



## Effect of water on the stability of Mo and CoMo hydrodeoxygenation catalysts: A combined experimental and DFT study

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### ABSTRACT

We report the study of the impact of water on the stability of Mo and CoMo sulfide catalysts in hydrodeoxygenation of phenolic compounds. The presence of water at reaction temperature leads to an additional deactivation of the catalyst, which is fully reversible on the CoMo catalyst, but partly irreversible on non-promoted Mo catalyst. IR and HRTEM characterizations as well as DFT simulations confirm the higher sensitivity of unpromoted MoS<sub>2</sub> toward water and show that large amounts of water at reaction temperature lead to the exchange of an important fraction of edge sulfur atoms on non-promoted MoS<sub>2</sub> catalysts, hence changing the nature of the active sites. For Co-promoted catalyst, the extent of water poisoning is much lower and reversible because Co atoms prevent sulfur–oxygen exchanges. Hence, in HDO conditions, Co does not only increase the intrinsic activity of the catalyst (promotion effect) but also stabilizes the active phase in the presence of water (passivation effect).

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### 1. Introduction

The European Union, the United States and many countries are promoting the use of non-edible lignocellulosic materials to produce biofuels to lower the consumption of fossil fuels and the emission of carbon dioxide without competing with a growing global demand for agricultural commodities [1]. Some green fuels, such as diesel, could be based on liquids derived from pyrolysis of lignocellulosic biomass. However, the bio-oil fraction produced by pyrolysis contains large amounts of oxygenated compounds (up to 45 wt.%) [2–4]. These molecules present multiple functions like aldehyde, ketone, acids and alcohols. High oxygen content leads to deleterious properties such as high viscosity, thermal and chemical instability as well as lower heating values than fossil sources [3–5]. The later was explained by the fact that combustion of oxygenated compounds is much less exothermic than that of hydrocarbons [6]. Hence, upgrading of bio-oils is mandatory to obtain usable fuels. Catalytic hydrodeoxygenation (HDO), a variant of hydroprocessing, refers to treatment of the feed under high

temperature and hydrogen pressure to lower the oxygen content of the feedstock. Oxygen is removed as water or carbon oxides.

Sulfided hydrotreating catalysts such as CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> appear to be good candidates for HDO processing [3–10]. They are well-known catalysts and are extensively used in commercial hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) processes; fundamental studies (in-depth experimental and theoretical investigations) greatly contributed to the understanding of their mode of action [7,11–18]. It is now well accepted that their active sites are located on the edges of MoS<sub>2</sub> nanocrystallites corresponding to the (1 0 0) edge planes of their layered structure [7,13,16]. This crystallographic (1 0 0) plane exhibits alternate rows of sulfur- (hereafter called S, or sulfur edge) and molybdenum-terminated layers (hereafter called M or molybdenum-edge) [13,16].

Lignocellulose is composed of cellulose (~40 wt.%), hemicellulose (~25 wt.%), lignin (~25 wt.%), extractives and inorganics (~10 wt.%). Lignin consists of aryl ether units connected by ether and alkyl bonds, and the cleavage of those bonds yields monomeric phenols and methoxyphenols [19]. Consequently, pyrolytic oils derived from such feedstocks contain a large amount of phenolic compounds, up to ~30% of the total oxygenated compounds

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[6,20,21]. Over sulfide-based catalyst, alkyl-phenols follow two main deoxygenation routes: one involves hydrogenation before C—O cleavage (HYD route) and the second one is a direct C—O bond cleavage (direct deoxygenation or DDO route) [22–31].

The stability of the sulfided catalysts in the presence of large amounts of oxygenated compounds and water is critical and may lead to modifications of the structure of the active edges of the sulfide phase [3,32]. Sulfided hydrotreating catalysts usually undergo a continuous deactivation caused by coke formation or partial reoxidation of the sulfide phase [3,4]. Water is known to have a slight inhibiting effect on the hydrodeoxygenation rate of phenolic compounds [23,33,34] or real feeds [35], which were related to a weak interaction between water and active sites at high temperature. Such an effect was also explained by the formation of a sulfate layer covering the active phase and reducing the catalytic activity [22]. However, water can also have a slight promoting effect in reactions such as HDN reactions [36].

The aim of the present study is to investigate the influence of water on the structure and activity of MoS<sub>2</sub>-based sulfide catalysts using CO adsorption monitored by infrared spectroscopy (IR), high-resolution transmission electron microscopy (HRTEM), periodic density functional (DFT) calculations and catalytic activity measurements in HDO of 2-ethylphenol. Such a study will lead to a better understanding of sulfide catalysts and their active sites in working HDO conditions.

## 2. Materials and methods

### 2.1. Materials

The Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by conventional incipient wetness impregnation and supplied by TOTAL. Their chemical composition and textural properties are given in Table 1.

### 2.2. IR spectroscopy

For the infrared (IR) study, the catalysts were grounded and pressed into self-supported wafers. After introduction in a low temperature IR cell, sulfidation was carried out in situ under a flow of H<sub>2</sub>S/H<sub>2</sub> (10/90) at 623 K during 2 h and followed by an evacuation during 1 h at the same temperature. CO was adsorbed on the sample cooled at 100 K. Small calibrated doses of CO were introduced in the IR cell up to an equilibrium pressure of 1 Torr. The sample was further evacuated from low temperature to 623 K. Subsequent water treatment (4.5 Torr of H<sub>2</sub>O at equilibrium) was carried out at 623 K for 2 h and followed by evacuation at 623 K for 1 h. CO adsorption was repeated in the same conditions than previously described.

### 2.3. HRTEM analysis

Before HRTEM analysis, the catalysts were sulfided in the same conditions as for IR experiments. A fraction of the sulfided sample was contacted with water at 623 K during 16 h and followed by evacuation at 623 K for 1 h. A blank experiment was also done

where the sulfided catalyst was heated (without water) in the closed cell at 623 K during 18 h and evacuated at 623 K for 1 h. After these various treatments, the samples were transferred under Ar in a glove box, gently crushed under Ar and stored under Ar before microscopic analysis. A drop of a suspension of the solid sample in *n*-butanol was deposited on a 300 mesh “holey carbon film” grid and dried at 298 K under argon flow before introducing in the high vacuum chamber of the microscope. HRTEM was performed on a JEOL 2010. The field emission gun was operated at 300 kV. For each sample, stacking degrees and lengths of ~1000 MoS<sub>2</sub> crystallites were measured.

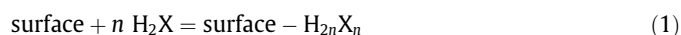
### 2.4. Computational settings

The density functional theory (DFT) calculations were performed with the Vienna Ab initio Simulation Package (VASP) [37] using the generalized gradient corrections proposed by Perdew et al. [38]. The wavefunction is expanded in a plane wave basis set, and the electron–ion interactions are described using the projector augmented plane wave (PAW) method [39]. The solution of the Kohn–Sham equations was improved self-consistently until a difference lower than 10<sup>−5</sup> eV was obtained between successive iterations. The calculations were performed with a cutoff energy of 450 eV and a Methfessel–Paxton smearing with  $\sigma = 0.1$  eV. Throughout this work, we used the large super cell (1.2641 × 1.2294 × 2.0000 nm<sup>3</sup>) shown in Fig. 1. It contains four elementary MoS<sub>2</sub> units in the *x* direction, four in the *z* direction and two layers along the *y*-axis. A *k*-point mesh (3, 1, 1) was chosen to give an accurate sampling of the Brillouin zone. A vacuum layer of 1 nm is located above the MoS<sub>2</sub> slab in the *z* direction in order to avoid interactions between slabs. The two upper rows were allowed to relax until forces acting on ions are smaller than 3 × 10<sup>−2</sup> eV Å<sup>−1</sup>. The two lower were kept fixed to simulate bulk constraints. Previous studies [16,17,40,41] showed that this model is suitable to predict the electronic and structural properties of the MoS<sub>2</sub> surface.

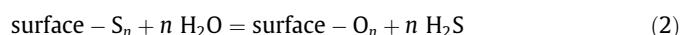
### 2.5. Thermodynamic treatment

Influence of the gas phase composition (H<sub>2</sub>O vs. H<sub>2</sub>S pressure) was taken into account by considering two reactions:

Adsorption of *n* H<sub>2</sub>X species (X = O or S) on the surface:



and S—O exchange reaction:



Gibbs free energy of Reaction (2), for example, was computed according to:

$$\Delta_r G = \mu(\text{surface} - \text{O}_n) - \mu(\text{surface} - \text{S}_n) + n(\mu(\text{H}_2\text{S}) - \mu(\text{H}_2\text{O}))$$

Assuming that the difference between the chemical potential of solid phases can be approximated by the difference in their electronic energy [42] led to:

$$\Delta_r G = \Delta_r G^0 + n RT \ln 10 \log P(\text{H}_2\text{S})/P(\text{H}_2)$$

where

$$\Delta_r G^0 = \Delta E_n + \Delta \mu^0(T)$$

and

$$\Delta E_n = E(\text{surface} - \text{O}_n) - E(\text{surface} - \text{S}_n) - n E(\text{H}_2\text{O}) + n E(\text{H}_2\text{S})$$

$\Delta E_n$  being the electronic energy contribution to the S—O exchange reaction.

**Table 1**  
Chemical composition, BET surface area and pore volume of the catalysts.

	Mo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>
BET area (m <sup>2</sup> /g)	251	255
Pore volume (cm <sup>3</sup> /g)	0.70	0.64
Mo (wt.%)	9.9	9.2
Co (wt.%)	–	4.2

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