The hydrogenation and direct desulfurization pathway in thiophene HDS over Co promoted and non-promoted MoS$_2$. A density functional theory study.

Poul G. Moses$^1$, Berit Hinnemann$^2$, Henrik Topsoe$^2$ and Jens K. Nørskov$^1$

$^1$Center for Atomic-scale Materials Design (CAMD), Department of Physics, Building 307, Technical University of Denmark, DK-2800 Lyngby, Denmark
$^2$Haldor Topsoe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark

*pgmoses@fysik.dtu.dk

Introduction
As the global energy consumption rapidly increases and environmental legislations become stricter the need to upgrade low quality oil becomes even more urgent. In order to meet present day environmental legislations, refiners must remove even the most refractory sulfur containing species. This has forced refiners to significantly improve hydrotreating processes and further improvements are needed in the future. Therefore, it is essential to understand the reaction mechanism of hydrodesulfurization in atomic detail to obtain a basis for future improvements.

Materials and Methods
We have performed extensive density functional theory DFT calculations using the atomic simulation environment (ASE) and the planewave DFT code DACAPO. We have in order to study the importance of van der Waals (vdW) interactions for adsorption energies implemented the recently developed exchange correlation functional vdW-DF which includes van der Waals interactions in the real space DFT code GPAW.

Results and Discussion
In order to obtain insight into the atomic details of the hydrodesulfurization (HDS) reaction we have presently carried out a DFT study of the full reaction mechanism of thiophene hydrodesulfurization on Co promoted and non-promoted MoS$_2$ catalysts. We have investigated adsorption of key intermediates on both the Mo edge (10 1 0) and the S edge (1 1 0) with sulfur and hydrogen coverage corresponding to HDS conditions and thereby determined the most stable adsorption configurations. We have subsequently determined barriers and reaction mechanisms of hydrogenation reactions, SC scission reactions and active site regeneration reactions on sites at both edges leading to the construction of possible hydrogenation (HYD) pathways and direct desulfurization (DDS) pathways. Knowledge of the detailed reaction mechanism of thiophene hydrodesulfurization has led to important understanding of the nature of the active sites including the role of the two different edges and their interaction. Figure 1 shows a schematic overview over the complicated reaction pathways and edge interactions. Furthermore, it has provided insight into the mechanisms of inhibition of hydrogenation by heterocyclic compounds.

The effect of Co promotion and formation of the CoMoS phase on the DDS and HYD pathway has been investigated by detailed calculations of adsorption energies and barriers on the Co promoted S edge. It is found that Co promotion introduces a non-vacancy active site. Co promotion is found to increase the hydrogenation properties of the catalysts and increase the relative importance of the DDS pathway. Finally the importance of including binding due to van der Waals forces will be discussed based on a recently developed and implemented xc-functional.

Significance
Hydrotreating and HDS are of key importance in all refineries and the present studies provide detailed atomic scale insight into the nature of the active sites and the effect of promotion, which is highly valuable for future optimization of HDS catalysts. Furthermore, the very recent possibility of including vdW forces in DFT has allowed us to calculate the influence of vdW forces on adsorption energies and it is found that the increase in adsorption energies is significant.

Figure
A schematic overview over the reactions and MoS$_2$ structures involved in HDS of thiophene.

References