Quantum-chemical-based microkinetics simulations of syngas conversion over MoS$_2$(1 0 0) surface

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**HIGHLIGTHS**

- Syngas conversion to methane and alcohols important for energy conversion.
- Multiscale modeling of syngas conversion on MoS$_2$ combining DFT and microkinetics.
- Bare Mo-edge poisoned for CO dissociation due to strong oxygen binding.
- Partial coverage of Mo-edge with sulfur lowers activation barriers.
- Microkinetic predictions for partially sulfur-covered surfaces close to experiment.

**ABSTRACT**

MoS$_2$ is a potential catalyst for the conversion of synthesis gas obtained from different carbon-containing feedstock into methane, hydrocarbons and alcohols. We performed a combined density functional theory and microkinetics simulation study of all relevant reaction pathways of CO and H$_2$ into methane, ethylene, ethane, formaldehyde, methanol, carbon dioxide and water at the bare and partially sulfided Mo-edge of MoS$_2$(1 0 0). Reaction barriers were substantially lower for the 25% sulfur-covered Mo-edge in comparison to the bare Mo-edge. H-assisted CO dissociation is preferred over direct CO dissociation for both surfaces. Microkinetics simulations predict a negligible methanation rate for the bare Mo-edge, which contradicts experiment. The discrepancy stems from oxygen poisoning of the surface. Oxygen removal barriers are substantially lowered at a sulfur coverage of 25%. The resulting CO conversion rate and product distribution are in good agreement with reported experimental data. These simulations show how density functional theory combined with microkinetics simulations can predict performance of catalytic surface used in complex chemical reactions.

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1. Introduction

The increasing global demand for energy leads to a more diversified use of fossil and renewable resources. At the fossil side of these resources, coal reservoirs remain plentiful and cheap and continue to be considered as a substitute for petroleum and natural gas. Synthetic natural gas can be obtained from coal via gasification into synthesis gas (a mixture of CO and H$_2$) and methanation. Methanation is already a large-scale industrial process to remove traces of CO during hydrogen production for ammonia production (Schaaf, 2014; Appl, 1999; Xu et al., 2006). Other sources of synthetic natural gas are biofuels, waste streams and renewable electricity, the latter requiring a source of carbon dioxide for conversion with green hydrogen, e.g. from electrolysis or gasification, via the Sabatier reaction. Natural gas is a convenient energy...
carrier as it can for instance be easily distributed in a gas grid. There is also increasing attention for natural gas as a fuel for heavy (marine) transport. On the other hand, natural gas prices are too low in many places to economically produce synthetic natural gas. Therefore, also other options involving synthesis gas as a platform to produce more valuable liquid hydrocarbon fuels are considered such as Fischer-Tropsch synthesis (Bell, 1981). Another interesting option is to convert synthesis gas to mixed alcohols, which are interesting octane-boosting fuel additives (Charles, 1991; Xu et al., 1987) as well as feedstock for olefins.

For methanation and mixed alcohols synthesis, MoS2 is one of the promising catalyst systems in addition to modified Cu and (expensive) Rh catalysts (Burch and Hayes, 1997; Hu et al., 2007; Fu et al., 1995; Bao et al., 2009; Dong et al., 2009; Sun and Robert, 2003; Liu et al., 2010). For methanation, MoS2-based catalysts are attractive, because their substantial water-gas shift activity allows converting synthesis gas at low H2/CO ratio. Another aspect of these catalysts is that they retain good activity in the presence of H2S, a common pollutant in synthesis gas derived from coal. On the other hand, their activity is currently too low to compete with Ni-based catalysts which are employed at the industrial scale. To employ MoS2 catalysts for CO hydrogenation on an industrial scale, we need to enhance the activity of MoS2 for which a detailed comprehension of the chemo-kinetic network is required. For mixed alcohols synthesis, conventional Fischer-Tropsch catalysts are not efficient enough (Bartholomew et al., 1982; Dalla Betta et al., 1975; Fitzharris et al., 1981; Anderson et al., 1965; Madon and Seaw, 1977). MoS2 is a more promising option for this purpose (Fu et al., 1995; Tatsumi et al., 1984). It has been found that alkali promotion of MoS2 is important in shifting the product distribution from hydrocarbons to mixed alcohols (Youchang et al., 1986; Lee et al., 1994; Li et al., 1999; Santos et al., 2013).

The mechanism of CO hydrogenation on MoS2 has already been studied by quantum-chemical calculations. Anderson and Yu investigated the conversion of CO and methane to ethane and ethanol on MoS2 (Anderson and Yu, 1989), using molecular orbital theory to study CO adsorption and energy barriers for CH4 + CH3, CH3 + CH3, CH3 + CH3, CH3 + CO and H + CH3CH2 coupling reactions. Klier et al. used density functional theory (DFT) to understand the influence of K and Ag promotion on MoS2 (Neiman et al., 2004). In order to study CO and H2 adsorption, they employed a Mo5S14 cluster, as its edges resemble the periodic MoS2 edges. Zeng et al. carried out a DFT study of CO adsorption at corners and edges of a Mo20S36 cluster (Zeng et al., 2005). They also studied CO adsorption on the coordinatively unsaturated (1010) surface on a Mo16S12 cluster (Zeng et al., 2005). Huang et al. performed a systematic DFT study of hydrogenation of synthesis gas on a periodic MoS2 model at 0% and 100% sulfur coverage of the Mo-edge (Huang and Cho, 2009). Formation of CH4 and CO2 were predicted to be dominant products on the unpromoted MoS2 surface. Shi et al. investigated reaction intermediates of CO hydrogenation on the Mo-edge at a 42% sulfur coverage and the S-edge at a 50% sulfur coverage of unpromoted MoS2 (Shi et al., 2009). This study showed formation of CH4 through C3-type intermediate surface species. Chen et al. conducted DFT calculations to investigate the mechanism of ethanol formation from methanol and synthesis gas on Mo25S24 and Mo20S36 clusters (Chen et al., 2010). In another DFT study, they carried out methanol dissociation on the bare Mo-edge, 50% sulfur covered Mo-edge and 50% sulfur covered S-edge of MoS2 clusters, demonstrating the ability of the clusters to break the O—H bond of methanol with low barrier (Chen et al., 2011). The coverage with sulfur species at the different surface terminations of MoS2 has been well studied. Travers et al. showed the dependence of sulfur coverage of the Mo and S edges of MoS2 on the H2/H2S ratio of the gaseous environment (Travers et al., 2001). Others have extensively studied this aspect as well (Shetty et al., 2009; Alfonso, 2013). An important corollary of these works is that the most stable structure for both Mo and S edges are 50% sulfur-covered under typical conditions with H2S/H2 ratios varying from 0.01 to 0.1. This has also been confirmed by Hansen et al. using high-resolution scanning TEM imaging of an industrial hydrodesulfurization catalyst under sulfidation conditions (Hansen et al., 2011). The Mo atoms at the Mo-edge with 50% sulfur coverage are coordinatively saturated. As such, one does not expect catalytic activity for such model and at least one S atom needs to be removed. Shi et al. used such a S-vacancy model to study CO hydrogenation on MoS2 (Shi et al., 2009). A drawback of their model is that CO and O were adsorbed on a single vacancy. CO2 adsorption at the single S-vacancy of this model is endothermic (+0.42 eV) (Kittel, 1966), whereas experimentally it has been found that CO2 inhibits the reaction rate of CO hydrogenation (Hou and Wise, 1985). A lower S coverage such as on the bare Mo-edge strongly adsorbs CO2 (Huang and Cho, 2009). Thus, in practice the sulfur coverage at the Mo-edge may be lower than predicted in these ideal model calculations.

Until now, no full microkinetic model is available for predicting the rate and selectivity of CO hydrogenation on MoS2. A potent approach is to couple or link these microkinetic models to the materials and energy balances for chemical reactor design. In this work, firstly we have chosen the bare Mo-edge for CO hydrogenation as it is universally accepted that coordinatively unsaturated sites at catalysts are responsible for catalytic activity. Mo atoms at the bare Mo-edge have the lowest coordination numbers and are thus expected to harbor the highest catalytic activity. As such, we want to understand the role of the one-dimensional array of Mo atoms in MoS2. Another inspiration for carrying out microkinetics for this surface was the DFT study of CO hydrogenation on the bare Mo-edge with very few selective elementary reaction steps (Huang and Cho, 2009). We have taken into consideration a comprehensive DFT study for detailed reaction network on the bare Mo-edge, and used computed kinetics parameters in microkinetics. We have studied CO hydrogenation, CO dissociation, different coupling as well as O removal and C hydrogenation reactions at the bare Mo-edge. Potential energy diagrams for these elementary reactions steps leading to methane, methanol, ethylene and ethane and water and carbon dioxide were computed. Microkinetics simulations were then used to predict CO hydrogenation turnover rates. Further investigations concerned the impact of co-adsorbed S atoms on the Mo-edge and the effect of sulfidryl (SH) groups on the reaction mechanisms. The presence of sulfur on the Mo-edge has a positive influence on oxygen removal rates in the form of CO2. In addition, dissociated H2 is more stable as MoH than as SH groups. The role of SH groups in CHO formation from CO hydrogenation is minor. We find that the simulated reaction rates and the product distribution on the partially sulfided Mo-edge are in good agreement with reported experimental data.

2. Methods

2.1. DFT calculations

Electronic structure calculations within the DFT framework were performed using the Vienna Ab initio Simulation Package (VASP) (Kresse and Hafner, 1994; Kresse and Furthmüller, 1996). Projector-augmented wave pseudo-potentials (Blochl, 1994) and a plane-wave basis set with an energy cut-off of 400 eV were used to describe the electron density (Kresse and Joubert, 1999; Perdew et al., 1996). Exchange-correlation was taken into account using the Perdew–Burke–Ernzerhof (PBE) parametrization of the generalized gradient approximation (Henkelman and Jónsson, 2000). Gaussian smearing-function with a width smaller than 0.1 eV was used to account for fractional occupancies (De Vita, 1992).
Bulk MoS$_2$ has a hexagonal structure with six atoms per unit cell, comprised of S-Mo-S layers. The basal (0 0 1) plane is terminated by sulfur atoms, which is usually regarded to be inactive in catalysis. Cleavage of bulk MoS$_2$ parallel to the (1 0 0) or (0 1 0) plane results in edge surfaces, namely the coordinatively unsaturated Mo-terminated (10 0) edge (named Mo-edge hereafter) and the S-terminated (10 1 0) edge (S-edge) (Helvey et al., 2000; Lauritsen et al., 2007). These edges are shown in Fig. 1. The slab model used is represented by a p(4 × 1) unit cell exposing the MoS$_2$(1 0 0) surface. Please note that every Mo atom can bind two sulfur atoms, thus a 100% sulfur coverage corresponds to 8 sulfur atoms. Thus, in terms of monolayer (ML) coverage, a sulfur coverage of 25% is the same as a 0.5 ML coverage. We used $a = 3.13$ Å and $c = 12.59$ Å for the lattice parameters. The vacuum layer thickness was set to 12.0 Å. To confirm that the vacuum layer was thick enough, we verified that the electron density as well as the electrostatic potential approached zero at the top and bottom border of the supercell. In all calculations, the geometry of the whole slab including adsorbates was relaxed on both sides. To significantly reduce the spurious dipole interactions between adjacent supercells, adsorbates were placed on both sides of the slab. Sampling of the Brillouin zone was done using a (3 × 3 × 1) $k$-point mesh, generated by the Monkhorst-Pack method (Monkhorst and Pack, 1976). Geometry optimization of gas-phase reference molecules was done using only the $\Gamma$-point with the molecules being placed at the center of a large unit cell (10 Å × 10 Å × 10 Å). Electronic convergence was set to $10^{-6}$ eV, and geometries were converged to $10^{-2}$ eV using a conjugate-gradient algorithm, which uses trial and corrector steps to converge both the energy and the forces on the ions. Transition states (TS) for elementary reactions were identified using the Climbing Image Nudged Elastic Band (CI-NEB) method as implemented in VASP (Henkelman and Jónsson, 2000). Typically, about 40 ionic steps were made with the NEB algorithm. Then, a frequency calculation was performed on the image with the highest energy. When frequency analysis showed one imaginary frequency in the direction of the reaction coordinate, the structure was further relaxed with a quasi-Newton algorithm until the forces were smaller than 0.01 eV/Å. Finally, the nature of the transition state was again confirmed by the occurrence of a single imaginary frequency in the direction of the reaction coordinate. Frequencies were obtained by Hessian vibrational analysis with a step size of 0.02 Å. Zero-point energy corrections were made to adsorption energies and activation energy barriers. Adsorption energies of adsorbates have been calculated using the following equation:

$$E_{\text{ads}} = \frac{E_{\text{lab,adsorbate}} - E_{\text{lab}} - 2E_{\text{adsorbate}}}{2}$$

(1)

The factor $\frac{1}{2}$ accounts for the fact that energies were computed with two adsorbates in the supercell.

2.2. Microkinetic simulations

The activation barriers and the corresponding vibrational frequencies of the initial, transition and final states were used to compute forward and backward rate constants for the elementary reaction steps relevant to the CO hydrogenation on the Mo-edge. The Eyring equation was used to calculate the rate constants of surface elementary reaction steps:

$$k = \frac{k_b T}{h \sqrt{2 \pi m k_b T}} e^{-\frac{Q}{k_b T}}$$

(2)

with $k$ being the rate constant in mol/s, $k_b$ the Boltzmann constant, $T$ the temperature in K, $h$ (Planck’s constant), $Q$ the partition function of the activated complex, $Q'$ the partition function of the complex in the pre-activated (initial) state and $E_z$ the ZPE-corrected electronic activation energy (Kittel, 1966; Chorkendorff and Niemantsverdriet, 2017). The partition functions for the activated and pre-activated complexes were taken as the product of translational, rotational and vibrational partition functions corresponding to the configurational degrees of freedom of the surface complexes. All the reported activation energies are zero-point-energy (ZPE) corrected (Einstein and Stern, 1913).

For non-activated molecular adsorption it was assumed that the complex loses one translational degree of freedom with respect to the gas phase in the transition state. The changes in the rotational degrees of freedom were neglected. Accordingly, the following expression was employed for the rate of molecular adsorption

$$k_{\text{ads}} = \frac{PA}{\sqrt{2\pi m k_b T}} S$$

(3)

With $P$ being the partial pressure of the adsorbate in the gas phase, $A$ the surface area of the adsorption site, and $m$ the mass of the adsorbate and $S$ the sticking coefficient.

For desorption, it was assumed that the complex has three rotational degrees of freedom and two translational degrees of freedom in the activated state, while in the adsorbed state it only has vibrational degrees of freedom. Accordingly, the rate of desorption is given by (Jansen, 2012)

$$k = \frac{k_b T^2}{h^4} \frac{A(2\pi k_b)_{\text{rot}}}{\sigma |\Omega_{\text{rot}}|} e^{-\frac{\lambda_s}{\sigma T}}$$

(4)

where $\sigma$ is the symmetry number, $\theta$ the characteristic temperature for rotation, and $E_{\text{des}}$ the desorption energy.

To carry out microkinetics simulations differential equations for all surface reaction intermediates were constructed using the rate constants as given in Eqs. (1)-(3). Given a system of $N$ elementary reaction steps, $2N$ rate expressions (i.e. $N$ forward and $N$ backward reactions) of the form

$$r_i = k_i |c_i|^j$$

(5)

are obtained, where $c_i$ is the concentration of the species $i$ on the surface, and $v$ is the stoichiometry coefficient of species $i$ in elementary reaction step $j$. These rate expressions were used to derive ordinary differential equations (ODEs) for each component.

The MKMCXX software was then used to solve the resulting set of ordinary differential equations (ODEs) by means of the Backward Differentiation Formula method (http://www.mkmcxx.nl; Filot et al., 2014; Brown et al., 1989; Byrne and Hindmarsh, 1975, 1987). Steady-state coverages were found by integrating the ODEs in time until the changes in the surface coverages were very small. These steady-state surface coverages were then used
to compute the rates of the individual elementary reaction steps and the overall rate per surface atom.

We determined the degree of rate control (DRC) as defined earlier (Filot et al., 2015). The DRC for a chemical reaction is defined as the relative change of the rate as a result of the relative change in the rate constant of a particular elementary reaction step keeping the equilibrium constant fixed. The DRC is defined as

$$Z_{i,C} = \left( \frac{\partial r_C}{\partial r_i} \right)_{k_i, K_i} = \left( \frac{\partial \ln (r_C)}{\partial \ln (k_i)} \right)_{k_i, K_i}$$

(6)

In the above equation, $Z_{i,C}$ is the DRC parameter of elementary reaction step $i$ for key component (i.e. a reactant or a product) $c$, $r_i$ is the overall reaction rate for key component $c$, and $k_i$ and $K_i$ are the overall reaction rate and equilibrium constants for the elementary reaction step $i$, respectively.

Lateral interactions and their influence on activation barriers were not implicitly taken into account in this study. The CO adsorption energy was set at $-1.66$ eV. This value is based on the adsorption energy of two CO molecules adsorbed at adjacent bridge Mo sites. The H$_2$ adsorption energy was set at $-0.72$ eV.

3. Results and discussion

3.1. DFT results for elementary steps on the bare Mo-edge

3.1.1. CO adsorption

We first studied CO adsorption on the Mo- and S-edges of the (1 0 0) surface termination of MoS$_2$. Stable adsorption geometries (see Fig. S1) and the corresponding adsorption energies are listed in Table 1. The adsorption energies are in good agreement with data reported by Huang and Cho (Zeng et al., 2005), but slightly higher than values mentioned by Huang and Cho (2009). CO binds strongest (2.22 eV) on the bridge-Mo site of the Mo-edge. CO adsorbs via its carbon atom and is tilted with respect to the normal of the Mo-edge. Top adsorption of CO is slightly less favorable (2.05 eV). In both these adsorption modes, CO is activated with slightly longer C=O bond than values mentioned by Huang and Cho (Zeng et al., 2005), but slightly stronger (2.24 eV) on the bridge-Mo site of the Mo-edge (see Fig. S4). Surface CH$_2$O is 0.12 eV less stable than co-adsorbed H and CHO, whereas CHOH is 1.39 eV less stable. The activation barriers for CH$_2$O and CHOH formation are 0.87 eV and 2.54 eV, respectively. Thus, formation of surface formaldehyde (CH$_2$O) is thermodynamically and kinetically favored over CHOH formation. Dissociation of CH$_2$O occurs with a lower energy barrier (0.43 eV) than for CHO dissociation (0.56 eV). This relates to the weakened C–O bond upon further hydrogenation of the C atom. The reaction energy associated with dissociation is $-1.43$ eV.

Formaldehyde can also be further hydrogenated to methane (CH$_4$) or methanol (CH$_2$OH) (see Fig. S5). The activation barrier for methanol formation (H + CH$_2$O → CH$_2$OH) is 1.18 eV and the reaction is endothermic by +0.73 eV. The activation barrier for methanol formation (CH$_2$O + H → CH$_2$OH) is +1.76 eV; this reaction is endothermic by +1.34 eV. Thus, on the basis of the activation barriers CH$_3$O bond dissociation is the preferred way of converting CH$_2$O.

3.1.3. Methane formation

The forward activation energies and reaction energies for all elementary steps leading to hydrogenation of surface CH$_x$ ($x = 0–3$) to gaseous methane (CH$_4$) are given in Table 2. The corresponding initial, transition and final states are shown in Fig. S6. It is not likely that atomic C is obtained by direct CO dissociation at the

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Adsorption site</th>
<th>E$_{ads}$ (eV)</th>
<th>d$_r$-O (Å)</th>
<th>Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>Atop-Mo</td>
<td>-2.05</td>
<td>1.17</td>
<td>9018; 1942; 1970</td>
</tr>
<tr>
<td>CO</td>
<td>Bridge-Mo</td>
<td>-2.22</td>
<td>1.23</td>
<td>1532; 1551; 1545</td>
</tr>
<tr>
<td>CO</td>
<td>Bridge-S</td>
<td>-0.63</td>
<td>1.20</td>
<td>1734; 1715; 1781</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Bridge-Mo</td>
<td>-1.97</td>
<td>1.26</td>
<td>-1.15</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>Bridge-Mo</td>
<td>-2.65</td>
<td>1.45</td>
<td>-822</td>
</tr>
</tbody>
</table>

*Zeng et al. (2005), Huang and Cho (2009)*
Mo-edge. Instead, it can for instance be formed by dehydrogenation of step of CH, obtained by C–O bond dissociation in formyl (CHO) species. The activation energy for methylidene (CH) dissociation into atomic C and H is 1.06 eV with a reaction energy of +0.09 eV. In the transition state of CH dissociation, the Mo–H and C–H bond distances are 1.77 Å and 1.80 Å, respectively. Compared with dehydrogenation, hydrogenation of CH to CH2 is more facile with a barrier of 0.87 eV; the reaction is slightly endothermic by +0.16 eV. In the transition state of CH2 formation from CH hydrogenation, the Mo–H and C–H bond distances are 1.72 Å and 1.74 Å, respectively. Another route that results in methylene is C–O bond dissociation in CH2O, whose barrier is 0.43 eV. The activation barrier for methyl formation at the bridge Mo-site is 0.89 eV with a reaction energy of +0.48 eV. The Mo–H and C–H bond distances in the transition state for CH2 formation are 1.76 Å and 1.75 Å, respectively. The activation barrier for CH3 formation is 1.48 eV. This reaction step is highly endothermic (+1.31 eV). In the transition state, both methyl and H are attached to the same Mo atom. The relevant Mo–C–Mo–H and C–H transition state are 2.35 Å, 1.78 Å, and 1.46 Å, respectively. The activation barrier for methane formation is higher than values reported in literature. Huang and Cho obtained a value of 0.58 eV at the bare Mo-edge, while at an S-coverage of single sulfur vacancy model a value of 0.53 eV was computed by Huang and Cho (2009), Shi et al. (2009). The higher value computed in the present work includes migration correction from the most stable adsorption sites of CH2 and H. Without these, we find a barrier for the recombinative desorption of CH4 of +1.12 eV, which is closer to the reported literature values.

3.1.4. Formaldehyde and methanol formation

In the previous section, we identified a pathway for CH2O formation. The adsorption energy of CH2O at the bridge-Mo site of the bare Mo-edge is ~2.65 eV. This adsorption is much stronger than values reported for transition metal surfaces such as Cu(1 1 1) and Ni(1 1 1) surfaces of ~0.33 eV and ~0.14 eV, respectively (Sun et al., 2013; Remediakis et al., 2004). The strong adsorption on the Mo-edge is in part due to the strong σ-bonds formed between adjacent Mo atoms with the C and O atoms of formaldehyde. As the adsorption energy of CH2O is higher than the activation barriers for CH2O dissociation or hydrogenation to CH3O, we do not expect that gas-phase formaldehyde will be observed as a reaction product during CO hydrogenation. We thus studied the hydrogenation of CH2O to methanol. Hydrogenation of CH2O starts from formaldehyde and atomic hydrogen adsorbed at adjacent bridge-Mo sites (see in Fig. 57). The activation energy is 1.18 eV and this reaction is endothermic by +0.74 eV. The Mo–H and Mo–C bond distances in the transition state are 1.74 Å and 2.44 Å, respectively. In comparison, activation barriers for methoxide formation on Cu(1 1 1) and Ni(1 1 1) surfaces are much lower (i.e. 0.36 eV and 0.42 eV, respectively). The higher activation barrier for this elementary step on the Mo-edge relates to the need to break additional σ-bonds. The product methoxide (CH3O) species, which only coordinates through its O atom, moves from the atop-Mo site to the bridge-Mo site. The methoxide species can then undergo either dissociation to methyl and oxygen or it can be hydrogenated to methanol. No transition state could be identified for CH3O dissociation in CH3 and O. For methanol formation, we used in the initial state methoxide and hydrogen co-adsorbed at adjacent bridge-Mo sites (see Fig. S7). The activation energy for methanol formation is 2.21 eV with a reaction energy of +1.84 eV. In the transition state, the Mo–H and Mo–O distances are 2.10 Å and 2.04 Å, respectively. The O–H bond distance in the methoxide in the transition state is 1.23 Å. In the final state, methanol is adsorbed atop-Mo with a Mo–O bond distance of 2.18 Å. The C–O bond length in methanol in this configuration is 1.46 Å, which is slightly elongated compared to the C–O bond distance in free methanol (1.43 Å). The top adsorption energy of methanol on Mo is ~0.98 eV. This value is only slightly lower than the adsorption energy of ~1.17 eV computed for methanol adsorbed on the Mo-edge of a Mo20S40 cluster (Chen et al., 2011).

3.1.5. CH3 + OH coupling reactions

The hydrogenation of CH3O intermediates to CH3OH (x = 1–3) involves high activation energies. Alternative pathways for CH3OH formation are the direct coupling reactions of CHx with surface OH species. As can be seen in Table 3, the reaction energies for such coupling reactions are even higher (1.26–2.50 eV). Accordingly, these reaction steps are likely kinetically irrelevant.

3.1.6. Oxygen removal as water and carbon dioxide

Atomic O derived from C–O bond scission can be removed as water or carbon dioxide. For water formation on the bare Mo-edge of MoS2, we studied two mechanisms, i.e. (i) H + OH → H2O and (ii) 2OH → H2O + O. The first step in both mechanisms is hydroxyl formation by reaction of O + H. The preferred adsorption sites for atomic O and H are bridge-Mo sites at the Mo-edge. In the initial state for OH formation, both O and H are adsorbed at adjacent bridge-Mo sites (Fig. S8). In the transition state, H is on the atop-Mo site and the O atoms on the bridge-Mo sites. The O–H bond distance is 1.36 Å, the Mo–H bond distance is 1.82 Å, and the Mo–O bond distances at bridge-Mo sites are 1.94 Å and 2.26 Å. The activation energy for OH formation is 1.99 eV and the reaction is endothermic by +1.02 eV. In the final state, the hydroxyl group is bound to the bridge-Mo site. For water formation by direct reaction of H with OH, OH and O are co-adsorbed at adjacent bridge-Mo sites (Fig. S8). In the transition state, both OH and H

### Table 2

<table>
<thead>
<tr>
<th>Elementary reaction</th>
<th>Ef (eV)</th>
<th>Eb (eV)</th>
<th>ΔH (eV)</th>
<th>Literature values</th>
<th>Ef (eV)</th>
<th>Eb (eV)</th>
<th>ΔH (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C + H → CH</td>
<td>1.06</td>
<td>1.15</td>
<td>0.09</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.64</td>
</tr>
<tr>
<td>CH + H → CH2</td>
<td>0.87</td>
<td>0.71</td>
<td>0.16</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.15</td>
</tr>
<tr>
<td>CH2 + H → CH3</td>
<td>0.89</td>
<td>0.40</td>
<td>0.48</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.01</td>
</tr>
<tr>
<td>CH3 + H → CH4</td>
<td>1.48</td>
<td>0.17</td>
<td>1.31</td>
<td>0.58</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.42</td>
</tr>
</tbody>
</table>

*a* Huang and Cho (2009).

*b* n.a means that the relevant value is not available.

### Table 3

<table>
<thead>
<tr>
<th>Elementary reaction</th>
<th>ΔH (eV)</th>
<th>Elementary reaction</th>
<th>ΔH (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C + OH → COH</td>
<td>+1.26</td>
<td>CH2 + OH → CH3OH</td>
<td>+1.76</td>
</tr>
<tr>
<td>CH + OH → COH</td>
<td>+1.84</td>
<td>CH3 + OH → CH4OH</td>
<td>+2.50</td>
</tr>
</tbody>
</table>
are bound to the same Mo atom; the O—H distance is 1.29 Å. The activation barrier for H$_2$O formation is 2.35 eV and this reaction is highly endothermic (1.81 eV). H$_2$O is adsorbed on the atop-Mo site. The adsorption energy for water at atop-Mo site is –0.85 eV. The Mo—O bond distance for adsorbed water on atop-Mo site is 2.21 Å. Another reaction pathway explored for water formation in this study is the disproportionation reaction, i.e. 2OH $\rightarrow$ H$_2$O + O. During our extensive exploration of the potential energy surface, we found that viable reactions always include dissociation of OH into O + H prior to OH + H recombination. Thus, only the pathway involving sequential addition of H atoms to O is reasonable.

The alternative O-removal pathway is as CO$_2$. On the bare Mo-edge, we have studied two mechanisms, namely (i) CO + O $\rightarrow$ CO$_2$ and (ii) 2CO $\rightarrow$ CO$_2$ + C. The latter reaction is commonly referred to as the Boudouard reaction. For CO$_2$ formation directly from CO with atomic O, the initial state involves co-adsorbed species at adjacent bridge-Mo sites. Then, the O atom migrates to an atop-Mo site, whereas CO remains at the bridge-Mo site with the C—O vector bending towards the Mo-edge as shown in Fig. S9. This highlights the repulsion between CO and atomic O on the bare Mo-edge. The activation barrier for CO$_2$ formation is 3.26 eV. Experimentally, it is observed that CO$_2$ is the main product that removes O atoms from the surface (Hou and Wise, 1985; Shi et al., 2009). The barrier for this reaction is found to be very high, because CO and O are strongly bound to the surface.

The second mechanism considered for CO$_2$ formation involves the reaction between two adsorbed CO molecules to give CO$_2$ and atomic C. This mechanism has amongst others been proposed to occur on exfoliated MoS$_2$ (Scholz and Morrison, 1989; Lund, 1996). When two CO molecules are co-adsorbed at adjacent bridge-Mo sites of MoS$_2$ (Fig. S9), the average CO adsorption energy decreases to ~1.60 eV, which is due to repulsive lateral interactions. Given the nature of the initial state, we could not identify a transition state for the Boudouard reaction.

### 3.1.7. C$_2$-species formation

#### 3.1.7.1. CH$_x$ adsorption

Stable adsorption geometries of CH$_x$ (with x = 0–3) (see Fig. S10). The most stable adsorption sites for C, CH, CH$_2$ and CH$_3$ are in the bridge-Mo sites. The Mo—C bond distances for C, CH, and CH$_2$ species are 1.95 Å, 2.02 Å and 2.15 Å, respectively. This distance becomes longer with increasing saturation of the C atom. For methyl (CH$_3$), we have compared adsorption at the top-Mo and the bridge-Mo site. Adsorption of methyl is more stable at the bridge-Mo site by 0.22 eV than at the atop-Mo site. The Mo—C distance for methyl adsorption at the atop-Mo site is 2.13 Å, while the distances at the bridge-Mo site are 2.05 Å and 2.21 Å. One of the C—H bonds of methyl adsorbed at the bridge-Mo site is elongated from 1.11 Å to 1.14 Å due to its interaction with a Mo-edge atom. This interaction of a methyl H atom with a surface Mo atom causes the asymmetric adsorption mode at the bridge-Mo site.

#### 3.1.7.2. CH$_4$ + CH$_x$ coupling reactions

CH$_4$ + CH$_x$ coupling reactions are relevant for the formation of higher hydrocarbons. We investigated 9 different coupling reactions at the Mo-edge of MoS$_2$, for which the kinetic parameters are given in Table 4. We first investigated coupling of the adsorbed C atom with CH$_4$ intermediates (see Fig. S11). Reactions with methylidyne (CH) and methylene (CH$_2$) are exothermic, whereas coupling of CH to methyl (CH$_3$) is slightly endothermic. Activation barriers for C + CH$_x$ are very high. The lowest activation barrier is for C + CH$_2$ coupling (2.01 eV), while activation barriers for coupling to CH and CH$_3$ are 2.70 eV and 2.81 eV, respectively. The C—C bond distances in the transition states for CCH, CCH$_2$ and CCH$_3$ formation are 2.21 Å, 2.35 Å and 2.17 Å, respectively. For C + CH coupling, C is located at the bridge-Mo site with CH at an adjacent atop-Mo site. In C + CH$_2$ coupling, C remains at the bridge site with methylene being in asymmetric two-fold coordination at the adjacent bridge Mo-site. The transition state of C + CH$_3$ coupling resembles that of C + CH coupling with C at the bridge site and CH$_3$ at the atop-Mo site. We then explored reactions of methylidyne with CH$_x$ (x = 1–3) intermediates (see Fig. S12). Reaction between two CH species starts from the co-adsorbed state on adjacent bridge Mo-sites. One of the CH species moves to the next bridge Mo-site (see Fig. S12). The co-adsorption at adjacent sites in bridged configuration is unfavorable. As a result of the repulsive interactions, the barrier for CH + CH coupling is 1.87 eV. The reaction energy for this reaction is endothermic by +0.29 eV. Formation of acetylene proceeds via a TS structure with a C—C bond length of 2.17 Å. The Mo—C bond lengths are 1.86 Å in the TS, while in the final twofold adsorbed acetylene state these distances are 2.11 Å.

For the CH + CH$_2$ coupling reaction, we start with methylidyne (CH) and methylene (CH$_2$) co-adsorbed at adjacent bridge-Mo sites. Compared to adsorption at infinite distance, the co-adsorbed configuration is less stable by 0.70 eV. The Mo—C bond distances of co-adsorbed methylene (CH$_2$) and methylidyne (CH) at the bridge-Mo site with a shared Mo atom are 2.60 Å and 2.02 Å, respectively. The difference in bond lengths indicates that CH is strongly bonded to the shared Mo atom in comparison to methylene (CH$_2$). The activation energy for CH + CH$_2$ coupling reaction is 1.39 eV. This elementary step is endothermic by +0.26 eV. The C—C bond distance in the transition state for this reaction is 2.49 Å. The Mo—C bond lengths of CH$_2$ and CH in the transition state for vinyl formation are 2.04 Å and 1.83 Å, respectively. In the final state, the vinyl group is adsorbed at the bridge-Mo site such that the CH-end of vinyl is at the top-Mo site with a Mo—C bond length of 1.95 Å (the Mo—C bond distance for the CH$_2$-end of vinyl is 2.18 Å). The C—C bond length of CHCH$_2$ at the bridge-Mo site in the final state is 1.45 Å.

### Table 4

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_r$ (eV)</th>
<th>$E_a$ (eV)</th>
<th>ΔH (eV)</th>
<th>d$_{C-C}$ (Å)</th>
<th>d$_{Mo-C}$ (Å)</th>
<th>d$_{Mo-Mo}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C + CH $\rightarrow$ CCH</td>
<td>2.70</td>
<td>3.60</td>
<td>-0.90</td>
<td>2.21</td>
<td>2.07</td>
<td>1.83</td>
</tr>
<tr>
<td>C + CH$_2$ $\rightarrow$ CCH$_2$</td>
<td>2.01</td>
<td>2.49</td>
<td>-0.48</td>
<td>2.35</td>
<td>2.04</td>
<td>2.13</td>
</tr>
<tr>
<td>C + CH$_3$ $\rightarrow$ CCH$_3$</td>
<td>2.81</td>
<td>2.68</td>
<td>+0.13</td>
<td>2.17</td>
<td>1.94</td>
<td>2.39$^a$</td>
</tr>
<tr>
<td>CH + CH $\rightarrow$ CCH</td>
<td>1.87</td>
<td>1.58</td>
<td>+0.29</td>
<td>2.17</td>
<td>1.86</td>
<td>1.86</td>
</tr>
<tr>
<td>CH + CH$_2$ $\rightarrow$ CCH$_2$</td>
<td>1.39</td>
<td>1.13</td>
<td>+0.26</td>
<td>2.49</td>
<td>1.83</td>
<td>2.04</td>
</tr>
<tr>
<td>CH + CH$_3$ $\rightarrow$ CCH$_3$</td>
<td>1.08</td>
<td>0.27</td>
<td>+0.80</td>
<td>2.06</td>
<td>2.18</td>
<td>2.33$^b$</td>
</tr>
<tr>
<td>CH$_2$ + CH$_2$ $\rightarrow$ CHCH$_2$</td>
<td>1.43</td>
<td>1.32</td>
<td>+0.11</td>
<td>2.65</td>
<td>1.98</td>
<td>1.98</td>
</tr>
</tbody>
</table>

$^a$ x and y represent number of hydrogen atoms varying from 1 to 3. $^b$ Adsorption atop-Mo.
We have also studied the CH + CH3 coupling reaction on the bare Mo-edge sites. Compared to adsorption at infinite distance, the co-adsorbed configuration is less stable by 0.57 eV. This destabilization is lower than for the CH2 + CH2 and CH + CH2 cases. The activation energy for CHCH3 formation by CH + CH3 coupling reaction is 1.08 eV. This reaction is endothermic by +0.27 eV. The C−C bond distance in the transition state for CH + CH3 coupling reaction is 2.06 Å. The Mo−C bond lengths of methylidyne (CH) at the bridge-Mo site in the transition state are 1.97 Å and 2.18 Å, whereas CH3 is adsorbed atop-Mo with a Mo−C bond length of 2.23 Å. The C−C and Mo−C bond lengths in the final CHCH3 state are 1.48 Å and 1.90 Å, respectively. The C−H bond is elongated from 1.11 Å in the initial to 1.17 Å in the final state due to the interaction of the H atom with a surface Mo atom. The Mo−H bond distance for CHCH3 in atop-Mo site in the final state is 1.99 Å. For CH2 + CH3 coupling reaction to ethylene, we considered co-adsorbed methylene species at adjacent bridge-Mo sites, where they are 0.65 eV less stable than adsorption at infinite distance. The activation barrier for ethylene formation on the bare Mo-edge is 1.43 eV. This elementary reaction is slightly endothermic by +0.11 eV. The C−C bond distance in the transition state for CH2 + CH3 coupling reaction is 2.65 Å. The Mo−C bond lengths in the transition state for ethylene formation from direct coupling of methylene groups are 1.97 Å and 1.99 Å. In the final state, ethylene is formed at the bridge-Mo site with a C−C bond distance of 2.48 Å, which is 0.15 Å larger than the C−C bond length in the gas phase. The Mo−C bond lengths for ethylene in the final state are 2.17 Å and 2.29 Å, consistent with the asymmetric adsorption mode at the bridge-Mo site (see Fig. S13).

We could not find a transition state for the CH2 + CH3 coupling reaction at the bare Mo-edge. This reaction is not feasible at the Mo-edge due to the unfavorable orientation of CH2 and CH3 in making the activated complex. The high barrier in formation of surface ethyl from CH2 + CH3 coupling has been claimed to be unfavorable due to repulsive interactions between the C−H bonds in surface methylene and methyl groups (Zheng et al., 1988). On the other hand, transition states have been identified for this reaction on Mo20S43 and Mo20S36 clusters, with values for the activation barrier of 2.30 eV and 1.12 eV, respectively (Chen et al., 2010). Identification of the transition state for direct coupling of two methyl fragments has not been explored, as it is expected to be very unstable due to steric hindrance of the adsorbed CH3 fragments (Zheng et al., 1988). Barriers for this reaction have been estimated to be 3.12 eV and 3.16 eV on Mo20S43 and Mo20S36 clusters, respectively (Chen et al., 2010). It is interesting to mention that ethane formation from two methyl species is also unfavorable on α-Mo5C (0 0 0 1) with an activation barrier of 4.28 eV (Ren et al., 2006).

### Table 5

Hydrogenation of CHx + CHy reactions on the bare Mo-edge of MoS2 (1 0 0) surface: computed forward and backward activation barriers (Eₐ and Eᵦ, respectively), reaction energies (ΔH) in relation to the most stable states, and structural parameters for the transition states.

<table>
<thead>
<tr>
<th>Index</th>
<th>Elementary reaction</th>
<th>Eₐ (eV)</th>
<th>Eᵦ (eV)</th>
<th>ΔH (eV)</th>
<th>Bond distances in TS</th>
<th>dₑ−ᵦ (Å)</th>
<th>dₑ−Mo (Å)</th>
<th>dᵦ−Mo (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>CCH + H → CHCH</td>
<td>1.03</td>
<td>0.42</td>
<td>+0.60</td>
<td>1.52</td>
<td>2.22</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>CCH₂ + H → CCH₂</td>
<td>0.99</td>
<td>0.05</td>
<td>+0.94</td>
<td>1.68</td>
<td>2.41</td>
<td>1.79</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>H + CCH → CCHCH</td>
<td>1.14</td>
<td>0.05</td>
<td>+1.09</td>
<td>1.61</td>
<td>2.03</td>
<td>1.80</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>H + CCH₂ → CCHCH₂</td>
<td>n.a.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>H + CCH₂ → CCH₂</td>
<td>1.09</td>
<td>0.62</td>
<td>+0.47</td>
<td>1.71</td>
<td>1.90</td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>CCH₁ + H → CCH₂</td>
<td>0.37</td>
<td>0.24</td>
<td>+0.14</td>
<td>1.69</td>
<td>2.21</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>CCH₂ + H → CCH₃</td>
<td>1.62</td>
<td>0.83</td>
<td>+0.78</td>
<td>1.71</td>
<td>2.49</td>
<td>1.75</td>
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<tr>
<td>17</td>
<td>H + CCH₂ + CH₂</td>
<td>1.07</td>
<td>0.16</td>
<td>+0.01</td>
<td>1.53</td>
<td>2.03</td>
<td>1.76</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>H + CCH₂ + CH₃</td>
<td>0.53</td>
<td>0.12</td>
<td>+0.41</td>
<td>1.82</td>
<td>2.48</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>H + CH₂ + CH₂</td>
<td>1.30</td>
<td>1.16</td>
<td>+0.12</td>
<td>1.67</td>
<td>2.46</td>
<td>1.74</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>H + CH₂ + CH₃</td>
<td>1.35</td>
<td>0.34</td>
<td>+1.01</td>
<td>1.45</td>
<td>2.47</td>
<td>1.76</td>
<td></td>
</tr>
</tbody>
</table>

* n.a means that the relevant value is not available.

3.1.7.3. Hydrogenation of CH₃CH₄ species. After formation of CH₃CH₄ species at the Mo-edge, the resulting species can either react further with surface CH₄ species or be hydrogenated to olefins or alkanes. For the sake of simplicity, we considered in this study only the formation of ethylene and ethane. The kinetic parameters for the hydrogenation steps that lead to formation of ethylene and ethane are listed in Table 5. We start this part of the discussion from the hydrogenation of CH₃ (x = 1–3) species (Figs. S14–S17). Hydrogenation of CCH and CH₂H₃ species at the Mo-edge results in CHCH and CHCH₂H₃, respectively. CCH and CH₂H₃ formation via association of C with CH and CH₃ at the bare Mo-edge involve high activation barriers. On the other hand, CH₂H₃ formation from direct coupling of C + CH₂ has a similar activation barrier (2.01 eV) and, once formed, this intermediate can be hydrogenated to CCH₃ with an activation energy of 0.92 eV or be dehydrogenated to CCH with an activation barrier of 0.42 eV. According to our calculations, hydrogenation of surface CCH₂ to CH₂H₃ at the bridge-Mo site is not feasible, as the C-end of CH₂H₃ is bonded at the atop-Mo site in such a way that it does not allow hydrogen to share the Mo atom for making a suitable transition state complex. Hydrogenation of CCH to CH₂H₃ is easier than its hydrogenation to surface acetylene (CHCH). The activation barriers for CH + H → CCH and CH + CH₂ → CHCH are 1.03 eV and 1.14 eV, respectively. Although the latter reaction has a slightly higher activation barrier, it is much more endothermic (+1.09 eV) than the former (+0.61 eV). The activation barriers for CCH₃ formation via hydrogenation of CCH are lower in comparison to direct C + CH₃ coupling. Once CH₂H₃ is formed, it can be hydrogenated to CH₂H₂ (CH₂H₂ + H → CH₂H₃) with activation and reaction energies of 0.92 eV and +0.87 eV, respectively. The activation barrier for surface vinyl (CH₂H₂) formation by hydrogenation of surface acetylene is very low (0.05 eV) and the reaction is slightly exothermic (ΔH = −0.15 eV). Surface vinyl (CH₂H₃) species formed by either of CH + CH₂ coupling or hydrogenation of surface vinyl may undergo hydrogenation either to CH₂H₂ or surface ethylene (CH₂H₃). Activation energies for CH₂H₂ and CH₂H₃ by hydrogenation of CH₂H₃ are 1.62 eV and 1.07 eV, respectively. The former reaction is highly endothermic (+0.78 eV) as compared to the latter (+0.01 eV). Thus, CH₂H₃ formation is thermodynamically more favorable than CH₃H formation. Another favorable route for surface CH₂H₃ formation can be via the hydrogenation of surface CCH₂. The activation barrier for the H + CCH₂ → CH₂H₃ reaction is 1.09 eV. The reaction is endothermic by 0.47 eV). The activation barriers for hydrogenation to ethyl and dehydrogenation to vinyl are 0.53 eV (ΔH = 0.41 eV) and 0.83 eV, respectively, showing that the hydrogenation reaction is kinetically favored. Surface ethyl formation is also possible by hydrogenation of surface ethylene. Ethylene (CH₂H₂) is strongly adsorbed (2.20 eV). In comparison, hydrogenation of surface ethylene to ethyl (CH₂H₃) is facile.
with an activation energy of 1.30 eV. The strong adsorption of ethylene and relatively low barriers for ethylene hydrogenation are consistent with the known ability of MoS$_2$ to hydrogenate alkenes to alkanes (Okuhara et al., 1977; Polyakov et al., 2008). The final step for ethane formation on the Mo-edge of MoS$_2$ is the hydrogenation for surface ethyl. The activation energy and reaction energy for ethane formation are 1.35 eV and 0.34 eV, respectively.

3.1.7.4. CH$_x$ + CO coupling reactions. When CH$_x$ species (x = 0–3) are co-adsorbed with CO at two adjacent bridge-Mo sites at the Mo-edge, the CH$_x$ species and CO adsorbates will repel each other and move to next-nearest neighbor bridge-Mo site due to the strong repulsion. We did not attempt to identify the transition states for these coupling reactions as they will be very high.

3.2. Microkinetics simulations on the bare Mo-edge of MoS$_2$

Microkinetics simulations were performed to predict the reaction rate and selectivity of CO hydrogenation on the Mo-edge of the MoS$_2$(1 0 0) surface. The kinetic parameters used in these simulations were determined using activation barriers and pre-exponential factors based on the DFT calculations. The microkinetics simulations with kinetics parameters for all relevant elementary steps for CO hydrogenation on the bare Mo-edge of MoS$_2$ is denoted as simulation I. Fig. 2 shows the turnover frequency (TOF) consumption of reactants (i.e., CO and H$_2$) and product formation (i.e., hydrocarbons, methanol, formaldehyde, CO$_2$, H$_2$O) as a function of temperature. At 975 K, the CO consumption rate is only $3.5 \times 10^{-3}$ s$^{-1}$. The maximum rate of $2.7 \times 10^{-4}$ s$^{-1}$ occurs at a very high temperature of 1225 K. At this temperature, the reaction order with respect to CO and H$_2$ are close to 1.5 and 0.5, respectively. Methane and water are the main products of CO hydrogenation and only small amounts of water and ethylene are formed as by-products, while the production of ethane and methanol remain very low. As a result of the higher overall barrier for CO$_2$ formation in comparison with that of H$_2$O formation, the dominant oxygen removal product is water. Investigation of the reaction network shows that CO dissociation only occurs via intermediate CHO formation (see Fig. 3).

Fig. 3 shows the surface coverage as a function of temperature. At relatively low temperature, the surface is completely covered by oxygen adatoms. The degree of rate control analysis shown in Fig. 4b indicates that at low temperature water formation is controlling the overall rate. Methane formation is rate inhibiting as its formation decreases the amount of hydrogen atoms at the surface needed to remove O adatoms. At very high temperatures when the surface is essentially empty, all DRC values are positive. OH hydrogenation and methane formation contribute equally to rate control under these conditions.

Clearly, the results of these simulations are inconsistent with experimental data with respect to reaction rates and product selectivity (Hou and Wise, 1985; Koizumi et al., 2004). The very strong binding of O to the bare Mo-edge leads to surface poisoning and too low predicted catalytic activity. A possible reason for this discrepancy is the presence of S atoms at the Mo-edge under reaction conditions (Gang et al., 1997). H$_2$S is known to play an important role in the water-gas shift activity of MoS$_2$ (Hou et al., 1983; Lund, 1996). It was shown that the presence of adsorbed S next to an adsorbed O atom lowers the energy for CO$_2$ formation. In order to obtain a first indication whether such effects may play a role here, we determined the barrier for CO$_2$ formation at different sulfur coverages (Fig. S18). Using CO$_2$ formation at the bare Mo-edge as a reference, the activation barrier for CO$_2$ formation at the Mo-edge is not reduced for a sulfur coverage of 12.5%. Increasing the sulfur coverage to 25% results in a substantial decrease of the barrier to 1.27 eV; the reaction energy is +0.86 eV. On the
37.5% sulfur-covered model, the activation barrier for CO₂ formation in the sulfur vacancy site is further reduced to 0.53 eV (Bollinger et al., 2001). In this model, an oxysulfide was formed. We failed to identify a stable structure with CO top adsorbed on Mo with O in the bridging site at a sulfur vacancy in the 37.5% sulfur-covered model. When we adopt the same model as in the literature (Shi et al., 2009), we find a barrier of 0.48 eV, which is close to the computed value (Shi et al., 2009) and consistent with the experimental activation energy for CO₂ formation in the water-gas shift reaction (Lund, 1996). Thus, our DFT calculations show that barrier of CO₂ formation is strongly reduced by co-adsorption of sulfur atoms.

We then carried out additional microkinetics simulations using a reduced barrier for CO₂ formation for the 25% sulfur-covered surface (termed as simulation II). The TOF as a function of temperature is given in Fig. 5. The corresponding product distribution is given in Fig. 6a. Assuming facile CO₂ formation results in formation of different products (see Fig. 7).

Hydrocarbons and carbon dioxide are formed in equimolar amounts over the whole temperature range, consistent with experimental data (Hou and Wise, 1985; Koizumi et al., 2004). Ethylene is the dominant hydrocarbon product below 675 K, while methane is the main product at higher temperatures. The amount of water formed is negligible, as are the rates of ethane, methanol and formaldehyde formation. At low temperature, the surface is mainly covered with CCH intermediates and a small amount of CO. At intermediate temperatures the surface contains CCH and H atoms, while at high temperature the surface is nearly empty. The DRC analysis (see Fig. 6b) shows that at low temperatures CH₃CH₂ desorption and association of surface CH with CH₃ are controlling the overall rate, while CH₃CH₂ hydrogenation to ethyl species has a
strong rate-inhibiting effect. The main reaction channel to form ethylene is \( \text{CH} + \text{CH}_2 \rightarrow \text{CHCH}_2 \) followed by the hydrogenation of the latter. Part of ethylene is desorbed. Some surface ethylene is hydrogenated to ethyl and then dehydrogenated to \( \text{CHCH}_3 \) and decomposed to \( \text{CH} \) and \( \text{CH}_3 \).

With increasing temperature, the reaction order with respect to hydrogen increases (see Fig. 8b), because the hydrogenation of \( \text{CH}_x \) to methane requires more \( \text{H} \) atoms than the hydrogenation towards ethylene. The reaction order with respect to \( \text{CO} \) becomes more negative with increasing temperature, as adsorption of \( \text{CO} \) lowers the coverage of \( \text{CH}_x \) species. Also, the DRC of \( \text{CH}_x \) hydrogenation to methane increases, while at the same time \( \text{CHO} \) dissociation becomes rate inhibiting. The apparent activation energy goes through a maximum.

3.3. DFT results for elementary steps on the 25% sulfur-covered Mo-edge

3.3.1. Adsorption energies

The adsorption energies related to the most stable geometries of the reactants, intermediates and products involved in CO hydrogenation on MoS\(_2\)(1 0 0) models with 0% and 25% sulfur coverages are given in Table 6. The adsorption energies for \( \text{CO}, \text{H}_2, \text{CO}_2, \text{ethylene} \) and formaldehyde are substantially lowered in the presence of co-adsorbed sulfur. The difference relates to the larger coordinative saturation of the Mo atoms to which these adsorbates bind as well as direct lateral interactions. The coordination number of Mo atoms of the bare Mo edge is 4, while two out of three Mo atoms of the 25%-covered Mo-edge have a coordination number of 5 and the other one has a coordination number of 4. It has been shown before that higher sulfur coverage at the Mo-edge results in lower occupation of the d-band of the Mo atoms (Raybaud et al., 2000). This explains why the adsorption energies of water and methanol, which preferentially adsorb on top of a Mo site with their oxygen-ends, are higher in the presence of co-adsorbed sulfur (less repulsion between the adsorbing O atom and the Mo atom with decreasing d-band occupation).

3.3.2. Formation of \( \text{C}_1 \) and \( \text{C}_2 \)-species

When \( \text{CO} \) and \( \text{H} \) are co-adsorbed on bridge-Mo sites of the 25%-sulfur-covered Mo-edge, the \( \text{H} \) atom cannot approach the C atom of adsorbed \( \text{CO} \) (Fig. S19). This means that \( \text{CHO} \) (formyl) formation, which is the dominant CO activation pathway at the bare Mo-edge, is not feasible on the partially sulfur-covered edge. A possible \( \text{CO} + \text{H} \) co-adsorbed state leading to \( \text{CHO} \) involves \( \text{CHO} \) adsorption on the bridge-Mo site with \( \text{H} \) present as a sulphydryl (−SH) species (see Fig. S20). In the initial state, the Mo−C bond distances for adsorbed \( \text{CO} \) are 1.99 Å and 2.19 Å, respectively for the 5- and 4-coordinated Mo edge atoms. The S−H bond distance in the initial state is 1.36 Å.

In the transition state, the S−H and C−H bond distances are 1.68 Å and 1.66 Å, respectively. The activation barrier for formyl
formation by hydrogenation of CO by sulhydryl is 1.19 eV; the reaction is exothermic by −0.44 eV. While CHO formation is kinetically favored at the bare Mo-edge, it is thermodynamically preferred at the partially sulfur-covered edge.

Surface formyl (CHO) can either be hydrogenated to CH₂O or dissociated into surface CH and O. We could not identify a transition state for CH₂O formation by hydrogenation of HCO involving the sulhydryl group. The activation energy for CHO dissociation into surface methylidyne (CH) and atomic oxygen (O) is 0.63 eV and the reaction energy is −1.37 eV. The activation barriers for these dissociation reactions are nearly similar for the bare and partially sulfur-covered Mo-edges. The reaction is however much more exothermic on the former. The reason is that the binding of the dissociated fragments CH and O is weaker in the presence of co-adsorbed sulfur.

The activation energy for surface formaldehyde (CH₂O) dissociation into surface methylene (CH₂) and atomic oxygen (O) is 0.76 eV and reaction energy is exothermic (−1.08 eV). In the initial state, the Mo–C and Mo–O bond distances of formaldehyde adsorbed at bridge-Mo site are 1.93 Å and 2.33 Å, respectively. The C–O bond length of formaldehyde is 1.40 Å. In the transition state, the Mo–C and Mo–O bond distances at the bridge Mo-site are 2.13 and 1.77 Å, respectively. In the transition state, the C–O bond is weakened as follows from the bond length of 2.23 Å. Similar to CHO dissociation, dissociation of adsorbed formaldehyde (CH₂O) becomes less thermodynamically and kinetically favored at the partially covered Mo-edge. Hydrogenation of surface formaldehyde to methoxide is not feasible on the 25% sulfur covered Mo-edge as the C atom in CH₂O cannot be approached by the Mo–H hydride species. This implies that methanol formation through methoxide hydrogenation is unlikely to occur on the partially sulfur-covered Mo-edge.

For methanol formation from hydrogenation of methoxide at the 25% sulfur covered Mo-edge, methoxide and hydrogen in the initial state (see Fig. S21) are co-adsorbed on the adjacent bridge-Mo sites. The activation energy for methanol formation by hydrogenation of methoxide (CH₃O) is 1.65 eV and reaction is endothermic by +0.79 eV. Table 7 shows that this elementary reaction is kinetically and thermodynamically more favorable at higher sulfur coverage. On the other hand, it should be mentioned that neither methoxide (CH₃O) nor methylol (CH₂OH) are likely to be formed on this surface.

### 3.3.3 Methane formation

The forward activation energies and reaction energies for all elementary steps in the hydrogenation of surface CH₃ (where x = 0–3) to gaseous methane (CH₄) are given in Table 7. The corresponding initial, transition and final states are shown in Fig. S22. Direct CO dissociation at the Mo-edge is difficult. Accordingly, it is more likely that CH is formed by CHO dissociation. The activation energy for methylene dissociation into atomic C and H is 1.30 eV with a reaction energy of −0.68 eV. In the transition state of CH dissociation, the Mo–H and C–H bond distances are 1.77 Å and 1.74 Å, respectively. Compared with dehydrogenation, hydrogenation of CH to CH₂ is more facile with a barrier of 0.54 eV; the reaction is exothermic by −0.23 eV. In the transition state of CH₂ formation from CH–hydrogenation, the Mo–H and C–H bond distances are 1.75 Å and 2.03 Å, respectively. Methylene can recombine with surface atomic O to form surface CH₂O, whose barrier is 1.84 eV. This barrier is higher than hydrogenation of CH₂ to methyl. The activation barrier for methyl formation at the bridge Mo-site is 0.99 eV with an exothermic reaction energy of −0.35 eV. The Mo–H and C–H bond distances in the transition state for CH₃ formation are 1.80 Å and 1.87 Å, respectively. The activation energy for CH₃ formation is 0.94 eV. This reaction step is endothermic by +0.48 eV. In the transition state, both methyl and H are attached to the same Mo atom. The relevant Mo–C, Mo–H and C–H distances in the transition state are 2.30 Å, 1.80 Å, and 1.57 Å, respectively. We have compared activation barriers for C hydrogenation to methane at the bare and partially sulfur-covered Mo-edges in Table 7. Clearly, the barriers of C and CH and CH₂ hydrogenation are significantly reduced and the reaction energy becomes more exothermic due to the presence of sulfur. On the other hand, the activation barrier for methylene hydrogenation to methyl is slightly higher at the partially sulfur-covered Mo-edge than at the bare Mo-edge. The activation barrier for methane formation is decreased from 1.48 eV at the bare Mo-edge to 0.94 eV at the 25% sulfur-covered Mo-edge. These

<table>
<thead>
<tr>
<th>Table 7</th>
<th>Comparison of activation energies and reaction energies for elementary reaction steps at the Mo-edge with 0% and 25% sulfur coverages. Computed forward and backward activation barriers (Eₐ and Eᵣ, respectively) and reaction energies (ΔH) are in relation to the most stable states found for the reactants and products, and include zero-point-energy (ZPE) corrections.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elementary reaction</td>
<td>0% S</td>
</tr>
<tr>
<td></td>
<td>Eₐ (eV)</td>
</tr>
<tr>
<td>CO + C → O</td>
<td>2.48</td>
</tr>
<tr>
<td>CO + H → CHO</td>
<td>0.94</td>
</tr>
<tr>
<td>SH + CO → CHO + S</td>
<td>−</td>
</tr>
<tr>
<td>CHO → CH + O</td>
<td>0.66</td>
</tr>
<tr>
<td>CH₂O + H + CH₂ + O</td>
<td>0.43</td>
</tr>
<tr>
<td>C + H → CH</td>
<td>1.06</td>
</tr>
<tr>
<td>CH + H → CH₂</td>
<td>0.87</td>
</tr>
<tr>
<td>CH₂ + H → CH₃</td>
<td>0.88</td>
</tr>
<tr>
<td>CH₄ + H → CH₄</td>
<td>1.48</td>
</tr>
<tr>
<td>CH + CH₂ → CHCH₂</td>
<td>1.38</td>
</tr>
<tr>
<td>CH + CH₂ → CHCH₃</td>
<td>1.02</td>
</tr>
<tr>
<td>CH₂ + CH₂ → CH₂CH₂</td>
<td>1.44</td>
</tr>
<tr>
<td>H + CH₂CH₂ → CH₂CH₃</td>
<td>1.61</td>
</tr>
<tr>
<td>H + CH₂CH₂ → CH₂CH₄</td>
<td>n.a.</td>
</tr>
<tr>
<td>H + CH₂CH₃ → CH₃CH₃</td>
<td>0.52</td>
</tr>
<tr>
<td>H + CH₂CH₃ → CH₃CH₄</td>
<td>1.31</td>
</tr>
<tr>
<td>O + CO → CO₂</td>
<td>3.26</td>
</tr>
<tr>
<td>CHO + H → CH₃</td>
<td>0.86</td>
</tr>
<tr>
<td>SH + CH₂O → CH₃O + S</td>
<td>−</td>
</tr>
<tr>
<td>CH₂O + H → CH₂O</td>
<td>1.17</td>
</tr>
<tr>
<td>SH + CH₂O → CH₃O + S</td>
<td>−</td>
</tr>
<tr>
<td>CH₂O + H → CH₃OH</td>
<td>2.25</td>
</tr>
</tbody>
</table>

* Not available, no transition state could not be identified for this elementary step.
calculated values are higher than reported values of 0.58 eV at the bare Mo-edge and 0.53 eV at a sulfur coverage of 37.5% (Huang and Cho, 2009; Shi et al., 2009).

### 3.3.4. CH + CH₄ coupling reactions

We have also determined at the 25% sulfur covered Mo-edge the energy barriers for the CH₂ + CH₃ coupling reaction steps that were earlier identified as the most facile ones at the bare Mo-edge. These elementary reactions and the corresponding computed kinetic parameters are given in Table 7. This table also includes the relevant data for hydrogenation steps resulting in ethylene and ethane.

We first investigated coupling of the adsorbed CH atom with CH₂ and CH₃ intermediates (see Fig. S23). For the CH + CH₂ coupling reaction, we considered methylidyne (CH) and methylene (CH₂) co-adsorbed on adjacent bridge-Mo sites. Compared to adsorption at infinite distance, the co-adsorbed configuration is less stable by 0.90 eV. The Mo–C bond distances of co-adsorbed methylene (CH₂) and methylidyne (CH) on the bridge-Mo site with a shared Mo atom are 2.32 Å and 2.29 Å, respectively. The difference in bond lengths indicates that CH is more strongly bonded to the shared Mo atom in comparison to methylene (CH₂). The activation energy for CH + CH₂ coupling is 1.17 eV. This elementary step is exothermic by −0.18 eV. The C–C bond distance in the transition state for this reaction is 2.44 Å. The Mo–C bond lengths of CH₂ and CH in the transition state for vinyl formation are 2.31 Å and 1.82 Å, respectively. In the final state, the vinyl group is adsorbed on the bridge-Mo site such that the CH-end of vinyl is at the top-Mo site with a Mo–C bond length of 1.90 Å (the Mo–C bond distance for CH₂-end of vinyl is 2.44 Å). The C–C bond length of CHCH₂ on the bridge-Mo site in the final state is 1.47 Å. We have also studied CH + CH₃ coupling at the partially sulfur-covered Mo-edge. Compared to adsorption at infinite distance, the co-adsorbed configuration is less stable by 1.28 eV. This destabilization is lower than for the CH₂ + CH₂ and CH + CH₂ cases. The activation energy for CHCH₃ formation by CH + CH₃ coupling is 1.76 eV. This reaction is thermoneutral (ΔH = +0.01 eV). The C–C bond distance in the transition state for CH + CH₃ coupling reaction is 2.13 Å. In the transition state, the Mo–C bond length of the methyldiene-end (CH) of CHCH₃ complex on the atop-Mo site is 1.84 Å, whereas the Mo–C bond length of methyl-end (CH₂) is 2.39 Å. In the final state, CHCH₃ is adsorbed on the atop-Mo site with the Mo–C bond length 1.90 Å. The C–H bond is elongated from 1.11 Å in the initial state to 1.17 Å in the final state due to the interaction of the H atom with a surface Mo atom. The Mo–H bond distance for CHCH₃ in atop-Mo site in the final state is 1.95 Å.

For CH₂ + CH₂ coupling to ethylene, we considered co-adsorbed methylidyne species at adjacent bridge-Mo sites, where they are 0.77 eV less stable than adsorption at infinite distance. The activation barrier for ethylene formation at the bare Mo-edge is 1.31 eV. This elementary reaction is slightly exothermic by −0.42 eV. The C–C bond distance in the transition state for CH₂ + CH₂ coupling reaction is 2.34 Å. The Mo–C bond lengths in the transition state for ethylene formation from direct coupling of methylene groups are 2.27 Å and 1.98 Å. In the final state, ethylene is formed at the bridge-Mo site with a C–C bond distance of 1.48 Å, which is 0.15 Å longer than the C–C bond length in gas phase. The Mo–C bond lengths for ethylene in the final state are 2.52 Å and 2.23 Å, consistent with the asymmetric adsorption mode at the bridge-Mo site (see Fig. S23 (bottom)). Comparison of ethylene formation via CH₂ + CH₂ coupling at the two edge models considered shows that the reaction becomes kinetically more favorable in the presence of sulfur. This partial sulfur coverage changes the nature of reaction from endothermic to highly exothermic. This is similar to the case for CH + CH₂ coupling.

### 3.3.5. Hydrogenation of CH₄CH₂ species

CH₄CH₂ species can either react further with surface CH₄ species or be (de)hydrogenated to olefins or alkanes. For the sake of simplicity, we considered in this study only the formation of ethylene and ethane. Structures involved in the hydrogenation of CH₄CH₂ species to ethylene and ethane are depicted in Fig. S24. We start this part of the discussion with the CHCH₂ₙ (n = 2–3) species. Hydrogenation of CHCH₂ and CH₂CH₃ species at the Mo-edge results in CH₂CH₂ and CH₂CH₃, respectively. We could not identify a transition state for the formation of CH₂CH₃. The activation barrier for surface ethylene formation by surface vinyl (CHCH₂) hydrogenation is 0.69 eV with an exothermic reaction energy (ΔH = −0.44 eV). The presence of sulfur on the Mo-edge shifts the reaction from endothermic without sulfur to exothermic. Adsorbed ethylene can be hydrogenated to ethyl or desorb. The adsorption energy of ethylene is 1.67 eV. In comparison, hydrogenation of surface ethylene to ethyl (CH₂CH₃) is easier with an activation energy of 0.84 eV. The strong adsorption of ethylene and relatively low barrier for ethylene hydrogenation are consistent with the known ability of MoS₂ to hydrogenate alkenes to alkanes (Okuhara et al., 1977; Polyakov et al., 2008). The final step for ethane formation at the Mo-edge of MoS₂ is the hydrogenation for surface ethyl. The activation energy and reaction energy for ethane formation are 1.23 eV and 0.34 eV, respectively.

### 3.4. Microkinetics simulations on 25% sulfur Mo-edge

Methane and ethylene formation rates as predicted by microkinetics simulations based on the complete reaction mechanism for the 25% sulfur-covered Mo-edge (model I) are shown in Fig. 9. Methane is the dominant product for three different models considered. Sticking coefficients for CO and H₂ were set to 10⁻³ and 10⁻², respectively, as they yielded kinetics in reasonable agreement with experimental data (vide infra, Table 8). We verified that simulations in which we only allowed CHO formation by reaction of adsorbed CO with SH groups yielded negligible methane formation rate (model II), whereas allowing only CHO formation through reaction of CO with Mo–H (model III) led to the same methane formation rates as predicted for model I.

In order to understand the very low consumption rate for model II in which reaction of CO with H as Mo–H is not included, Fig. 10 shows turnover frequencies in s⁻¹ for the formation of methane and ethylene as a function of temperature for CO hydrogenation on the MoS₂ edge for the full microkinetic model (model I), the microkinetic model in which CHO can only be formed via reaction of CO with SH (model II) and the microkinetic model where CHO forms only via reaction of CO with H (model III). Products not included in the graph have rates lower than 10⁻¹¹ s⁻¹ (reaction conditions: H₂:CO = 1, p = 20 atm).

![Fig. 9. Turnover frequencies (in s⁻¹) for the formation of methane and ethylene as a function of temperature for CO hydrogenation on the MoS₂ edge for the full microkinetic model (model I), the microkinetic model in which CHO can only be formed via reaction of CO with SH (model II) and the microkinetic model where CHO forms only via reaction of CO with H (model III). Products not included in the graph have rates lower than 10⁻¹¹ s⁻¹ (reaction conditions: H₂:CO = 1, p = 20 atm).](image-url)
shows the surface coverages and degree of rate control (DRC) values. H atoms are predominantly present as hydride species (Mo\(\text{H}^\text{A}\)) with a negligible amount of sulfhydryl (\(\text{A}\text{SH}\)) groups. H\(_2\) adsorption with respect to gas phase is exothermic on Mo sites, but endothermic on the sulfur atoms on the partially covered Mo-edge. CO and H compete for the Mo sites in this model at temperatures below 575 K. The rate-determining step at low temperatures is the formation of CHO by reaction of adsorbed CO with a sulfhydryl group (Fig. 10b). The low rate is then due to the very low SH coverage. With increasing temperature the rate-determining step shifts to direct CO dissociation. At higher temperature, the reaction order with respect to CO becomes unity as the surface becomes nearly empty. At 700 K, the highest rate is obtained with reaction orders with respect to CO and hydrogen being 1 and –0.02, respectively. CH\(_4\) and CO\(_2\) are the dominant products formed in equimolar amount in the simulations of model II.

Table 8

<table>
<thead>
<tr>
<th>Reaction conditions</th>
<th>(E_{\text{apparent}}) (kJ/mol)</th>
<th>Reaction orders</th>
<th>Turnover frequencies TOF (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P \text{ (bar)})</td>
<td>(T \text{ (K)})</td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>1</td>
<td>139</td>
<td>31</td>
<td>0.45</td>
</tr>
<tr>
<td>20</td>
<td>–80</td>
<td>80</td>
<td>0.21</td>
</tr>
<tr>
<td>80</td>
<td>585</td>
<td>62</td>
<td>–0.32</td>
</tr>
</tbody>
</table>

Experimental data taken from Santos et al. (2013), Hou and Wise (1985) and Kim et al. (2013).

We further concentrate on the complete microkinetic model I and show the rates of formation of different products (Fig. 11) and the surface coverages and DRC values (Fig. 12). Methane and carbon dioxide are the dominant products, which implies that the O atoms originating from CO dissociation are removed as CO\(_2\), while most of the C atoms are hydrogenated to CH\(_4\). Formaldehyde and ethylene are minor by-products, while the for- mation rates of methanol and ethane are negligible. As expected, the surface S groups are not hydrogenated during CO hydrogenation, that is to say the surface coverage with S atoms remains 50% throughout the simulation.

Different kinetic regimes can be distinguished on the basis of the surface coverages (Fig. 12a) and the degrees of rate control (Fig. 12b). The other relevant kinetic parameters are given in Fig. 13. In the 500–600 K range, besides 50% coverage with S atoms, the surface is covered by O atoms and methyl groups. In this temperature range, the rate-controlling steps are methyl hydrogenation to methane and CO oxidation to CO\(_2\). CHO dissociation to CH and O is strongly inhibiting the rate, because this reaction increases the surface coverage. It results in a negative reaction order with respect to H\(_2\). The apparent activation energy is high because of the high surface coverages. In the 600–900 K range, the O coverage decreases from nearly 50% to zero. In this regime, CO oxidation becomes less rate-controlling, while CHO dissociation will change from rate-inhibiting to rate-controlling. Moreover, CHO formation by hydrogenation of CO becomes also one of the rate-controlling steps. The maximum rate occurs just above 700 K. At the rate maximum, the only rate-controlling step is CO
oxidation with an O coverage of ca. 25%. At this temperature, the only other compound significantly covering the surface is H at a coverage of ca. 1%. The reaction orders with respect to CO and H2 at this temperature are 1 and 0.21, respectively.

At higher temperatures, the surface becomes nearly empty (except for the S atoms). Under these conditions, CHO formation and dissociation are the rate-controlling steps. In the high-temperature limit, CHO formation will control the overall reaction rate. As the reaction between adsorbed CO and H is controlling the overall rate, the reaction orders with respect to CO and H2 are 1 and 0.5, respectively. The negative apparent activation energy arises from the strong adsorption of CO and H as compared to the activation energy of the rate-limiting surface reaction step.

We have compared the simulated and experimental reaction orders and apparent activation barrier for CO hydrogenation on MoS2 at different reaction conditions in Table 8). The computed TOF and reaction orders at 800 K and 1 bar for model I are in close agreement with experimental data (Hou and Wise, 1985). The values of reaction order with respect to H2 and CO for these simulations are 0.45 and 1, respectively. On the other hand, whilst experimentally a positive apparent activation energy was reported under such conditions (Zaman and Smith, 2012), the simulations predict a strongly negative apparent activation energy. This may be largely due to overestimation of the binding energies in the DFT simulations. Below 585 K, the computed apparent activation energy is in much better agreement with experimental data in another study (Santos et al., 2013).

4. General discussion

We have employed combined DFT and microkinetics simulations to comprehend CO hydrogenation mechanism on the bare as well as partially sulfided Mo-edge of MoS2. The extensive DFT calculations done at the bare Mo-edge of the MoS2(1 0 0) surface show that this surface is active in CO hydrogenation. The potential energy surface for CO hydrogenation to methane, methanol and water is shown in Fig. 14. The energies for the elementary steps relevant to methanol formation are calculated relative to clean MoS2 surface and one CO and two H2 molecules. The diagram includes activation barriers for all elementary steps.

A microkinetic model based on parameters obtained for the bare Mo-edge predicts that methane and water are the predominant products with very low reaction rates. These predictions are at odds with experimental data (Hou and Wise, 1985; Koizumi et al., 2004). The reason is the strong binding of O to the bare Mo-edge as is evident from high activation barriers for water and CO2 formation. In an attempt to estimate the effect of co-adsorbed S atoms on the Mo-edge, we demonstrated that O removal via CO2 is much more facile in the presence of co-adsorbed S atoms. We used a simplified model in which we only
used the lowered barrier for CO₂ formation to determine the influence on the microkinetics and then found that methane and carbon dioxide are produced in equimolar ratio at relatively high temperature (T > 800 K), consistent with experiment (Hou and Wise, 1985; Koizumi et al., 2004). At lower temperatures, CHₓ + Cₓ Hᵧ coupling reactions become possible, resulting in ethylene as the main product. We predict that longer hydrocarbon chains will also be formed by similar chain growth mechanism; such reactions were excluded from the current model. The finding that higher hydrocarbons are formed is at odds with the predictions of Huang and Cho (Huang and Cho, 2009), emphasizing the need to carry out microkinetics simulations to predict product distribution based on complex potential energy diagrams. On the other hand, ethylene as a main product of CO hydrogenation on MoS₂ has been experimentally found, e.g. by Nielsen et al. for CO hydrogenation on (Co-promoted) MoS₂ (Nielsen et al., 1995). Consistent with our predictions, ethane is usually observed in relatively small amounts, an example being studies of CO hydrogenation on unsupported MoS₂ (Lee et al., 1994; Li et al., 1999). It is interesting to note the metallic character of the bare Mo-edge, also confirmed by DFT calculations and STM studies (Bollinger et al., 2001). CO hydrogenation on metallic Mo(1 0 0) resulted in a mixture of ethylene and methane (Logan et al., 1985). Possibly, other sides at for instance the S-edge may be involved in ethylene hydrogenation to ethane.

The observation that methane is the main hydrocarbon product at temperatures with reasonable CO consumption rates is consistent with literature (Hou and Wise, 1985; Koizumi et al., 2004). Although care has to be taken in comparing absolute rates from microkinetics simulations with experiment, it is interesting to note that the predicted TOF for simulation II (4.2 x 10⁻² s⁻¹) is much closer to the experimental value (0.017 s⁻¹) reported for MoS₂ (Kim et al., 2013) than the TOF for simulation I (<10⁻² s⁻¹). These values are compared at a temperature of 773 K, a pressure of 20 bar and a H₂/CO ratio of 1:1. On the other hand, it needs to be mentioned that kinetic parameters such as apparent activation energy and reaction orders do not correspond between experiment and predictions.

Nevertheless, from the viewpoint of the mechanism the finding that CO bond scission occurs hydrogen-assisted involving formyl (CHO) is consistent with spectroscopic and kinetic data from literature (Santos et al., 2013; Zaman and Smith, 2012). The reason for adopting hydrogen-assisted CO dissociation route compared to direct CO dissociation is relatively overall lower barrier (1.63 eV, derived from 0.66 eV for CHO formation and 0.97 eV for CHO dissociation into CH + O) for former compared to the barrier (1.53 eV) for direct CO dissociation. The preference of CHO dissociation into CH + O over CHO hydrogenation to formaldehyde (CH₂O) is due to the lower activation barrier for former (0.66 eV) than the activation barrier for the latter (0.87 eV). In addition, gaseous formaldehyde may not form due to its very high desorption energy (i.e. 2.65 eV).
on the bare Mo-edge. It rather prefers to dissociate into methylene and surface O with activation barrier of 0.43 eV, and reaction energy of $-1.43$ eV. Hydrogenation of CH$_2$O to CH$_2$OH is also not a feasible pathway due to higher activation barrier ($i.e.$ 1.76 eV). In the next step, methylene is hydrogenated to methyl with the activation barrier of 0.89 eV and the reaction energy of 0.70 eV. In the last step, surface methyl (CH$_3$) undergoes hydrogenation to methane (CH$_4$) with the activation barrier of 1.48 eV. This elementary reaction step is endothermic by $+1.30$ eV. Methanol is not formed in our simulations in agreement with experimental works showing that only traces of methanol were observed on unpromoted MoS$_2$ (Santos et al., 2013). Only a single report described formation of ethanol during CO hydrogenation on unpromoted MoS$_2$ supported on $\gamma$-Al$_2$O$_3$ (Chiang et al., 2012). The absence of methanol formation is due to the higher rate of CH$_2$O dissociation as compared with its hydrogenation. For methanol formation (green line in Fig. 14), formaldehyde is hydrogenated to methoxide with a barrier of 1.18 eV, which is much higher than formaldehyde dissociation. Hydrogenation of methoxide to methanol on the bare Mo-edge may not be a favorable reaction due to its high activation barrier of 2.21 eV. A possible reason is the high reactivity of the metallic Mo-edge.

The microkinetics simulations for CO hydrogenation over a partially sulfur-covered (25% S) Mo-edge of MoS$_2$ shows that reaction proceeds via a hydrogen-assisted CO dissociation mechanism, which is consistent with kinetic and spectroscopy indications reported in experimental literature (Santos et al., 2013; Koizumi et al., 2004). Predicted CO conversion rates are in the same range as experimental reaction data (Filot et al., 2015). Methane and carbon dioxide are the dominant products of CO hydrogenation obtained in a 1:1 M ratio, which is also in keeping with experimental reaction data (Hou and Wise, 1985; Chen et al., 2002). This indicates that the O atoms derived from CO dissociation are only removed from the surface as CO$_2$. In these simulations, the amounts of ethylene and ethane are negligible. Experimentally, ethane has been observed as a by-product formed in very small amounts during CO hydrogenation on unsupported MoS$_2$ (Woo et al., 1992; Liu et al., 2013; Kim et al., 2013).

A detailed reaction network analysis on the basis of the microkinetics simulations is shown in Fig. 15. CO dissociation occurs solely via the formyl intermediate. The formyl species is formed by reaction of adsorbed CO with H species adsorbed to Mo. SH groups are not stable under the given reaction conditions. Accordingly, CHO formation through the facile reaction of CO with SH does not contribute to the overall rate. The surface methyldiene fragment resulting from CHO dissociation is then converted to methane through consecutive CH$_x$ hydrogenation steps. The very small amount of ethylene is formed mainly through coupling of adsorbed CH$_2$ fragments. The removal of surface O atoms proceeds through recombination with CO. A DRC analysis shows that oxygen removal as CO$_2$ step is the rate-controlling step.

Overall, introducing sulfur atoms at the Mo-edge of MoS$_2$ leads to destabilization of the reaction intermediates. Consequently, association reactions become more exothermic and their activation barriers are lowered. While in the absence of S atoms the surface is poisoned by O atoms at reaction temperatures typically used in experiment, lateral interactions with co-adsorbed S atoms result in much lower O coverage. Consequently, reaction rates increase and are in reasonable agreement with experimental values.

### 5. Conclusion

Combined DFT calculations and microkinetics simulations performed to explore the mechanism of CO hydrogenation at the bare (as well as partially sulfided) Mo-edge of the MoS$_2$ (1 0 0) termination show that methane is the major product. Ethane, ethylene and methanol formation are produced in trace amounts in both models. Oxygen removal takes place as water or as carbon dioxide, depending on the model. Microkinetics simulations based on the kinetic data for the bare Mo-edge predict a very low reaction rate, inconsistent with experimental data. The low rate is due to surface poising by atomic O produced by C–O bond scission. In other words, the rate of O removal is too slow. In order to explore the effect of S atoms adsorbed on the Mo-edge, we studied the removal of O as CO$_2$ at a partially sulfur-covered Mo-edge model. This results in a strongly reduced barrier for CO$_2$ formation. Preliminary microkinetics simulations show that this reduced barrier for CO$_2$ formation provides improved catalytic reaction rates resulting in equimolar ratio of hydrocarbons ad CO$_2$ consistent with the experiment. It also explains the experimentally observed positive effect of H$_2$S on CO hydrogenation on MoS$_2$. Ethylene is predicted to be the dominant product at temperatures below 675 K, whereas methane is the dominant product at higher temperature.

According to our DFT calculations, reaction intermediates relevant to CO hydrogenation to methane and higher hydrocarbons become destabilized upon co-adsorption of S atoms at the Mo-edge of MoS$_2$. This results in substantial decrease in activation barrier for hydrogenation reactions as well as CO$_2$ formation. Microkinetics simulations show that methanation rates on the partially (25%) sulfur-covered Mo-edge are much closer to experiment than the very low predicted rates on the bare Mo-edge. In these simulations, hydrogen atoms are predominantly present as molybdenum hydride (–MoH). Sulphhydril (-SH) groups are present in negligible amounts during CO hydrogenation. As a result, CHO formation mainly occurs via hydrogenation of adsorbed CO from molybdenum hydrides. CHO dissociation provides surface methyldiene species which are hydrogenated to methane. Atomic oxygen produced is removed as CO$_2$ which is the rate controlling step under experimental reaction conditions reported in the literature. The kinetics of the partially sulfur covered Mo-edge results in reaction rates and reaction orders in close agreement with experimental data. Methane and carbon dioxide are the dominant products, indicating that CO$_2$ formation is the main oxygen removal pathway on MoS$_2$. Formaldehyde and ethylene are minor by-products, while the formation rates of methanol and ethane are negligible. Ethylene is produced by direct coupling of surface methylene species. The main conclusion is that the partially sulfur-covered Mo-edge provides a better model for CO hydrogenation to methane than the bare Mo-edge.

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### Appendix A. Supplementary material

Supplementary data to this article can be found online at [https://doi.org/10.1016/j.ces.2018.10.040](https://doi.org/10.1016/j.ces.2018.10.040).

### References


