The direct deoxygenation reaction pathway of phenol and 2-ethylphenol over MoS$_2$-based catalysts: a DFT study

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Introduction

The increase in crude oil prices and desire to limit carbon dioxide emissions from fossil fuels implies the substitution of 20% of the conventional fuels with alternative fuels in the road transport sector by the year 2020 [1]. One possibility is to produce oil by pyrolysis of biomass such as wood waste, which is a renewable source. However, wood-derived bio-oil fractions resulting from this pyrolysis contain very important amounts (up to 45 wt%) of oxygenated compounds [2-4]. Therefore, upgrading of bio-oils by reducing their oxygen content is required to obtain a usable fuel. Hydrodeoxygenation (HDO), which occurs during hydroprocessing, refers to the high temperature hydrogen treatment of the feed to obtain oxygen-free molecules. Oxygen is then removed in the form of water. HDO of model compounds like phenol was carried out over typical hydrotreating catalysts but mechanisms remains unclear [5,6].

In this context, we investigated the adsorption and direct deoxygenation (DDO) reaction of phenol and 2-ethylphenol over MoS$_2$ and CoMoS catalysts, after finding the stable surfaces under HDO conditions. The DDO reaction is desirable since it limits hydrogen consumption compared to the hydrogenation pathway.

Computational Methods

The periodic density-functional theory (DFT) calculations were performed with the Vienna Ab initio Simulation Package (VASP) [7,8], including optimized projector augmented plane wave (PAW) method to describe the electron–ion interactions [9]. The transition state was located using the Nudged Elastic Band (NEB) method [10], and characterized by numerical frequency calculations.

Results and Discussion

We have first pointed out that the adsorption of an oxygenated compound through its oxygen atom (η_1) over insatured Mo or Co atoms was the most likely mode for the DDO reaction and leads to the activation of the C-O bond. According to the proposed mechanism, vacancy creation and electrophilic aromatic substitution to form a Wheland intermediate are the crucial steps of the mechanism. The rate determining step (rds) depends on the nature of the edge (metallic M or sulfur S) and on the promoter. Indeed, formation of the Wheland intermediate is the rds on the M edge of MoS$_2$ (Figure 1) whereas vacancy creation is the one on the S edge.
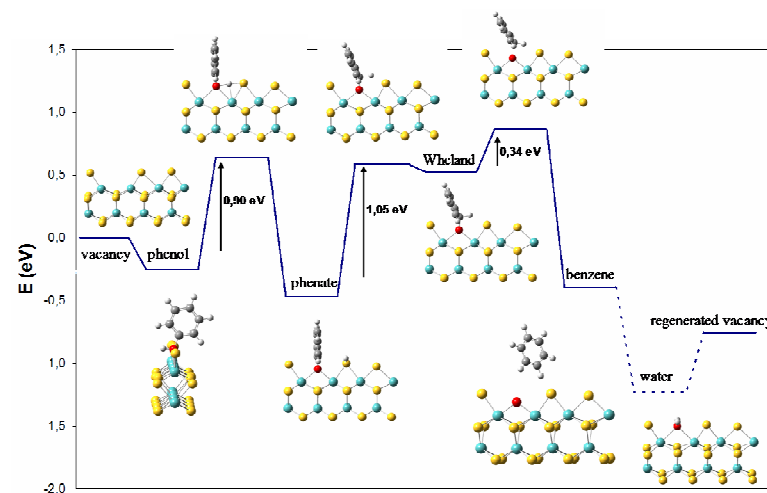

Figure 1. Direct Deoxygenation pathway of phenol over the M edge of MoS$_2$.

Nevertheless, on a cobalt promoted sulfur edge, the vacancy formation is easier which may explain the promoter effect of Co observed in the DDO pathway in experimental studies [5,6]. The understanding of the role of the promoter atoms in HDO process will favor the development of new catalytic formulations.

References

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