CO Hydrogenation Reaction on Sulfided Molybdenum Catalysts

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ABSTRACT

Adsorption of reaction intermediates appearing during CO hydrogenation at the sulfur covered MoS\textsubscript{2}(10-10) surfaces, Mo-termination with 42\% S coverage and S-termination with 50\% S coverage, are investigated systematically using periodic density functional theory methods. Computed vibrational frequencies of all intermediates are compared with observed data from infrared (IR) spectroscopy allowing a detailed interpretation and assignment of the different features in the experimental spectra. The pathway for CO hydrogenation on both terminations has been studied in detail where the most likely reaction path involves C\textsubscript{1} type surface species in the sequence

\[
\text{CO} \rightarrow \text{CHO} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CH}_2 \rightarrow \text{CH}_3 \rightarrow \text{CH}_4
\]

in agreement with experiment.
1. INTRODUCTION

Sulfided Mo catalysts have been widely used in hydrodesulfurization (HDS) and hydrogenation (HDN) processes and exhibit also high activity for methanation and for the Fischer-Tropsch synthesis of light hydrocarbons from CO hydrogenation [1–7]. In particular, CO hydrogenation on sulfided Mo catalysts has been studied extensively because of the tolerance of these catalysts to sulfur poisoning [2–7]. Using in-situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, Koizumi et al. [8] identified the main products of CO hydrogenation on pure MoS₂ catalyst to be CO₂ and CH₄. However, the modification of the pure MoS₂ surface by alkali promoters yields alcohols instead of hydrocarbons as while additional promoters, such as Ni or Co, are found to increase the selectivity of ethanol and higher alcohols [9–11].

The CO hydrogenation mechanism, involving formation and breaking of C-H, O-H, and C-C bonds, is rather complicated and various reaction schemes have been proposed [12–15] so far. The basic process has been described by reaction steps (1)

\[
\text{CO} + 3\text{H} \rightarrow \text{CHO} + 2\text{H} \rightarrow \text{CH}_2\text{O} + \text{H} \rightarrow \text{CH}_3\text{O} \quad (1)
\]

occurring at the catalyst surface followed by competing steps (2) [16]

- \( \text{CH}_3\text{O} + 2\text{H} \rightarrow \text{CH}_3 + (\text{H}_2\text{O})_{\text{gas}} \) followed by
  \( \text{CH}_3 + \text{H} \rightarrow (\text{CH}_4)_{\text{gas}} \) or by \( \text{CH}_3 + \text{CO} + 3\text{H} \rightarrow (\text{CH}_3\text{CH}_2\text{OH})_{\text{gas}} \) (2a)
- \( \text{CH}_3\text{O} + \text{H} \rightarrow (\text{CH}_3\text{OH})_{\text{gas}} \) (2b)
- \( \text{CH}_3\text{O} + \text{CO} + \text{H} \rightarrow \text{CH}_3\text{COO} + \text{H} \rightarrow (\text{HCOOCH}_3)_{\text{gas}} \) (2c)

producing alcohols (steps (2a), (2b)) or formate (steps (2c), the latter will also form alcohols in subsequent reaction steps). In this context, the existence and details of reaction intermediates have been discussed for a long time but still remain unclear. As examples we mention temperature programmed desorption (TPD) experiments that suggest that formyl (CHO) intermediates are formed at the catalyst surface which, depending on the reaction conditions and the nature of the active sites, may be hydrogenated to yield alcohols or may react to form other hydrocarbons [17–19]. It is also suggested that the primary product is methanol and the methanol could then undergo secondary reactions to produce methane. \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) formation may take place before methanol desorbing from the surface during high-pressure CO hydrogenation. Further, experiments of CO hydrogena-
tion on a sulfided Mo/γ-Al₂O₃ catalyst using in-situ DRIFT spectroscopy show vibrational frequency bands where those at 1590, 1420 and 1385 cm⁻¹ are claimed to indicate surface formate (HCOO), while an additional band at 1470 cm⁻¹ could originate from acetate (CH₃COO), methoxy (CH₃O), or from carbonate (CO₃) species [8]. Despite these experimental efforts theoretical work has been restricted mainly to CO, H₂ adsorption and surface properties of MoS₂ [20−31]. Using a periodic two-sheet model (for the definition of sheets see Sec. 2 below) of the ideal MoS₂(10-10) surface, Cristol et al. [29] found that dissociative H₂ adsorption is endothermic at the Mo terminated sheet with 50% S coverage while it is exothermic for 33% S coverage forming one S-H and one Mo-H group.

Using a periodic single-sheet model, Sun et al. [28] studied H₂ adsorption and dissociation on MoS₂ and NiMoS, and found that homolytic H₂ dissociation to form two S-H groups is thermodynamically preferred over heterolytic dissociation yielding one S-H and one Mo-H group, and the latter is kinetically favored. On the other hand, Bollinger et al. [27] found the most stable hydrogen adsorption to be the formation of two S-H groups on the S edge. By means of IR spectroscopy and applying a two-sheet periodic model Travert et al. [32] reported CO adsorption on sulfided Mo catalysts and compared the results of spectroscopic with theoretical studies. They found that under reductive condition adsorption of one CO molecule at the sulfur edge with about 50% S coverage is the most stable and exothermic by 0.7 eV. They also identified three thermodynamically stable surfaces for different H₂/H₂S pressure ratios which were also studied by Schweiger et al. [24], Bollinger et al. [27], Raybaud et al. [33] and Cristol et al. [34].

While a considerable amount of experimental studies have been carried out, theoretical investigations on CO hydrogenation at the pure MoS₂ surface are still lacking. Recently, Huang and Cho have studied CO hydrogenation at the MoS₂(10-10) surface [35] where they considering two terminations reflecting full Mo metal and full sulfur coverage. They found that the most likely products of CO hydrogenation are CH₄ and CO₂, in agreement with the experiment results [8]. However, according to the studies of Travert et al. [32], Cristol et al. [29,34], Raybaud et al. [33], and Sun et al. [28,36], the two terminations considered by Huang and Cho [35] do not seem to reflect the realistic catalyst. They are not stable for H₂S/H₂ pressure ratios in the range 0.0001 < p(H₂S)/p(H₂) < 10000 [34]. For p(H₂S)/p(H₂) < 0.05 corresponding to the realistic catalytic system the MoS₂(10-10) surface is terminated by Mo metal sheets covered with about 50% sulfur and by S sheets with about
50% sulfur vacancies [28,29,32–34,36] as mentioned above. These terminations have been considered in the present work.

We apply ab initio density functional theory (DFT) methods together with periodic surface models to examine all intermediates of the above described CO hydrogenation reaction steps [16]. We focus on geometric and energetic parameters of the adsorbed species as well as on their vibrational properties in connection with the interpretation of the corresponding experimental data from IR measurements. The intermediates are C \(_1\)-type CH \(_x\), CH \(_x\)OH (x = 0, 1, 2), CH \(_x\)O (x = 1, 2, 3), HCOO and CO\(_3\) which lead to C \(_1\)-type products found over pure MoS\(_2\) catalysts [16]. We also consider C \(_2\)-type intermediates CH\(_3\)COO, CH\(_3\)CO, CH\(_3\)CHO and CH\(_3\)CH\(_2\)O. In addition, possible reaction paths of CO hydrogenation have been explored.

Sec. 2 describes briefly model geometries and computational methods while Sec. 3 presents the theoretical results and discussion. Finally, we summarize our conclusions in Sec. 4.

2. THEORETICAL DETAILS

Clean MoS\(_2\) forms a hexagonal lattice with two elemental units in the elementary cell. The lattice is layer type with weakly coupling MoS\(_2\) sheets oriented along the (0001) direction of the crystal. The orientation of the reactive surface is assumed to be (10-10) [36] where the ideal bulk terminated geometry is described by parallel pairs of MoS\(_2\) sheets perpendicular to the surface (Fig. 1a). Each pair consists of two differently terminated sheets, one of Mo and one of S termination which may offer active sites for catalytic reactions. Theoretical thermodynamic studies on the MoS\(_2\)(10-10) surface at different H\(_2\)S/H\(_2\) exposures [28,29,32–34,36] have shown that under hydrogen-rich conditions i.e.; for H\(_2\)S/H\(_2\) pressure ratios < 0.05 reflecting realistic reaction conditions, the two non-equivalent sheets are both terminated by sulfur, one sulfur atom per surface molybdenum, however, with the surface sulfur positioned differently. Compared with the ideal surface this sulfur reconstructed geometry (Fig. 1b) corresponds to sulfur addition at the initial Mo terminated sheet (denoted T\(_1\) termination) and sulfur depletion at the S terminated sheet (denoted T\(_2\) termination). Lauritsen et al. [37] observed C\(_4\)H\(_2\)S species adsorbed at the brim edge of triangular MoS\(_2\) nanoclusters by scanning tunneling microscopy (STM) and concluded that the brim edge is a new
kind of active site for HDS. However, so far there is no experimental evidence to indicate that CO hydrogenation can also occur at this brim edge. Triangular MoS$_2$ nanoclusters observed by Lauritsen exist usually under H$_2$S rich conditions during the HDS process which is not considered in this work.

The T$_1$ and T$_2$ terminated sheets, including adsorption of reaction intermediates, are examined in separate calculations where supercell model systems with only one sheet termination are used. Here slabs of identical sheets, either T$_1$ or T$_2$ terminated, containing four rows of molybdenum atoms and corresponding rows of sulfur atoms in each slab (Fig. 2a, b) are placed periodically with a separation of 10 Å of vacuum along the (0001) direction. The slabs are repeated periodically along the surface normal (equal to the (10-10) direction) with a vacuum separation of 10 Å between them. Test calculations confirmed that the chosen separation was sufficient to avoid electronic coupling between adjacent slabs. Theoretical studies for the T$_1$ model system have shown [28] that for low H$_2$S/H$_2$ pressure ratios the surface can become more stable thermodynamically if the sulfur concentration at the top is smaller than one S atom per underlying Mo atom. This can be achieved by including surface sulfur vacancies (leaving coordinatively unsaturated molybdenum surface sites) where, assuming H$_2$S/H$_2$ pressure ratios below 0.001, a reasonable value is one vacancy per six surface sulfur atoms corresponding to 42% relative S coverage (100% S coverage corresponds two surface S atoms per Mo atom [33]) at the real MoS$_2$(10-10) surface as sketched in Figs. 1b, 2a. [28] This model geometry, labeled T$_1'$, is described by a sheet supercell with six MoS$_x$ units along the surface edge and will be considered in the following. Adsorption of reaction intermediates at the sheet edges of the T$_1'$ and T$_2$ model systems is considered in corresponding geometry optimizations where the adsorbates and the top-most substrate layers are allowed to relax freely while the two bottom layers of the slabs (Fig. 2) are fixed at the geometry of bulk MoS$_2$.

The electronic structure and equilibrium geometries of the model systems are calculated using the DMol$^3$ program package [38,39] where the generalized gradient corrected functional according to Perdew and Wang (PW91) is employed [40,41]. Extended numerical all-electron basis sets (double-zeta plus polarization, DNP) are used to describe the electronic structure of all atoms in the model systems except molybdenum where the 28-electron core is approximated by an effective core potential (ECP) [42,43] and a DNP basis is used to account for the valence electron structure. All electronic states are determined by calculations including spin polarization for the open shell species.
in gas phase and for appropriate multiplet states of the adsorption systems. As a result of the large supercells the k point integration during the electronic structure calculations is restricted to one k point in the Brillouin zone. Geometry optimizations are performed with a numerical displacement accuracy of the atom centers of $5 \times 10^{-3} \text{ Å}$. Possible transition states (TS) are located by using the complete linear and quadratic synchronous transit (LST, QST) method \[44\] connecting the most stable reactants and products. Corresponding adsorption energies, $E_{\text{ads}}$, are computed from appropriate differences of total energies of supercells of the MoS$_2$ slabs with adsorbates in their equilibrium geometries, $E_{\text{tot}}(\text{slab/ads})$, of the pure MoS$_2$ slabs, $E_{\text{tot}}(\text{slab})$, and of the free adsorbates in gas phase, $E_{\text{tot}}(\text{ads})$, i.e. by

$$E_{\text{ads}} = E_{\text{tot}}(\text{slab/ads}) - E_{\text{tot}}(\text{slab}) - E_{\text{tot}}(\text{ads}) \quad (3)$$

where negative $E_{\text{ads}}$ values correspond to exothermic adsorption while positive $E_{\text{ads}}$ means endothermic adsorption. The adsorption energies (3) are evaluated using total energies $E_{\text{tot}}(\text{ads})$ of the gas phase species in their neutral ground states. This is justified since the corresponding experiments have been carried out at $T = 500$-$700$ K where there is no solvent to provide charges. However, the corresponding adsorbates may become charged at the surface as a result of charge transfer which is accounted for by the selfconsistent treatment of the combined adsorbate-substrate system (slab/ads) in its neutral state.

The present calculations consider periodic slabs where the molecular adsorbates and reactants are added only on one side of the slab. This yields a non-symmetric slab system where in strongly polar systems charge rearrangements may result in large dipole contributions affecting the accuracy of the adsorption energies $E_{\text{ads}}$. This was studied in test calculations for the adsorption of formyl, CHO and formate, HCOO, at the T$_1'$ terminated MoS$_2$ surface employing the Vienna Ab Initio Simulation Package (VASP) \[45,46\] (The DMol$^3$ code does not allow including dipole corrections in a straightforward way.) Dipole corrections were found to contribute to $E_{\text{ads}}$ less than 0.04 eV for CHO and 0.05 eV for HCOO, respectively (2% of $E_{\text{ads}}$ in both cases) which suggests strongly that these corrections can be ignored for the present purpose. The non-symmetric slab system has also been successfully applied by other groups using the DMol$^3$ code in theoretical studies on CO, H$_2$ adsorption, surface properties, and surface reactions at MoS$_2$ surfaces \[28,35,36,47\]. As specific examples, we mention work by Todorova et al. \[47\] on the hydrogenolysis reaction of CH$_3$SH to
CH$_4$ at the MoS$_2$(10-10) surface and by Huang et al. [35] on CO hydrogenation at prefect MoS$_2$(10-10) corresponding to our T$_1$ model.

In addition to geometric and energetic quantities, adsorbate charges $q$ are determined by Mulliken charges summed over all atoms of the adsorbates. (It should be emphasized that all adsorbate charges based on Mulliken populations can be considered only as qualitative guidelines and not taken as quantitative entities of chemical relevance. In particular, they cannot represent formal valence charges.) Further, vibrational frequencies of the adsorbates are calculated following the harmonic approach using Hessian matrices where all substrate centers are fixed and only intra-adsorbate displacements are considered.

The calculations include reactions of the different intermediates of CO hydrogenation at the MoS$_2$(10-10) surface. For a reaction A + B $\rightarrow$ AB we define two different reaction scenarios. First we consider two separate species A, B at the surface which approach and react to form the product AB. This is described by a reaction energy $\Delta E_{\text{sep}}$ with

$$\Delta E_{\text{sep}} = [E_{\text{tot}}(\text{slab/AB}) + E_{\text{tot}}(\text{slab})] - [E_{\text{tot}}(\text{slab/A}) + E_{\text{tot}}(\text{slab/B})], \quad (4)$$

where $E_{\text{tot}}$ are total energies (per unit cell) of the corresponding systems. Second, we consider the two species A, B in a coadsorption geometry where they stabilize at nearby sites followed by a reaction to form AB. This is described by a reaction energy $\Delta E_{\text{coad}}$ with

$$\Delta E_{\text{coad}} = E_{\text{tot}}(\text{slab/AB}) - E_{\text{tot}}(\text{slab/(A+B)coad}) \quad . \quad (5)$$

where $E_{\text{tot}}(\text{slab/(A+B)coad})$ denotes the total energy of the coadsorption system. Obviously, the difference ($\Delta E_{\text{coad}} - \Delta E_{\text{sep}}$) characterizes the interaction between A and B in the coadsorbed state at the surface with negative values for attraction and positive ones for repulsion. In Sec. 3, we will focus on the discussion of results for $\Delta E_{\text{coad}}$.

3. RESULTS AND DISCUSSION

3.1. Adsorption of reaction intermediates
Table 1 lists the computed adsorption energies $E_{\text{ads}}$ and adsorbate charges $q$ of 16 possible intermediates occurring in CO hydrogenation reactions discussed above where stabilization at $T_1'$ and $T_2$ terminated MoS$_2$ model surfaces is considered. As mentioned above, adsorption energies are evaluated using total energies $E_{\text{tot}}(\text{ads})$ of the gas phase species in their neutral ground states where charging like in the presence of a solvent is excluded. In addition, Figs. 3, 4 and 5 show the corresponding equilibrium geometries of the intermediates for both terminations. Here only adsorbate sites and geometries with largest $E_{\text{ads}}$ are included while many more have been evaluated. In addition, for $T_1'$ terminated MoS$_2$ we focus only on adsorption near the coordinatively unsaturated molybdenum surface site which is well accepted to play a major role in the adsorption and activation of the reactants [48–50]. All intermediate adsorbates stabilize at $T_1'$ and $T_2$ terminated MoS$_2$ surfaces resulting in basically two different adsorption geometries where the adsorbate is bound to either one or two molybdenum centers as will be discussed in the following.

3.1.1. **Adsorbed C$_1$H$_x$O$_y$ species**

Extended optimizations of formyl, CHO, at the MoS$_2$ model surface yield for $T_1'$ and $T_2$ termination three different local energy minima each where those of the most stable states for each termination are shown by their equilibrium geometries in Fig. 3a. Here the CO part is always found to bridge two adjacent molybdenum centers resulting in $E_{\text{ads}}$ of -2.01 eV ($T_1'$) and -1.98 eV ($T_2$) (Table 1a). Further, the C-O bond of the adsorbate is activated compared with free CHO increasing its C-O bond length from 1.19 Å to 1.25 ($T_1'$) and 1.26 Å ($T_2$), respectively. Such C-O distance increase has also been obtained for COH, CH$_2$O, CH$_3$O, CHOH and CH$_2$OH (see below), where the effect is smallest for COH adsorbed at $T_2$ terminated MoS$_2$. The latter is explained by the fact that the adsorbate binds only with its carbon end to one Mo substrate atom (Fig. 3b), affecting the C-O bond only little. For hydroxy carbine, COH, two different local energy minima are obtained for $T_1'$ and one for $T_2$ terminated MoS$_2$ surface. Here the most stable adsorbate geometry for $T_1'$ yields the carbon end of the adsorbate binding to two adjacent 5-fold coordinated molybdenum centers (Fig. 3b top), while at $T_2$ termination the carbon end binds only with one Mo center. Consequently, the corresponding $E_{\text{ads}}$ differ substantially, -3.49 eV for $T_1'$ and -2.71 eV for $T_2$; revealing that COH prefers adsorption at $T_1'$ terminated MoS$_2$ surface over $T_2$. 
Geometry optimizations hydroxy methine, \textbf{CHOH}, at the MoS$_2$ model surface yield for T$_1$' and T$_2$ termination two different local energy minima each where those of lowest total energy for each termination are shown by their equilibrium geometries (Fig. 3c). In both cases the adsorbate is found to bridge two adjacent molybdenum centers with its carbon center which accounts for $E_{\text{ads}}$ of -2.60 eV (T$_1$') and -2.61 eV (T$_2$) (Table 1a). This indicates very similar adsorbate binding for both surface terminations. The most stable adsorption geometries of the formaldehyde species, \textbf{CH$_2$O}, at the two differently terminated MoS$_2$ surfaces (of three local equilibrium geometries found for each termination) are sketched in Fig. 3d. While the $E_{\text{ads}}$ at both sites are almost identical, -0.50 eV (T$_1$') and -0.52 eV (T$_2$) (Table 1a), the binding mechanisms are rather different. For T$_1$' termination the CO part of the adsorbate bridges two adjacent molybdenum centers whereas at T$_2$ terminated surface the molecule binds with its CO part to only one center yielding a 6-fold coordinated Mo species. The calculated $E_{\text{ads}}$ value for CH$_2$O is found to be the smallest amongst all C$_x$H$_y$O$_z$ species considered. In addition, the adsorbate charge of CH$_2$O is very close to zero (Table 1), yielding an almost neutral species. These results are obvious since CH$_2$O forms a stable closed-shell molecule interacting more weakly with the substrate compared with the other C$_x$H$_y$O$_z$ species which represent highly reactive species. Weak adsorptive binding of CH$_2$O has also been observed on other substrates like e. g. the Pt(111) surface [51].

The most stable adsorption geometries of hydroxy methylen, \textbf{CH$_2$OH}, at the two MoS$_2$ surfaces (of two local equilibrium geometries found for each termination) are sketched in Fig. 3e. Here the adsorbate binding geometry is rather similar with the case of CH$_2$O. For T$_1$' termination the CO part of the adsorbate bridges two adjacent molybdenum centers whereas at T$_2$ terminated surface the molecule binds with its CO part to only one center yielding a 6-fold coordinated Mo species. The calculations yield $E_{\text{ads}}$ of -1.99 eV (T$_1$') and -1.53 eV (T$_2$) (Table 1a), suggesting stronger binding for T$_1$' compared with T$_2$ termination.

Methoxy, \textbf{CH$_3$O}, stabilizes at T$_1$' and T$_2$ terminated MoS$_2$ surfaces with most favorable adsorption geometries that are similar. Here the oxygen end of the adsorbate binds between two adjacent molybdenum centers (Fig. 3f, two local equilibrium geometries for each termination are found). As for CH$_2$OH, binding is weaker at T$_2$ compared with T$_1$' terminated surface yielding $E_{\text{ads}}$ of -3.20 eV (T$_1$') and -2.67 eV (T$_2$), respectively. Adsorption of formate, \textbf{HCOO}, and carbonate, \textbf{CO$_3$}, species, although not appearing in reaction steps (1) and (2a-c), is also considered for completeness.
Both species result in most stable adsorption geometries with oxygen of the corresponding OCO part bridging two adjacent molybdenum centers of the substrate, independent of the termination (Fig. 4a, b). The $E_{\text{ads}}$ for HCOO, -2.95 eV ($T_1'$) and -2.90 eV ($T_2$), differ only slightly between the terminations while for CO$_3$ the difference between the $E_{\text{ads}}$ values, -3.95 eV ($T_1'$) and -4.25 eV ($T_2$), is larger, suggesting weaker binding for $T_1'$ compared with $T_2$ termination. The $E_{\text{ads}}$ for CO$_3$ is the largest amongst all adsorbates considered in this study. This shows that this adsorbate is very strongly binding with the substrate where ionic contributions become important. The latter is confirmed by the relatively large negative charge of -0.6 to -0.7 calculated for the adsorbate (Table 1). Interestingly, the two C-O distances of the OCO part, common to both adsorbates, are not changed by the adsorption (i.e. distance differences are below 0.01 Å). This suggests that the OCO part is almost inert and cannot be activated easily.

3.1.2. Adsorbed C$_2$H$_x$O$_y$ species

Geometry optimizations of acetyl, CH$_3$CO, at the MoS$_2$ model surface yield for $T_1'$ and $T_2$ termination two different local energy minima each where those of lowest total energy for each termination are shown by their equilibrium geometries in Fig. 4c. In both cases the CO part of the adsorbate is found to bridge two adjacent molybdenum centers resulting in $E_{\text{ads}}$ of -1.98 eV ($T_1'$) and -2.03 eV ($T_2$) (Table 1b), indicating very similar adsorbate binding for both surface terminations. For both terminations the C-O distance of free CH$_3$CO is increased from 1.19 to 1.25 Å in the adsorbed state which can be understood as an adsorption-induced activation of the C-O bond in CH$_3$CO. The most stable adsorption geometries of acetaldehyde, CH$_3$CHO, at the two differently terminated MoS$_2$ surfaces are shown in Fig. 4d. Obviously, the resulting binding scheme is similar in both cases: CH$_3$CHO binds with its oxygen tail at one molybdenum atom. This yields quite small $E_{\text{ads}}$ of -0.40 eV ($T_1'$) and -0.34 eV ($T_2$) (Table 1b), which are the smallest amongst all C$_2$H$_x$O$_y$ species considered in the present work. This is, in analogy with the previous result for CH$_2$O, explained by CH$_3$CHO forming a stable closed-shell molecule which, therefore, interacts weakly with the substrate. The C-O distance in free CH$_3$CHO is increased by only 0.02 Å due to adsorption at $T_1'$ or $T_2$ terminated surface. This can be understood, analogous to the findings for COH, by the fact that CH$_3$CHO binds only with its carbon end to one Mo substrate atom (Fig. 4d), influencing the
C-O bond only little. CH$_3$CHO species has been identified by temperature programmed desorption (TPD) measurements in CO hydrogenation on Co/Cu-based catalyst [18,19].

Ethoxy, CH$_3$CH$_2$O, stabilizes at T$_1'$ and T$_2$ terminated MoS$_2$ surfaces with most favorable adsorption geometries, are also similar. The oxygen tail of the adsorbate binds in both cases between two adjacent molybdenum centers (Fig. 4e). Here binding is stronger at T$_1'$ compared with T$_2$ terminated surface with $E_{\text{ads}}$ of -3.16 eV (T$_1'$) and -2.67 eV (T$_2$), respectively. Finally, acetate, CH$_3$COO, leads to most stable adsorption geometries with oxygen of the corresponding OCO part bridging two adjacent molybdenum centers of the substrate, independent of the termination (Fig. 4f). The $E_{\text{ads}}$ amount to -2.87 eV (T$_1'$) and -2.73 eV (T$_2$), respectively, which yields a slight energetic preference for T$_1'$ termination of the MoS$_2$ surface. As for HCOO and CO$_3$ discussed above, the two C-O distances of the OCO part of CH$_3$COO are not affected by adsorption suggesting that the OCO part of the adsorbate cannot be activated easily.

### 3.1.3. Adsorbed CH$_x$ and OH$_x$ species

Atomic carbon was found to adsorb at both the T$_1'$ and T$_2$ terminated MoS$_2$ surfaces bridging two adjacent molybdenum centers and coupling with the nearest sulfur center, see Fig. 5a, and forming fairly strong bonds as indicated by $E_{\text{ads}}$ values of -5.40 (T$_1'$) and -5.56 eV (T$_2$). Both CH and CH$_2$ adsorbates exhibit the most stable adsorption geometries also with carbon bridging two adjacent molybdenum sites by strong adsorption bonds, see Fig. 5b, c. In addition, CH couples with the nearest sulfur center, analogous to atomic carbon, whereas CH$_2$ binds only with molybdenum centers. The computed adsorption energies $E_{\text{ads}}$ are -5.73 (T$_1'$) and -6.03 eV (T$_2$) for CH while they amount to -4.26 (T$_1'$) and -4.41 eV (T$_2$) for CH$_2$. The most stable adsorbate geometry for CH$_3$ yields the carbon end of the adsorbate binding to only one molybdenum center such that the carbon is 4-fold coordinated in a distorted tetrahedral environment, see Fig. 5d. In this geometry the adsorption bond is relatively weak leading to $E_{\text{ads}}$ values of -1.71 (T$_1'$) and -1.59 eV (T$_2$), respectively. Finally, atomic oxygen and OH are also found to stabilize at both the T$_1'$ and T$_2$ terminated MoS$_2$ surfaces where the oxygen bridges two adjacent molybdenum centers. The computed adsorption energies $E_{\text{ads}}$ amount to -5.43 (T$_1'$) and -5.17 eV (T$_2$), respectively, for atomic oxygen and to -3.86 (T$_1'$) and -3.49 eV (T$_2$) for OH.
3.2. Vibrational properties of reaction intermediates

Koizumi et al. [8] examined CO hydrogenation at unpromoted MoS$_2$/$\gamma$-Al$_2$O$_3$ catalysts using in situ DRIFT spectroscopy and observed six different peaks at 2060 cm$^{-1}$, 2010 cm$^{-1}$, 1590 cm$^{-1}$, 1470 cm$^{-1}$, 1420 cm$^{-1}$, and 1385 cm$^{-1}$. The peaks at 2060 cm$^{-1}$ and 2010 cm$^{-1}$ were attributed to CO adsorption and also confirmed by separate experiments and calculations [32]. Here we restrict ourselves to the peak region between 1280 and 1600 cm$^{-1}$ ignoring CHx and OH vibrations which lie outside this frequency range. All the other reaction intermediates are examined in their vibrational behavior by corresponding normal mode analyses in the adsorbed state. Characteristic frequencies for each adsorbate at the T$_1$' and T$_2$ terminated MoS$_2$(10-10) surfaces are listed in Table 2 where the calculated values are restricted to a range between 1280 and 1600 cm$^{-1}$ reflecting the experimental range considered in the DRIFT experiments for an MoS$_2$/$\gamma$-Al$_2$O$_3$ catalyst [8]. In addition, Table 3 compares the computed vibrational frequencies of the adsorbates with the experimental DRIFT data [8] where vibrations of the different adsorbates in a given frequency range are combined for the comparison with experimental peaks (given by their peak center). The comparison confirms most of the experimental assignments by theory but yield also additional information from the calculations.

The calculations yield vibrations for the four adsorbates CHOH, COH, CHO and CH$_3$CO in the frequency range between 1286 and 1336 cm$^{-1}$ which could explain the rather weak structure in the experimental infrared spectrum slightly above 1300 cm$^{-1}$. Further, the experimental spectrum shows two broadened peaks with additional structure between 1370 and 1400 cm$^{-1}$ where the peak at lower frequency near 1385 cm$^{-1}$ was assigned [8] to formate, HCOO, while the higher peak was not identified. In the calculations the frequency region between 1349 and 1403 cm$^{-1}$ accommodates vibrational excitations from five different adsorbates listed in Table 3. This includes HCOO at 1374 (T$_1$') and 1372 cm$^{-1}$ (T$_2$) (Table 2), which is consistent with the previous interpretation of the experimental lower peak. In addition, the higher experimental peak near 1395 cm$^{-1}$ is assigned in the calculations to a combination of the four CH$_3$ containing adsorbates CH$_3$CO, CH$_3$CHO, CH$_3$COO and CH$_3$CH$_2$O where the relative importance of the difference species can be determined only in separate experiments.

There is an additional structure between 1415 and 1440 cm$^{-1}$ in the experimental spectrum
where lower end at 1420 cm\(^{-1}\) was assigned \([8]\) also to HCOO. The latter cannot be confirmed by the present calculations. The experimental frequency range between 1413 and 1443 cm\(^{-1}\) is described in the calculations by vibrations of the six CH\(_2\) and CH\(_3\) containing adsorbates CH\(_2\)O, CH\(_2\)OH, CH\(_3\)O, CH\(_3\)CO, CH\(_3\)CHO and CH\(_3\)COO (Table 3), with no contribution from formate. The peak region near 1470 cm\(^{-1}\) in the experimental spectrum was assigned \([8]\) to vibrations of the three adsorbates CH\(_3\)COO, CH\(_3\)O and CO\(_3\). This is only partly compatible with our computed results where the experimental frequency range between 1447 and 1488 cm\(^{-1}\) is covered by vibrations of the six adsorbates CH\(_3\)COO, CH\(_3\)O, CHO, COH, CH\(_3\)CO and CH\(_3\)CH\(_2\)O (Table 3), with CO\(_3\) missing. Instead, vibrations of adsorbed CO\(_3\) are calculated to yield frequencies of 1747 cm\(^{-1}\) (T\(_1\prime\)) and 1744 cm\(^{-1}\) (T\(_2\)) (Table 2), where there is no clear structure in the experimental spectrum. This may indicate that carbonate species do not appear in the CO hydrogenation experiment under the conditions described in Ref. \([8]\) (Note that vibrations of adsorbed bridging CO\(_3\) on Pt catalysts have been measured to yield 1725 cm\(^{-1}\) \([52]\).) Finally, the experimental spectrum shows a broad asymmetric peak between 1560 and 1600 cm\(^{-1}\) where a frequency of 1590 cm\(^{-1}\) was assigned \([8]\) to vibrations of the HCOO. This is confirmed by the calculations which yield HCOO vibrations at 1535 and 1562 cm\(^{-1}\) giving further evidence that the formate adsorbate appears in the CO hydrogenation experiment described in Ref. \([8]\).

### 3.3. CO hydrogenation at the MoS\(_2\) surface

CO hydrogenation on pure MoS\(_2\) is found to yield mainly C\(_1\) type products. Therefore, we focus in the following on reaction steps producing C\(_1\) species. Corresponding reaction energies, \(\Delta E_{\text{coad}}\) and \(\Delta E_{\text{sep}}\), as well as activation energies \(E_a\), involving all reaction intermediates discussed in Sec. 3.1 have been evaluated and are listed in Table 4. Figs. 6, 7 sketch calculated geometric structures of the optimized reactants, transition states, and products at the T\(_1\prime\) and T\(_2\) terminated MoS\(_2\) surfaces for the most favorable reaction paths each. Further, Fig. 8 shows corresponding energetic reaction schemes based on the results of Table 4 where the most favorable reaction path is highlighted by thick lines. Overall, the results in Table 4 show that reaction energies starting from completely separated surface species, \(\Delta E_{\text{sep}}\) of definition (4), and from coadsorbed nearby species, \(\Delta E_{\text{coad}}\) of definition (5), yield the same trends. (The same conclusions have been arrived at in studies on the
dehydrogenation of methanol over Pt (111) surface [51].) They quantify thermodynamic reaction properties and are used in the following to characterize relative thermodynamic reaction probabilities (only $\Delta E_{\text{coad}}$ values will be mentioned). In contrast, the energy barriers $E_a$, given in Table 4 and discussed in the following, characterize kinetic probabilities of corresponding reactions. It should be emphasized that our reaction studies are always based on Langmuir-Hinshelwood [53] type reaction schemes (which may also be connected with hydrogen spillover [28,31]) where only adsorbed species are considered and additional adsorption/desorption processes are ignored.

3.3.1. Initial reaction of CO with hydrogen

Fig. 6a shows that coadsorption of CO and H at the $T_1'$ terminated MoS$_2$ edge yields CO adsorbed near the 5-fold Mo site with H at the nearby top S site. Starting from this coadsorption, CHO formation is more favorable than COH both kinetically ($E_a = 1.45$ vs. 1.75 eV) and thermodynamically ($\Delta E_{\text{coad}} = 0.36$ vs. 0.79 eV), see Table 4. Subsequent dissociation of adsorbed CHO to yield CH and O is connected with a barrier of 1.46 eV and is endothermic by 0.80 eV. Obviously, CHO will be the first intermediate of CO reacting with hydrogen. The same qualitative results, with, however, larger barriers are found for the $T_2$ terminated MoS$_2$ edge, see Fig. 7a.

The CHO adsorbate may react with another hydrogen adsorbate to form CH$_2$O or CHOH surface species. The coadsorbate geometry at the $T_1'$ terminated MoS$_2$ edge yields CHO assuming the geometry of the previous hydrogenation reaction and the hydrogen stabilizing at a nearby top S site, either close to the carbon or close to the oxygen of the CHO adsorbate. While two coadsorbate configurations are close in energy the first geometry leads to CH$_2$O as a reaction product as shown in Fig. 6b while the latter results in CHOH. Here CH$_2$O formation is more favorable than CHOH both kinetically ($E_a = 0.79$ vs. 1.06 eV) and thermodynamically ($\Delta E_{\text{coad}} = -0.48$ vs. 0.00 eV). Subsequent dissociation of adsorbed CH$_2$O into CH$_2$ and O is connected with a barrier of 1.47 eV and is exothermic by -0.28 eV. The same qualitative results, with, however, larger barriers are found for the $T_2$ terminated MoS$_2$ edge, see Fig. 7b. Thus the second intermediate for CO hydrogenation will be CH$_2$O.

The CH$_2$O adsorbate can react with another hydrogen adsorbate to form CH$_3$OH or CH$_3$O
surface species. As before the coadsorbate geometry at the T$_1$' terminated MoS$_2$ edge allows for hydrogen stabilizing at a top S site, either close to the carbon or close to the oxygen of the CH$_2$O adsorbate where the two configurations are close in energy. Here the first geometry leads to CH$_3$O as a reaction product as illustrated in Fig. 6c while the latter results in CH$_2$OH. The numerical results in Table 4 show that both CH$_2$OH and CH$_3$O formation are favorable thermodynamically ($\Delta$$E_{\text{coad}}$ = -0.52 vs. -1.36 eV) where the former is kinetically more favorable ($E_a$ = 0.88 vs. 1.60 eV). Subsequent dissociation of adsorbed CH$_2$OH into CH$_2$ and OH is connected with a barrier of 0.95 eV and is exothermic by -0.29 eV. On the other hand, CH$_3$O dissociation into surface CH$_3$ and O is neither kinetically ($E_a$ = 2.59 eV) nor thermodynamically feasible ($\Delta$$E_{\text{coad}}$ = 1.35 eV). Altogether, the dissociation of adsorbed CH$_2$OH into CH$_2$ and OH is more likely to happen. As another competing step, CH$_2$OH may react with surface hydrogen to form CH$_3$OH. However, our calculations show that the hydrogenation of CH$_2$OH, while gaining more energy than the dissociation, is less likely to occur due to its reaction barrier, 1.26 eV, see Table 4, which is higher than that of the dissociation process, 0.95 eV. Qualitatively similar results are found for the T$_2$ terminated MoS$_2$ edge, see Fig. 7c. Thus the third intermediate for CO hydrogenation will be CH$_2$OH followed by cleavage of its C-O bond.

### 3.3.2. Reaction of CH$_2$ with hydrogen

As discussed above, CO hydrogenation at the MoS$_2$(10-10) surface will yield, amongst other products, surface CH$_2$. This species can react further with adsorbed hydrogen yielding CH$_4$ in two reaction steps. The coadsorbate geometry at the T$_1$' edge yields CH$_2$ bridging two Mo centers and the hydrogen stabilizing at a nearby top S site. This leads to adsorbed CH$_3$ as a reaction product as shown in Fig. 6d where the reaction is exothermic ($\Delta$$E_{\text{coad}}$ = -0.20 eV) and connected with a moderate barrier of $E_a$ = 0.97 eV. In a subsequent reaction the adsorbed CH$_3$ can combine with another hydrogen to produce CH$_4$ where the reaction is strongly exothermic ($\Delta$$E_{\text{coad}}$ = -1.26 eV) and connected with a barrier of only $E_a$ = 0.53 eV. For comparison, adsorbed CH$_3$ reacting with surface OH to form CH$_3$OH is found to yield a rather high barrier, $E_a$ = 1.68 eV, and is much less exothermic, $\Delta$$E_{\text{coad}}$ = -0.38 eV, than CH$_4$ formation. The same qualitative results are found for the T$_2$ terminated MoS$_2$ edge, see Fig. 7d. Altogether, the calculations show that CH$_2$ reacting with hydrogen at the MoS$_2$(10-10) surface to form adsorbed CH$_4$ is a very likely process. The resulting CH$_4$ species can
be assumed to bind very weakly with the surface and may easily desorb.

3.3.3. Optimized reaction paths

Fig. 8 shows energetic reaction schemes for sequential CO hydrogenation at the MoS$_2$(10-10) surface for both T$_1$' (Fig. 8a) and T$_2$ edges (Fig. 8b) which consider all reaction steps discussed above where reaction intermediates and products are assumed in their adsorbed states at the surface resulting in Langmuir-Hinshelwood type reactions. This yields optimized reaction paths combining energetically lowest reaction intermediates and lowest reaction barriers which are highlighted by thick lines in Fig. 8. Obviously, the most favorable reaction path is qualitatively the same for both terminations and involves C$_1$ type surface species in the sequence

$$\text{CO} \rightarrow \text{CHO} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CH}_2 \rightarrow \text{CH}_3 \rightarrow \text{CH}_4 \quad (6)$$

This pathway is consistent with experimental findings [8] but disagrees in some details with recent theoretical studies [35] where the MoS$_2$(10-10) surface was modeled with pure Mo metal and pure sulfur termination. The authors find for the pure Mo metal termination that both adsorbed CHO and CH$_2$O species can dissociate breaking its C-O bond in an exothermic reaction with a rather low barrier. (The corresponding $E_a$ and $\Delta E_{\text{coid}}$ values are included in Table 4.) This misses the reaction intermediates CH$_2$OH and CH$_3$O found in the present study and leads to a shortened reaction path which involves C$_1$ type surface species in the sequence

$$\text{CO} \rightarrow \text{CHO} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CH}_3 \rightarrow \text{CH}_4 \quad . \quad (7)$$

The discrepancy is most likely due to the different MoS$_2$ surface terminations considered Ref. [35] as compared to the present study where the present surface terminations are believed to be more realistic. It should be noted that on both the sulfur covered and the pure metal surface, formyl (CHO) is the first intermediate for the activation of CO. Surface formyl is also found as the most important intermediate in Fischer-Tropsch process on metal surfaces [54] and in the reforming of CO$_2$ to methane on Ni surfaces [55].
4. CONCLUSIONS

The present theoretical studies give a clear account of the adsorption of reaction intermediates appearing during CO hydrogenation at the sulfur covered MoS$_2$(10-10) surface as well as of the elementary reaction steps. Periodic density functional theory calculations using the generalized gradient corrected functional due to Perdew and Wang [40,41] provide adsorption energies of the different adsorbates. The results, considering two different surface terminations of MoS$_2$(10-10), show highly localized strong adsorbate - molybdenum interaction for all (slightly charged) adsorbates with adsorption energies ranging between -1.6 eV and -6.0 eV. Adsorption of the (neutral) molecular reaction intermediates CH$_2$O and CH$_3$CHO is found to be much weaker yielding adsorption energies $E_{\text{ads}}$ of -0.5 eV and -0.4 eV, respectively.

The reaction intermediates C$_{1}$H$_{x}$O$_{y}$ and C$_{2}$H$_{x}$O$_{y}$ are examined in their vibrational behavior by corresponding normal mode analyses in the adsorbed state. A comparison of the computed vibrational frequencies with experimental data from measurements applying infrared (DRIFT) spectroscopy to a MoS$_2$/γ-Al$_2$O$_3$ catalyst [8] confirms most of the experimental assignments but yields also new information. In particular, the frequency analyses give clear evidence that formate species, HCOO, appears in the CO hydrogenation experiment under the conditions described in Ref. [8] while they suggest that carbonate species, CO$_3$, may not participate in the reaction. More detailed information can be obtained only after experimental spectra with higher resolution have been carried out in CO hydrogenation experiments under well defined conditions where additional measurements are performed to identify possible reaction intermediates.

Further, systematic density-functional theory studies on possible reaction steps during CO hydrogenation at the sulfur covered MoS$_2$(10-10) surface are used to identify optimized reaction paths which are found to involve C$_{1}$ type surface species in the sequence

$$\text{CO} \rightarrow \text{CHO} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CH}_2 \rightarrow \text{CH}_3 \rightarrow \text{CH}_4$$

In particular, the dissociation of adsorbed CH$_2$OH results in CH$_2$ and OH products where CH$_2$ can react further to form CH$_4$. In addition, surface OH formed during the reactions may dissociate into adsorbed O and H or react with hydrogen to form water species undergoing a water-gas-shift reaction. These processes merit a separate discussion which goes beyond the scope of the present work.
and will be considered in a subsequent study. The above pathway is consistent with experimental findings [8] but disagrees in some details with recent theoretical studies [35] where the MoS$_2$(10-10) surface was modeled with pure Mo metal and pure sulfur termination. The disagreement is most likely due to differences in the MoS$_2$ surface terminations considered in the studies. The present results cannot confirm the existence of formate, HCOO, intermediates found in the experiment [8]. This may be explained by the fact that in CO hydrogenation experiments on MoS$_2$ catalysts there is always a high probability of the water-gas shift reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$, occurring in parallel. The latter is bond to produce formate as a reaction intermediate [56–60] which was discussed elsewhere [61].

ACKNOWLEDGEMENTS

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Table 1. Adsorption energies $E_{\text{ads}}$ (in eV) and adsorbate charges $q$ (in atomic units) of all reaction intermediates at the MoS$_2$(10-10) surface considered in this work. The data are listed for both the T$_1'$ and T$_2$ termination. Corresponding adsorption geometries are shown in Figs. 3, 4.

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_{\text{ads}}$(T$<em>1'$) / $E</em>{\text{ads}}$(T$_2$)</th>
<th>$q$(T$_1'$) / $q$(T$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$H$_x$O$_y$ and CO$_3$ species</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHO</td>
<td>-2.01 / -1.98</td>
<td>0.11 / 0.14</td>
</tr>
<tr>
<td>COH</td>
<td>-3.49 / -2.71</td>
<td>0.22 / 0.44</td>
</tr>
<tr>
<td>CHOH</td>
<td>-2.60 / -2.61</td>
<td>0.20 / 0.16</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>-0.50 / -0.52</td>
<td>-0.06 / -0.01</td>
</tr>
<tr>
<td>CH$_2$OH</td>
<td>-1.99 / -1.53</td>
<td>0.17 / 0.17</td>
</tr>
<tr>
<td>CH$_3$O</td>
<td>-3.20 / -2.67</td>
<td>-0.20 / -0.18</td>
</tr>
<tr>
<td>HCOO</td>
<td>-2.95 / -2.90</td>
<td>-0.21 / -0.23</td>
</tr>
<tr>
<td>CO$_3$</td>
<td>-3.95 / -4.25</td>
<td>-0.62 / -0.67</td>
</tr>
<tr>
<td>C$_2$H$_x$O$_y$ species</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$CHO</td>
<td>-1.98 / -2.03</td>
<td>0.18 / 0.18</td>
</tr>
<tr>
<td>CH$_3$CHO</td>
<td>-0.40 / -0.34</td>
<td>0.23 / 0.21</td>
</tr>
<tr>
<td>CH$_3$CH$_2$O</td>
<td>-3.16 / -2.67</td>
<td>-0.16 / -0.16</td>
</tr>
<tr>
<td>CH$_3$COO</td>
<td>-2.87 / -2.73</td>
<td>-0.16 / -0.18</td>
</tr>
<tr>
<td>CH$_x$ species</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-5.40 / -5.56</td>
<td>0.07 / 0.09</td>
</tr>
<tr>
<td>CH</td>
<td>-5.73 / -6.03</td>
<td>0.10 / 0.10</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>-4.26 / -4.41</td>
<td>0.10 / 0.15</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>-1.71 / -1.59</td>
<td>0.24 / 0.29</td>
</tr>
</tbody>
</table>
Table 2. Vibrational frequencies ν (in cm\(^{-1}\)) of all reaction intermediates at the MoS\(_2\)(10-10) surface considered in this work. The data are listed for both the T\(_1\)' and T\(_2\) termination. The corresponding adsorption geometries are shown in Figs. 3, 4.

<table>
<thead>
<tr>
<th></th>
<th>ν(T(_1)')</th>
<th>ν(T(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHO</td>
<td>1336, 1488</td>
<td>1310, 1483</td>
</tr>
<tr>
<td>COH</td>
<td>1298</td>
<td>1468</td>
</tr>
<tr>
<td>CHOH</td>
<td>1286</td>
<td>1317</td>
</tr>
<tr>
<td>CH(_2)O</td>
<td>1418</td>
<td>1422</td>
</tr>
<tr>
<td>CH(_2)OH</td>
<td>1424</td>
<td>1437</td>
</tr>
<tr>
<td>CH(_3)O</td>
<td>1421, 1440, 1465</td>
<td>1420, 1443, 1455</td>
</tr>
<tr>
<td>HCOO</td>
<td>1355, 1374, 1535</td>
<td>1358, 1372, 1562</td>
</tr>
<tr>
<td>CO(_3)</td>
<td>1747</td>
<td>1744</td>
</tr>
<tr>
<td>CH(_3)CO</td>
<td>1327, 1386, 1434, 1467</td>
<td>1329, 1419, 1450, 1517</td>
</tr>
<tr>
<td>CH(_3)CHO</td>
<td>1349, 1391, 1423, 1441</td>
<td>1373, 1383, 1431, 1442</td>
</tr>
<tr>
<td>CH(_3)CH(_2)O</td>
<td>1373, 1392, 1454, 1466, 1476</td>
<td>1357, 1381, 1450, 1458, 1485</td>
</tr>
<tr>
<td>CH(_3)COO</td>
<td>1379, 1413, 1439, 1448, 1534</td>
<td>1356, 1403, 1442, 1447, 1531</td>
</tr>
</tbody>
</table>
Table 3. Comparison of the computed vibrational frequencies $\nu$ (in cm$^{-1}$) of reaction intermediates adsorbed at the MoS$_2$(10-10) surface with experimental data from DRIFT spectroscopy for CO hydrogenation at the unpromoted MoS$_2$/γ-Al$_2$O$_3$ catalyst [8].

<table>
<thead>
<tr>
<th>Theory</th>
<th>Assignment</th>
<th>Experiment</th>
<th>$\nu$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1286, 1336]</td>
<td>CHO, COH ($T_1'$), CHO, CH$_3$CO</td>
<td>-</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>[1349, 1403]</td>
<td>HCOO, CH$_3$CO ($T_1'$), CH$_3$CHO, CH$_3$COO, CH$_3$CH$_2$O</td>
<td>1385</td>
<td>HCOO</td>
<td></td>
</tr>
<tr>
<td>[1413, 1443]</td>
<td>CH$_2$O, CH$_2$OH, CH$_3$O, CH$_3$CO, CH$_3$CHO, CH$_3$COO</td>
<td>1420</td>
<td>HCOO</td>
<td></td>
</tr>
<tr>
<td>[1447, 1488]</td>
<td>CH$_3$COO, CH$_3$O, CHO, COH ($T_2'$), CH$_3$CO, CH$_3$CH$_2$O</td>
<td>1470</td>
<td>CH$_3$COO, CH$_3$O, CO$_3$</td>
<td></td>
</tr>
<tr>
<td>[1535, 1562]</td>
<td>HCOO</td>
<td>1590</td>
<td>HCOO</td>
<td></td>
</tr>
<tr>
<td>[1744, 1747]</td>
<td>CO$_3$</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>
Table 4. Reaction energies, $\Delta E_{\text{sep}}$ and $\Delta E_{\text{coad}}$, and reaction barriers, $E_a$, of different elementary steps for CO hydrogenation at the MoS$_2$(10-10) surface. For definitions of $\Delta E_{\text{sep}}$, $\Delta E_{\text{coad}}$, $E_a$, see text. All energies are given in eV. The numbers in parentheses refer to theoretical values for a pure Mo metal termination [35], also labeled with “a”, see Fig. 1 and text.

<table>
<thead>
<tr>
<th>Reaction step</th>
<th>$T_1'$ termination</th>
<th>$T_2$ termination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta E_{\text{sep}}$</td>
<td>$\Delta E_{\text{coad}}$</td>
</tr>
<tr>
<td>CO + H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO + H \rightarrow CHO</td>
<td>0.11</td>
<td>0.36 (0.51$^a$)</td>
</tr>
<tr>
<td>CO + H \rightarrow COH</td>
<td>0.54</td>
<td>0.79 (1.71$^a$)</td>
</tr>
<tr>
<td>CHO \rightarrow CH + O</td>
<td>0.21</td>
<td>0.80 (-0.69$^a$)</td>
</tr>
<tr>
<td>CO + 2H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHO + H \rightarrow CH$_2$O</td>
<td>-0.13</td>
<td>-0.48 (0.20$^a$)</td>
</tr>
<tr>
<td>CHO + H \rightarrow CHOH</td>
<td>0.36</td>
<td>0.00 (1.00$^a$)</td>
</tr>
<tr>
<td>CH$_2$O \rightarrow CH$_2$ + O</td>
<td>0.04</td>
<td>-0.28 (-0.73$^a$)</td>
</tr>
<tr>
<td>CO + 3H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$O + H \rightarrow CH$_3$O</td>
<td>-1.48</td>
<td>-1.36</td>
</tr>
<tr>
<td>CH$_2$O + H \rightarrow CH$_2$OH</td>
<td>-0.65</td>
<td>-0.52</td>
</tr>
<tr>
<td>CH$_3$O \rightarrow CH$_3$ + O</td>
<td>0.68</td>
<td>1.35</td>
</tr>
<tr>
<td>CH$_2$OH \rightarrow CH$_2$ + OH</td>
<td>-0.32</td>
<td>-0.29</td>
</tr>
<tr>
<td>Misc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$OH + H \rightarrow CH$_3$OH</td>
<td>-0.46</td>
<td>-0.78</td>
</tr>
<tr>
<td>CH$_2$ + H \rightarrow CH$_3$</td>
<td>-0.84</td>
<td>-0.20 (-0.01$^a$)</td>
</tr>
<tr>
<td>CH$_3$ + H \rightarrow CH$_4$</td>
<td>-0.70</td>
<td>-1.26 (0.42$^a$)</td>
</tr>
<tr>
<td>CH$_3$ + OH \rightarrow CH$_3$OH</td>
<td>0.67</td>
<td>-0.38</td>
</tr>
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</table>
FIGURE CAPTIONS

Fig. 1. Crystal structure of hexagonal MoS$_2$ at the (10-10) surface with (a) ideal bulk termination, (b) sulfur reconstructed termination, see text. Molybdenum (sulfur) centers are shown by small dark (large light) balls with connecting sticks visualizing atom coordination. The two differently Mo and S terminated layers are labeled accordingly.

Fig. 2. Slabs of (a) T$_1$' terminated, (b) T$_2$ terminated MoS$_2$ sheets used for the supercell model systems, see text. Molybdenum (sulfur) centers are shown by small dark (large light) balls with connecting sticks visualizing atom coordination. Vector $R_s$ denotes the supercell periodicity along the sheet edge including six MoS$_x$ units.

Fig. 3. Computed equilibrium geometries of selected C$_1$ reaction intermediates at T$_1$' and T$_2$ terminated edges of the MoS$_2$(10-10) surface, (a) CHO; (b) COH; (c) CHOH; (d) CH$_2$O; (e) CH$_2$OH; and (f) CH$_3$O. The atom centers are shown by shaded balls of different size and labeled in Fig. 3a. Connecting sticks are meant to visualize atom coordination.

Fig. 4. Computed equilibrium geometries of selected C$_1$ and C$_2$ type reaction intermediates at T$_1$' and T$_2$ terminated edges of the MoS$_2$(10-10) surface, (a) HCOO; (b) CO$_3$; (c) CH$_3$CO; (d) CH$_3$CHO; (e) CH$_3$CH$_2$O; (f) CH$_3$COO. The atom centers are shown by shaded balls of different size and labeled in Fig. 4a. Connecting sticks are meant to visualize atom coordination.

Fig. 5. Computed equilibrium geometries of selected CH$_x$ species at T$_1$' and T$_2$ terminated edges of the MoS$_2$(10-10) surface, (a) C; (b) CH; (c) CH$_2$; (d) CH$_3$. The atom centers are shown by shaded balls of different size and labeled in Fig. 5a. Connecting sticks are meant to visualize atom coordination.

Fig. 6. Sequential CO hydrogenation steps at the T$_1$' edge for the most favorable reaction path: The structures to the left denote initial reactants, those on the right refer to products, and the center structures sketch corresponding transition states.

Fig. 7. Sequential CO hydrogenation steps at the T$_2$ edge for the most favorable reaction path: The structures to the left denote initial reactants, those on the right refer to products, and the center structures sketch corresponding transition states.

Fig. 8. Energetic reaction schemes for sequential CO hydrogenation at the (a) T$_1$' edge and (b) T$_2$ edge assuming reaction intermediates and products in their adsorbed states at the surface. The most favorable reaction paths are highlighted by thick lines. Alternative intermediates are labeled accordingly and listed at the bottom of the graph. The barriers between the reaction intermediates refer to corresponding reaction barriers.
REFERENCES


(a) CO + H → CH₂O
(b) CHO + H → CH₂O
(c) CH₂O + H → CH₂OH
(d) CH₂ + H → CH₃
(a) $\text{CO} + \text{H} \rightarrow \text{CHO}$

(b) $\text{CHO} + \text{H} \rightarrow \text{CH}_2\text{O}$

(c) $\text{CH}_2\text{O} + \text{H} \rightarrow \text{CH}_2\text{OH}$

$\text{CH}_2\text{OH} \rightarrow \text{CH}_2 + \text{OH}$

(d) $\text{CH}_2 + \text{H} \rightarrow \text{CH}_3$

$\text{CH}_3 + \text{H} \rightarrow \text{CH}_4$