated XANES spectra of the unpromoted Mo catalyst at the Mo K-edge during 1-propanol vs H₂S cycling at 400 °C are shown in Figure 10a,b, recorded at the inlet and outlet of the quartz microreactor, respectively. Corresponding time-resolved spectra are given in the Supporting Information, Figure S10, where no changes were observed, showing that the bulk phase for MES was MoS₂. The features observed at the inlet of the reactor are stronger and better resolved compared to those observed at the outlet. This could be due to interaction of the catalyst with the formed propene. Figure 10c,d gives the comparison of the features of the demodulated spectrum with the maximum amplitude observed at Δφ = 150° for the inlet and at Δφ = 120° for the outlet, respectively, together with the difference spectrum of the MoS₂ and MoO₃ references. At the inlet, good agreement between the two spectra shows that S-O exchange also occurred on Mo sites during 1-propanol/H₂ and H₂S/H₂ cycling. For the outlet, though the demodulated spectrum features are less resolved, they still show similarity with MoS₂-MoO₃ indicating the S-O exchange, as expected for water and 1-propanol interacting with the catalyst. Also, as observed from values of Δφ for the maximum amplitude, the changes at the outlet occur slightly faster. The demodulated spectra observed in this case showed some deviation from the expected behavior as some of the spectra do not have zero crossing on the Y-axis at the same energy, i.e., no clear isosbestic point can be observed. This can be attributed to different reasons, e.g., that there are more than two species or that different parts of the sample have different reaction rates. The observed deviation is higher at the outlet than at the inlet. As mentioned above, a higher concentration of the products (propene and water) is present at the outlet, which may cause multiple-step transition or different reaction rates leading to dampening of features generally observed in the presence of two different phases.

The cycling experiments with 1-propanol were also performed at 450 °C (both inlet and outlet positions), and results are given in the Supporting Information, Figure S10. As expected, at 450 °C, a comparatively high amplitude of the demodulated spectra, i.e., 0.0020 vs 0.0016 at 400 °C, indicates that with higher temperature, the amount of S-O exchange at Mo sites increased during 1-propanol vs H₂S cycling, like for H₂O vs H₂S cycling. At 450 °C the maximum amplitude was observed at Δφ = 150° (Figure S10) for both the inlet and outlet positions. From the MS traces (Figure 9), it was also observed that the conversion of 1-propanol to propene and water increased significantly, as expected, and the catalyst deactivated further during the first 8−9 cycles at 450 °C.

Similarly, MES experiments were performed with the CoMo 2 catalyst when cycling 1-propanol vs H₂S at the inlet position of the quartz microreactor. The maximum amplitude
Demodulated spectra along with the difference spectra of references at the Mo K-edge and Co K-edge are shown in Figure 11a,b, respectively. Corresponding time-resolved spectra and demodulated spectra are given in the Supporting Information, Figure S11. The changes observed at the Mo as well as Co sites during 1-propanol vs H2S cycling were similar to those observed for this catalyst during H2O vs H2S cycling, i.e., at Mo sites, S-O exchange was observed, and at Co sites, oxidation of the sulﬁde phase was observed. The maximum amplitude of the demodulated spectra was observed at $\Delta \phi = 0^\circ$ at both the Mo and Co K-edges (Figure S11), indicating that maximum changes occurred initially. In the case of CoMo 2, the amplitude of the demodulated spectrum at the Mo K-edge was observed to be quite low (0.0005) as compared to that of the unpromoted Mo sample (0.0016) as shown in Figure 11c. Thus, in the case of propanol, there was an almost 70% decrease in the amplitude due to Co promotion, which is almost double as compared to that in the case of water where a 35% decrease in the amplitude was observed (cf. Figure 8d). This indicates that promotion with Co makes the catalyst comparatively more stable toward S-O exchange for 1-propanol than H2O. In general, for the Mo and CoMo samples, similar trends were observed with H2O and 1-propanol cycling, i.e., high temperature enhances S-O exchange and promotion with Co lowers this effect.

Figure 12 gives the comparison of the maximum amplitude of the demodulated spectra obtained from the two different cycling experiments, H2O vs H2S and 1-propanol vs H2S, at similar temperatures. A higher amplitude was observed with H2O for both the Mo and the CoMo 2 catalysts. Thus, it can be concluded that H2O is more effective for S-O exchange compared to 1-propanol. For the CoMo 2 catalyst, the difference between the amplitude of the demodulated spectra under the influence of two oxygenate reactants was very pronounced at both Mo and Co sites, which indicates that promotion with Co made the catalyst more stable against such processes when induced by a primary alcohol, i.e., 1-propanol.

4. CONCLUSIONS

Modulation excitation spectroscopy coupled with time-resolved X-ray absorption spectroscopy can provide valuable insight and complement to surface science studies by unraveling the minute levels of reversible S-O exchange at the active sites of Co promoted and unpromoted MoS2 hydrotreating catalysts. Due to its more selective and higher sensitive nature compared to conventional XAS, MES coupled XAS showed that the degree of S-O exchange was affected by the metal loading, promotion, temperature, and oxygenate reactant. For CoMo catalysts, increasing the metal loading at 400 °C stabilized the catalyst against the undesired S-O exchange at Mo sites whereas increasing the temperature made the catalyst more prone to such processes. Transient XAS could successfully detect the reversible oxidation/sulﬁdation occurring over sulﬁded Co sites, even in the presence of multiple phases. For the unpromoted Mo catalyst, with an increase of 100 °C (from 400 to 500 °C), the fraction of Mo sulﬁde sites undergoing S-O exchange almost doubled, substantiating the reactive nature of Mo sites. For both CoMo and Mo catalysts, a comparison of cycling experiments using 1-propanol vs H2S with H2O vs H2S showed that H2O
was more effective for S-O exchange than 1-propanol. For the CoMo catalyst, the difference was more pronounced at both Mo and Co sites under 1-propanol cycling as compared to H₂O cycling, which indicated that promotion with Co makes the catalyst more stable against such processes.

Thus, it has been shown that MES coupled with suitable time-resolved spectroscopic measurements can not only resolve the changes taking place on catalyst surfaces but can also evaluate the comparative degree of changes due to the variation in reaction conditions, e.g., temperature and sample composition, i.e., metal loadings. These parameters play important roles in defining the activity and stability of the catalytic system, and hence, such sensitive measurements will be helpful in general to examine catalysts under operando conditions for characterization of the active site on the atomic scale.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c04767.

Additional time-resolved and demodulated XAS data at Mo K- and Co K-edge for CoMo (different metal loadings)/Mo catalysts at different temperatures during H₂O vs H₂S cycling; EXAFS fitting results for calcined and in situ sulfided catalysts at Mo K- and Co K-edge for CoMo/Mo catalysts; LCF results for calcined and in situ sulfided CoMo catalysts at Co K-edge; additional time-resolved and demodulated XAS data at Mo K- and Co K-edges for Mo/CoMo 2 catalysts at different temperatures during 1-propanol vs H₂S cycling at the inlet and outlet positions of the quartz microreactor (PDF).

**AUTHOR INFORMATION**

**Corresponding Authors**

Abhijeet Gaur — Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen D-76344, Germany; Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe D-76131, Germany; orcid.org/0000-0001-5328-9280; Email: abhijeet.gaur@kit.edu, abhijeetgaur9@gmail.com

Martin Høj — Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Kgs. Lyngby DK-2800, Denmark; orcid.org/0000-0002-8482-3359; Email: mh@kt.dtu.dk

**Authors**

Matthias Stehle — Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe D-76131, Germany; orcid.org/0000-0002-7382-5666

Marc-André Serrer — Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen D-76344, Germany; Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe D-76131, Germany

Magnus Zingler Stummann — Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Kgs. Lyngby DK-2800, Denmark; orcid.org/0000-0001-6319-4429

Figure 12. Comparison of the maximum amplitude of the demodulated spectra obtained from the two different cycling experiments H₂O vs H₂S and 1-propanol vs H₂S (inlet position of the quartz microreactor) at the Mo K-edge for (a) Mo at 400 °C, (b) Mo at 450 °C, (c) CoMo 2 at 400 °C, and (d) at the Co K-edge for CoMo 2 at 400 °C.
Camille La Fontaine — SOLEIL Synchrotron, UR1-CNRS, L’Orme des Merisiers, BP48, Gif-sur Yvette F-91129, France
Valérie Brois — SOLEIL Synchrotron, UR1-CNRS, L’Orme des Merisiers, BP48, Gif-sur Yvette F-91129, France
Jan-Dierk Grunwaldt — Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen D-76344, Germany; Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe D-76131, Germany; orcid.org/0000-0003-3606-0956

Complete contact information is available at: https://pubs.acs.org/10.1021/acscatal.1c04767

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work at the ROCK beamline was supported by a public grant overseen by the French National Research Agency (ANR) as part of “Investissements d’Avenir” program (reference: ANR-10-EQPX-45). M.H. thanks DanScatt for funding travels to the SOLEIL synchrotron. We thank HGF for support in the programs “storage and crosslinked infrastructures” (SCI), “science and technology of nanosystems” (STN) and “Materials and Technologies for the Energy Transition” (MTET). We also thank KIT’s synchrotron radiation source (operated by KIT-IBPT) for ex situ XAS measurements conducted at the CAT-ACT beamline.

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