



## Bio-oil hydrodeoxygenation: Adsorption of phenolic compounds on sulfided (Co)Mo catalysts

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### ABSTRACT

This paper reports the interaction of aromatic compounds (as phenol, ethylphenols, and guaiacol) representative of oxygenated functions of pyrolysis bio-oils, with sulfided (Co)Mo/Al<sub>2</sub>O<sub>3</sub> catalyst in order to determine the origin of catalyst deactivation in hydrodeoxygenation (HDO) reaction.

Infrared spectroscopy shows that all the studied phenolic compounds anchor on the alumina support as phenate-type species, whereas only the most basic ones (2(4)-ethylphenol and guaiacol) interact also with the sulfide phase. At 623 K (typical temperature of the HDO reactions), only phenate species on the support are formed that is confirmed by study of the catalyst tested in HDO reaction. Phenate-type species anchored on alumina hinder the accessibility of the sulfide edge sites. This shows that the nature of the oxygenated compound (basicity and nature of the substituent) as well as the surface properties of the catalyst support are crucial in the mode and extent of HDO active sites poisoning.

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### 1. Introduction

The increase in crude oil prices and environmental concerns in limiting carbon dioxide emissions implies the substitution of conventional fuels by new products issued of renewable sources. In European Union, 20% of the conventional fuels should be replaced by alternative fuels in the road transport sector by 2020 [1]. Since the development of bio-fuels should avoid competition with human food production, it is widely admitted that a sustainable route is the use of lignocellulosic biomass issued from agricultural and wood residues [2–6]. From the various thermochemical processes developed to produce liquids from solid lignocellulosic materials, fast-pyrolysis seems the most promising one because it does not need neither high pressure nor H<sub>2</sub> supply [7,8]. However, lignocellulosic-derived bio-oils resulting from fast-pyrolysis contain very important amounts of oxygenated compounds (up to 45 wt% O) [2,4,9]. Resasco [10] underlines that these bio-oils include three main families of compounds: (i) small acids, aldehydes and ketones, (ii) sugar-derived compounds, and (iii) lignin-derived phenolics. Consequently, the main challenges for production of bio-fuel from pyrolytic bio-oils are the elimination of oxygen, while retaining the carbon in the product, and with minimum hydrogen con-

sumption. In this aim, activity, selectivity, and stability of the HDO catalyst have to be optimized.

As recently reviewed, hydrodeoxygenation (HDO) appears as a very promising route that could produce bio-fuel at reasonable prices compare to fossil fuel [11]. The number of papers dealing with HDO have considerably increased in the last 10 years [3,5,12–14]. As emphasized by Hicks [7], the most important issue is the development of highly selective and durable catalysts.

Hydrodesulfurization/hydrodenitrogenation (HDS/HDN) catalysts based on mixed sulfides of (Co, Ni) and (Mo, W) dispersed on high surface area supports like  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are interesting candidates for HDO reaction. Some papers report their use in HDO of pyrolysis bio-oils [15,16]. But, as important quantities of oxygenated aromatic compounds are present in pyrolytic bio-oils [17], and as these molecules are known to be the most refractory ones, most of the HDO studies concentrate on oxygenated aromatics like anisole, phenol, 2-methoxyphenol (guaiacol), and other phenolic compounds.

It is generally reported that deoxygenation reaction occurs via two main routes: HYDrogenation (HYD) and Direct DeOxygenation (DDO) [18,19], this latter route allowing deoxygenation while minimizing H<sub>2</sub> consumption. Within the most recent papers, Bui et al. [20] shows that the DDO route involved in 2-methoxyphenol conversion is strongly increased versus HYD route after Co addition to MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. Romero et al. [18] emphasize the increase in the HDO rate with the addition of Co or Ni to Mo/Al<sub>2</sub>O<sub>3</sub> for

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2-ethylphenol HDO and point out a highest DDO/HYD selectivity for CoMo/Al<sub>2</sub>O<sub>3</sub>. Finally, Senol et al. [21] shows that CoMo catalyst exhibits higher activity than NiMo for phenol HDO. Therefore, the CoMo catalyst seems promising. Furthermore, on CoMo/ZrO<sub>2</sub>, the DDO/HYD selectivity is even better, showing that support change is an interesting way for H<sub>2</sub> economy [22].

However, deactivation of HDO catalyst is a key problem, and deactivation mechanisms are still unclear. Deactivation can be related to water effect (that can modify active phase or support), sintering of the active phase, or coking [23]. In our previous work [24], we showed that water effect is not the main factor in the deactivation of phenol HDO, and that Co addition to Mo/Al<sub>2</sub>O<sub>3</sub> allows to reduce this effect.

Therefore, deactivation of HDO catalyst is likely related to active phase sintering or poisoning by carbon deposition. Previous studies on HDS or HDN catalysts show that carbon is deposited under the form of polyaromatic species and can block the active sites of the catalyst [25]. Carbon deposition strongly depends on the type of feed. Due to their stronger interaction with the catalytic surface, alkenes and aromatics have the largest affinity for carbon formation relative to saturated hydrocarbons [11]. Besides, for oxygen-containing compounds, those with more than one oxygen atom appear to have a higher affinity for carbon formation by polymerization reactions [25]. Indeed, it has been shown that the interaction of phenolic compounds with sulfided catalysts produces these types of poison species [26–28]. Note that coking increases with increasing acidity of the catalyst, while acid sites are required in the mechanism of HDO [11].

The positive effect of H<sub>2</sub>S against deactivation has been shown in various papers [19,21,29–32]. H<sub>2</sub>S allows reactivating the sulfided phase. H<sub>2</sub>S could also prevent poison species formation. But besides, too much of H<sub>2</sub>S is known to inhibit HDO reaction [33].

To specify the role of the various components of the catalyst in the deactivation process, in our first work [34], we focused on the adsorption mechanisms of phenolic model compounds on oxides usually used as supports for hydrotreatment catalysts. Therefore, the adsorption of phenol, anisole and 2-methoxyphenol on alumina, silica, and silica–alumina was studied by IR spectroscopy. The main results show that at room temperature (RT), while phenolic-type compounds mainly interact via H-bonding with silica, chemisorption is the main adsorption mode on alumina, probably due to interaction of phenol with the Lewis acid–base pairs of alumina. At typical temperatures of HDO operating conditions ( $\approx 673$  K), the phenate species cover 2/3 of the alumina surface. These species are likely responsible for the deactivation of the catalysts supported on alumina.

To validate this hypothesis, we investigate the influence of phenolic-type molecules (phenol, ethyl-phenol, anisole, 2-methoxyphenol) on supported sulfided (Co)Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. In this aim, this paper focuses on (i) the identification of the adsorption modes of the oxygenated molecules on catalysts, (ii) the measurement of the accessibility of catalyst sites, (iii) the analysis of poison species on spent catalysts, and (iv) the validation of these results by a quantitative model.

## 2. Experimental

### 2.1. Materials

The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and (Co)Mo/Al<sub>2</sub>O<sub>3</sub> catalysts were supplied by TOTAL. Cobalt composition was measured by X-ray fluorescence spectroscopy (XRF) and the molybdenum content by Inductively Coupled Plasma (ICP) method. The origin and the properties of the oxides studied are given in Table 1.

Commercial oxygen-containing compounds phenol, ethylphenols, and 2-methoxyphenol were used (Prolabo for phenol and eth-

**Table 1**  
Characteristics of the support and catalysts.

	Al <sub>2</sub> O <sub>3</sub>	Mo/Al <sub>2</sub> O <sub>3</sub>	CoMo/Al <sub>2</sub> O <sub>3</sub>
Mo (wt%)	–	9.9	9.2
Co (wt%)	–	–	4.2
S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	252	258	243
Average slab length (nm)	–	2.4	2.6

ylphenols with purity of 99.5 wt%, Johnson Matthey Company for 2-methoxyphenol with purity of 98 wt%).

### 2.2. IR spectroscopy measurements

The IR experiments were performed using a FTIR Nicolet Magna AEM spectrometer equipped with a DTGS detector. Each spectrum corresponds to the accumulation of 64 scans at 4 cm<sup>-1</sup> of resolution using one zero filling level. Most of the spectra displayed correspond to difference spectra, that is, spectrum after adsorption (or desorption) minus the spectrum of the corresponding activated sample. All spectra are normalized to a constant mass (10 mg of dried catalysts for a disk of 2 cm<sup>2</sup>).

Each sample was pressed into a self-supported wafer (2 cm<sup>2</sup>, between 10 and 20 mg but precisely weighed), under a pressure of 10<sup>7</sup> Pa. Activation and adsorption/desorption steps of the various experiments were performed in situ in the infrared cell according to the procedures described in the following sections.

#### 2.2.1. Sulfidation procedure

The wafer was flushed under argon gas flow for 1 h at 423 K to remove adsorbed water and air traces and further cooled down to RT. Then, the sample was sulfided by heating from 298 K (RT) up to 623 K (ramp 3 K/min) under H<sub>2</sub>S/H<sub>2</sub> (10/90) flow at 30 mL/min. After 2 h sulfidation at 623 K, the temperature was decreased to room temperature. Then, an activation procedure was followed at 623 K (5 K/min) for 30 min to remove H<sub>2</sub>S.

#### 2.2.2. Phenolic compounds adsorption

Oxygenated compounds (20 Pa) were introduced on the pellet at RT or at 623 K maintained at this temperature for 15 min and further evacuated the adsorption temperature for 15 min.

#### 2.2.3. CO adsorption

**2.2.3.1. Experimental protocol.** In order to identify the catalyst sites involved in the interaction of oxygenated molecules, CO adsorption was applied before and after oxygenated compound introduction. Firstly, CO was introduced at about 100 K at equilibrium pressure of 133 Pa on the sulfided catalyst. After desorption of CO at 298 K, oxygenated compound (pressure of 20 Pa) was introduced on the sample at room temperature, followed by evacuation for 15 min at the adsorption temperature. Then, CO adsorption was performed in similar conditions than previously. In a second step, oxygenated compound was adsorbed at 623 K following the same procedure. CO was again adsorbed in the same conditions than previously.

**2.2.3.2. Calculation of the site concentration.** On sulfided CoMo/Al<sub>2</sub>O<sub>3</sub>, the adsorption of CO at  $\sim 100$  K gives rises to several bands characteristic of various species:  $\nu(\text{CO}/\text{Al}^{3+})$  at 2185 cm<sup>-1</sup>,  $\nu(\text{CO}/\text{OH})$  at  $\sim 2154$  cm<sup>-1</sup>,  $\nu(\text{CO}_{\text{physisorbed}})$  at  $\sim 2141$  cm<sup>-1</sup>,  $\nu(\text{CO}/\text{MoS}_2)$  at  $\sim 2109$  cm<sup>-1</sup>,  $\nu(\text{CO}/\text{CoMoS})$  at  $\sim 2070$  and  $\sim 2050$  cm<sup>-1</sup>. To quantify these species, spectral decomposition is required. The  $\nu(\text{CO})$  zone was fitted using Gaussian/Lorentzian curves. Area of each band was then obtained using the fitting procedure of the OMNIC

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