



# Atomic scale analysis of sterical effects in the adsorption of 4,6-dimethyldibenzothiophene on a CoMoS hydrotreating catalyst



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## ABSTRACT

The low catalytic hydrodesulfurization (HDS) activity toward sterically hindered sulfur-containing molecules is a main industrial challenge in order to obtain ultra-low sulfur diesel. In this study we report a combined Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) investigation of the adsorption of the sterically hindered sulfur-containing molecule 4,6-dimethyldibenzothiophene (4,6-DMDBT) onto a hydrotreating model catalyst for the Co promoted MoS<sub>2</sub> (CoMoS) phase. The molecular adsorption occurs exclusively on the Co-promoted S-edge, most predominantly in a precursor-like diffusive physisorption referred to as delocalized  $\pi$ -mode. 4,6-DMDBT adsorption directly in a S-edge sulfur vacancy is observed exclusively in S-edge corner vacancies in an adsorption configuration reflecting a  $\sigma$ -coordination. STM movies reveal dynamic conversion between the  $\sigma$ -mode and an on-top  $\pi$ -adsorption providing a link between different adsorption sites and hence between the hydrogenation and direct desulfurization pathways in HDS. The low overall direct desulfurization activity of 4,6-DMDBT and related molecules is consistent with the low occurrence of S-vacancies on CoMoS S-edges predicted under HDS conditions in this study.

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## 1. Introduction

In hydrodesulfurization (HDS) catalysis, a major challenge is the removal of sulfur from sterically hindered sulfur-containing molecules containing sulfur in a position spatially shielded by the remaining functional groups of the molecule [1]. Improvement on this matter is of key importance to meet with new legislation demanding still lower sulfur content for transportation fuels [2–4] and the catalysis industry is hence compelled to find novel methods to increase the catalytic reactivity toward the refractory sulfur, mainly locked up in sterically hindered molecules.

This category of molecules includes alkyl-substituted dibenzothiophenes (DBT) among which the hardest to desulfurize are those having the alkyl placed in the 4th and/or 6th position of the molecule [5] such as 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), respectively. These molecules are especially challenging as the position of the methyl groups causes the sulfur atom to be spatially unavailable for adsorption [6,5]. Such components (4-MDBT, 4,6-DMDBT

and related molecules) are responsible for the majority of the residual sulfur content in the refined crude oil and hence generate a lower bar for the sulfur content in the treated oil. In order to increase the catalytic activity a deeper fundamental understanding of the molecular interaction between this category of molecules and the catalyst is needed.

Cobalt promoted single-layer MoS<sub>2</sub> (CoMoS) is the active phase of the MoS<sub>2</sub>-based industrial HDS catalyst. The CoMoS structure has been revealed in detail in previous atom-resolved microscopy and theory studies to reflect predominantly hexagonal MoS<sub>2</sub>-like nanoparticles terminated by two different edge types called Mo-edge and S-edge. The structural effect of the cobalt was concluded to be related to a selective substitution of Mo atoms along the S-edge [7–12]. In the literature there is broad consensus that the desulfurization activity of the CoMoS catalyst proceeds through two different pathways: the direct desulfurization (DDS) and the hydrogenation (HYD) pathway [13–16]. In the DDS pathway the sulfur atom is directly cleaved from the molecule upon hydrogenolysis of the C–S bonds, whereas in the HYD pathway the hydrogenation of the aromatic ring happens prior to desulfurization [14,17,18]. Studies have suggested that DDS and HYD occur at different active sites [19] and it has further been proposed that a

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diffusion step may be necessary for the HYD pathway [20–22]. The sulfur extrusion involved in both the DDS pathway and as the final step in the HYD pathway is believed to happen through molecular interaction with coordinative unsaturated sites (CUS) on the cluster edge, such as sulfur vacancies. There exists, however, some debate in the literature about the nature of such CUS and their role in the DDS and HYD pathway. Furthermore are S–H groups on the cluster edge speculated to be involved in both pathways as the source of H.

The sterically hindered sulfur containing molecules such as alkyl substituted DBTs (e.g. 4-MDBT and 4,6-DMDBT) are primarily desulfurized through the HYD pathway and generally have a very low DDS reactivity. The HYD pathway has the advantage that bonding flexibility is added by hydrogenating the benzene rings of the DBTs which distorts the planar structure of the molecule, allowing additional available adsorption-configurations onto sulfur vacancies which are generally believed to be unavailable for direct adsorption of the intact alkyl-substituted DBTs. Several adsorption geometries on MoS<sub>2</sub> have been considered for the HYD active sites including multiple vacancies and perimeter sites. It has been proposed that the first hydrogenation step in the reaction for sterically hindered molecules in the HYD pathway occurs in a planar configuration in which the molecule is adsorbed onto the cluster interacting through the conjugated  $\pi$ -system of the molecules [23]. Studies have proposed the active site for the HYD pathway to be the perimeter sites along the cluster edges, denoted the cluster brim. The conclusion was based on STM studies which first showed that the MoS<sub>2</sub> edges express a modified electronic structure visible as a bright brim in STM images [24], together with the finding that the small  $\pi$ -conjugated molecules, such as thiophene and pyridine preferentially interact with the brim of unpromoted MoS<sub>2</sub> nanoclusters [22,20,25].

Relative to the unpromoted MoS<sub>2</sub> nanoclusters, molecular adsorption is less studied on CoMoS due to the more complex morphology of the system arising from an additional element, Co, and the presence of two, instead of one, edge types in the CoMoS structure [26,7] (further discussed in Section 3.1). Previously DBT, 4-MDBT and 4,6-DMDBT adsorption on unpromoted MoS<sub>2</sub> has been studied; however, for CoMoS only DBT adsorption was reported until now [27].

Here we combine Scanning Tunneling Microscopy (STM) imaging and Density Functional Theory (DFT) calculations to study the adsorption of 4,6-DMDBT on a well-characterized CoMoS model system [10,7]. We activate the CoMoS phase by exposing the sample to atomic hydrogen to introduce S–H groups and sulfur vacancies to the cluster edges and then investigate the available adsorption modes. The most predominant 4,6-DMDBT adsorption mode appears on top of the cluster brim and we exclusively see this interaction on the Co-promoted S-edge on the CoMoS nanocluster as a diffusive  $\pi$ -bonded species. This configuration is considered to be a possible precursor state for HYD reaction as the mobility of the molecule indicates that it can scavenge multiple H atoms adsorbed on the edge sulfurs under HDS conditions. Static chemisorption of 4,6-DMDBT is observed in the experiment exclusively in corner S-vacancies in a  $\sigma$ -bonded adsorption, which is considered a precursor state to direct sulfur extrusion. Interestingly it was observed in a STM movie that the  $\sigma$ -adsorbed 4,6-DMDBT could reversibly transform into a static  $\pi$ -mode adsorption revealing strong evidence for a direct link between the adsorption on brim and sulfur vacancies. To explore the possible extent of the static chemisorption of 4,6-DMDBT in a corner vacancy, under catalytic relevant conditions, the vacancy formation energies were calculated for HDS conditions. The calculations however, predict a very low concentration of corner vacancies in CoMoS under HDS conditions and hence explain the low DDS activity for 4,6-

DMDBT in the industrial catalyst and, thus, confirm the preference for this molecule to react through the HYD pathway.

## 2. Experimental

### 2.1. Scanning tunneling microscopy

The experiment is carried out in a homebuilt, standard ultra-high vacuum (UHV) chamber equipped with a homebuilt Aarhus type STM. The synthesis is made on a Au(111) single crystal cleaned using sputtering and anneal cycles. The CoMoS nanoclusters were synthesized by e-beam evaporation of Mo and Co in an H<sub>2</sub>S atmosphere as reported in [10,7]. H<sub>2</sub>S was dosed into the chamber through a doser tube providing a controlled leak from a high pressure reservoir. This resulted in a local H<sub>2</sub>S pressure at approximately 10<sup>-6</sup> mbar at the sample surface. Simultaneously, Mo was evaporated onto the surface at a deposition rate of approximately 0.02 monolayer (ML) per minute to reach a 0.1 ML coverage. In the last part of the deposition Co was co-deposited to reach a Co coverage of 0.02 ML. Next the sample was annealed at 673 K for 10 min, still in the H<sub>2</sub>S atmosphere resulting in the CoMoS nanoparticles. The CoMoS is subsequently activated through exposure to atomic hydrogen to introduce vacancies and possibly SH-groups on the cluster edges [27]. Atomic hydrogen is used here as in previous studies, since molecular hydrogen at vacuum compatible pressures was not sufficiently reactive to create vacancies. The activation procedure was carried out by backfilling the chamber to 8 × 10<sup>-8</sup> mbar with molecular hydrogen and crack the hydrogen using an Oxford Applied Research TC-50 thermal gas cracker while keeping the sample at room temperature (RT). Subsequently the activated sample was flashed to 500 K.

Prior to the 4,6-DMDBT dosing the activated CoMoS/Au(111) sample was cooled in the STM body to approximately 190 K. 4,6-DMDBT was heated to 60 °C in a vacuum glass tube, to increase the vapor pressure, and dosed through a leak valve onto the sample at a chamber pressure of 2 × 10<sup>-9</sup> mbar for 2 min. The sample is transferred to the STM and investigated at both low temperatures (190 K) and again when the sample has reached RT. The cooling of the sample proved to be essential for the adsorption process; however once adsorbed, the molecules are still observed as the sample reached RT. In the full monolayer limit the molecules tend to pack in a ordered structure on the gold whereas lower coverages resulted in layer of mobile molecules partly fixed around the cluster perimeter.

### 2.2. Density functional theory

DFT calculations [28,29] were carried out using the DFT package GPAW, ASE [30–32] with the BEEF-vdW exchange-correlation functional using a real-space grid with a spacing of 0.18 Å. In order to computationally study different adsorption sites on the Co-promoted S-edge nanoparticle two different models were constructed representing the Co-promoted S-edges and the corners of the nanocluster. All the models were constructed using the calculated lattice constant of monolayer MoS<sub>2</sub>,  $a = 3.173$  Å, which agrees well with the experimental obtained value as well as other theoretical work [33]. The 4,6-DMDBT adsorption on gold was studied using a Au slab model with the calculated fcc lattice constant,  $a = 4.215$  Å, which agrees with experiments and other theoretical values [34,35]. The S-edge has been modeled with 6 × 4 stripes periodic in the  $x$ -direction. The Mo atoms on the S-edge are replaced by Co atoms as observed in MoS<sub>2</sub> nanoparticles promoted with Co [36,7]. The Co promoted S-edge is terminated in S monomers (50% sulfur coverage) as shown in previous studies [7]. Corners were modeled as a stepped stripe with four Co atoms

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