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# Effect of H<sub>2</sub>S and CO on the transformation of 2-ethylphenol as a model compound of bio-crude over sulfided Mo-based catalysts: propositions of promoted active sites for deoxygenation pathways based on an experimental study

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Promoted (CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub>) and unpromoted (Mo/Al<sub>2</sub>O<sub>3</sub>) catalysts were tested in the hydrodeoxygenation of 2-ethylphenol as a model compound of bio-crude under various partial pressures of H<sub>2</sub>S and CO. The catalytic tests were carried out at 340 °C under 7 MPa of total pressure in a fixed-bed microreactor. H<sub>2</sub>S, needed to maintain the sulfidation level of the catalysts, showed promoting or inhibiting effects depending on the catalyst tested and the deoxygenation pathway considered. Over the three catalysts, H<sub>2</sub>S was found to slightly promote the HYD pathway, which first involves the hydrogenation of the aromatic ring, whereas it strongly inhibited the DDO pathway, which consists of a direct C–O bond scission, particularly on the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. In addition, a strong though reversible inhibition by CO was found over CoMo/Al<sub>2</sub>O<sub>3</sub>. Differences in inhibition induced by H<sub>2</sub>S and CO observed over both promoted catalysts suggested that different active sites are involved in the hydrodeoxygenation of 2-ethylphenol, depending on the nature and the localisation of promoters and on the transformation pathway.

### Introduction

During the last century, economic development for a better standard of living has been instrumental in damaging the environment. We are now in a position whereby we are consuming more resources than ever, particularly fossil ones for transportation. However, many major improvements have already been achieved in the last decades regarding emission abatement, energy consumption and development of alternative technologies. The goals must be to give a positive answer in topics such as to use renewable feedstocks, to reduce the total mass consumed and the amount of energy needed, to improve recyclability, to lessen waste production.

Most of the world's energy demand is currently met by fossil fuels and they are being depleted fast.<sup>1</sup> This makes the development of new liquid fuels coming from biomass an attractive alternative.<sup>2,3</sup> Following the fourth recommendation of Anastas and Warner,<sup>4</sup> the European Union is committed to use non-food cellulosic and lignocellulosic biomass as a sustainable alternative for bio-fuel production.<sup>5</sup> Bio-oils derived from biomass, however, present a high oxygen content (between 20-55 wt%) depending on the biomass source and the transformation process used<sup>6-11</sup> due to numerous oxygenated compounds, such as acid derivatives, aldehydes, alcohols and phenolic compounds.<sup>12-14</sup> All these oxygenated compounds are responsible for some detrimental properties of bio-oils such as high viscosity, low volatility, corrosiveness, immiscibility with fossil fuels, thermal instability and a tendency to polymerize under exposure to air. Therefore, bio-oil upgrading to liquid fuel requires oxygen removal which can be achieved by a hydrodeoxygenation (HDO) process. Such a process is carried out under hydrogen pressure (4-10 MPa) and at moderate temperature (300-500 °C) where the catalysts usually used are sulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, promoted by metals of group VIII (Co, Ni).<sup>3,15-17</sup> Nevertheless, the sulfur content of bio-oils being very low, the addition of sulfur-containing compounds to the processed feed is required to maintain the sulfided state of such catalysts. As organosulfur compounds present in petroleum feedstocks lead to the formation of H<sub>2</sub>S by desulfurization, a co-hydrotreatment of bio- and fossil oils could be a solution, as already proposed recently in the literature.<sup>18-21</sup> This would allow operating the same production units and therefore obtaining an upgraded bio-fuel at affordable prices. The study of the effect of H<sub>2</sub>S during the HDO process using sulfided catalysts is therefore relevant.

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In order to ease the understanding of complex catalytic reactions, model molecules are often used. For the evaluation of sulfided catalysts in HDO, benzofuran,22-25 phenolic compounds,<sup>21,22,26-32</sup> and acid derivatives such as methyl heptanoate<sup>28,30,33-36</sup> were recently chosen as probe oxygenated molecules. The effect of H<sub>2</sub>S seems to be very dependent on the oxygenated molecule used, the experimental conditions and the type of catalyst (Ni(Co)Mo based catalysts). For example, in a similar temperature range (300-340 °C), it was reported that H<sub>2</sub>S inhibited the transformation of benzofuran over NiMo/Al<sub>2</sub>O<sub>3</sub> under 3.45 MPa of total pressure<sup>24</sup> but enhanced its conversion over NiMoP/Al<sub>2</sub>O<sub>3</sub> under 7 MPa.<sup>22</sup> An inhibiting effect of H<sub>2</sub>S during the HDO of phenolic compounds using sulfided catalysts is often described, <sup>26,30,35,37,38</sup> even if a promoting effect of H<sub>2</sub>S on the transformation of 2-ethylphenol over a NiMoP/Al<sub>2</sub>O<sub>3</sub> catalyst was recently reported.<sup>22</sup> It is also known that H<sub>2</sub>S strongly affects the selectivity of the catalysts. Indeed, phenolic compounds mainly lead to aromatics and cycloalkanes as deoxygenated products and their proportion depends on the partial pressure of  $H_2S$  used. In general, the formation of aromatic compounds is more affected by H<sub>2</sub>S than the formation of cycloalkanes, whatever the catalyst used (NiMo/Al<sub>2</sub>O<sub>3</sub> or  $CoMo/Al_2O_3$ ).

During the HDO process, the oxygen atom can be eliminated through water and/or carbon oxides production. In the case of benzofuran and phenolic compounds, water is the only oxygenated by-product while for acid derivatives, in addition to water, CO and/or  $CO_2$  are expected. It has been shown that water has a limited effect on deoxygenation of either phenolic compounds<sup>37,39,40</sup> or acid derivatives.<sup>34</sup> However, carbon oxides may have a negative impact on the deoxygenation rate. Indeed, carbon monoxide is frequently used as an infra-red probe molecule to characterize sulfided phases, since it is known to strongly interact with the edge sites of sulfided catalysts.<sup>41-44</sup> The high adsorption observed in these conditions suggests that some catalytic drawbacks can be expected if CO is formed during the HDO process or through the reverse water-gas shift reaction from CO<sub>2</sub>. Indeed, an important inhibiting effect of CO was recently reported over sulfided catalysts for hydrodesulfurization (HDS) reactions.45,46 However, to the best of our knowledge, its impact on hydrodeoxygenation has never been reported.

The aim of the present paper is first to confirm the influence of the promoter type (Co and Ni) on the activity and selectivity of three sulfided catalysts (Mo/Al<sub>2</sub>O<sub>3</sub>, NiMo/Al<sub>2</sub>O<sub>3</sub> and  $CoMo/Al_2O_3$ ) in the transformation of 2-ethylphenol used as a model oxygenated molecule. The effect of different partial pressures of H<sub>2</sub>S, produced in the reactional mixture by decompositon of dimethyldisulfide (DMDS), as well as the effect of CO are also investigated over the three catalysts. Despite many proposals from different studies, a complete understanding of the influence of H<sub>2</sub>S on the activity and selectivity of sulfided catalysts is still missing. In addition, as infra-red measurements of CO adsorption allow to distinguish promoted from unpromoted sites of sulfided catalysts, it can be expected that active sites could have a specific interaction with CO under reaction conditions. Potential differences in activity and selectivity in the course of a catalytic test might therefore lead to valuable information and help determine the nature and/or location of the active sites involved in

 Table 1
 BET area, pore volume and chemical composition of the catalysts in their oxide form<sup>29</sup>

	$Al_2O_3$	Mo/Al <sub>2</sub> O <sub>3</sub>	CoMo/Al <sub>2</sub> O <sub>3</sub>	NiMo/Al <sub>2</sub> O <sub>3</sub>
BET area (m <sup>2</sup> g <sup>-1</sup> ) Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	252 0.85	251 0.70	255 0.64	257 0.66
Mo(wt%)		9.9	9.2	9.3
Ni (wt%)	_	_	<b>4.</b> 2	3.9

**Table 2** Partial pressures in the gas phase in sulfidation and reactionconditions $^{29}$ 

	P <sub>total</sub> (MPa)	$P_{\rm H_2}$ (MPa)	P <sub>toluene</sub> (MPa)	P <sub>2-EtPh</sub> (kPa)	$P_{\rm H_2S}$ (kPa)	$P_{CH_4}$ (kPa)	P <sub>co</sub> (kPa)
Sulfidation conditions	4	2.674	1.068	_	129	129	_
Reaction conditions	7	5.750– 5.813	1.103– 1.181	49	10–49	10–49	0–30

HDO, with respect to the deoxygenation pathway and/or the promoter.

#### Experimental

#### Chemicals and catalysts

Dimethyldisulfide (DMDS, 98%), 2-ethylphenol (2-EtPh, 99%) and toluene (99%) were purchased from Aldrich. Carbon monoxide (1% in H<sub>2</sub>) and hydrogen (H<sub>2</sub>O < 5 ppm, O<sub>2</sub> < 5 ppm) were provided by Air Liquide. 2-Ethylphenol was distilled prior to use.

The three catalysts (Mo/Al<sub>2</sub>O<sub>3</sub>, NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub>) were provided by Total. The same alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was used to support all catalysts. Textural properties of the catalysts were determined by nitrogen physisorption on a ASAP 2000 Micromeritics instrument. The specific surface area was calculated from the linear portion of BET plots (*P*/*P*<sub>0</sub> = 0.05–0.30) and the pore volume at *P*/*P*<sub>0</sub> = 0.99. The Co or Ni composition was measured by XRF and the Mo content by ICP. Catalysts composition and support textural properties are presented in Table 1 for non-sulfided catalysts. All catalysts have comparable textural properties and Mo and/or promoter content.

The extrudates were crushed and sieved to a 250–315  $\mu$ m size range. The catalysts (50 mg of NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> or 100 mg of Mo/Al<sub>2</sub>O<sub>3</sub>) were diluted in carborundum to keep the volume of the catalytic bed constant. The catalyst weight was chosen in order to obtain a total molar conversion of 2-EtPh near 20%.

#### Sulfidation and reaction conditions

The catalysts were sulfided *in situ* in a dynamic flow reactor (length: 40 cm, inner diameter: 1.25 cm) using a sulfiding feed (Table 2) made up of hydrogen, DMDS and toluene. The sulfiding solution was injected at a starting temperature of 150 °C. After 1 h, the temperature was raised to 350 °C at a 5 °C min<sup>-1</sup> rate and then kept at 350 °C for 14 h. It was finally lowered to the reaction temperature (340 °C).

The catalytic tests were performed right after sulfidation in the same fixed-bed microreactor at 340 °C under 7 MPa of total pressure. DMDS was added to the feed to generate a constant partial pressure of H<sub>2</sub>S ranging from 10 to 49 kPa. The partial pressure of 2-EtPh was fixed at 49 kPa. The effect of H<sub>2</sub>S was measured with independent experiments. However, the effect of carbon monoxide was evaluated during a single experiment for each catalyst. CO was introduced after catalyst stabilization (after about 20 h on stream) at partial pressures set in the range of 2.5-30 kPa. After each exposition to CO (about 4 h), the catalytic activity was measured without CO until stabilization was observed. The total pressure was kept constant at 7 MPa by adjusting the partial pressure of hydrogen (Table 2). For a typical run, the contact time, defined as the ratio between the volume of the catalyst and the gas flow of 2-EtPh was close to 1.1 min for promoted catalysts (NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub>) and near 2.3 min for the unpromoted catalyst  $(Mo/Al_2O_3)$ . No transformation of toluene was observed under these experimental conditions.

#### Product analysis

The reactor effluents were condensed and liquid samples were periodically analyzed with a Varian 430 chromatograph equipped with a DB1 capillary column (length: 30 m; inside diameter: 0.25 mm; film thickness: 0.25  $\mu$ m) and a flame ionization detector. The oven temperature was first set during 5 min at 55 °C, then raised to 175 °C at a rate of 4 °C min<sup>-1</sup> and kept at 175 °C for 5 min.

Gaseous effluents (CO,  $CO_2$ ,  $H_2S$  and  $CH_4$ ) were analyzed online with a Varian 450 chromatograph equipped with an automatic sampling valve, two HayeSep Q columns (length: 0.5 m; inside diameter: 1/8 in; film thickness: 2.0 mm), a 13X molecular sieve (length: 1.5 m; inside diameter: 1/8 in; film thickness: 2.0 mm) and a thermal conductivity detector. A backflush procedure allowed the removal of organic compounds. The oven, block and filament temperatures were set at 40, 160 and 200 °C, respectively.

For example, the total catalyst activity (global reaction rate) was calculated according to the following equation:

$$A_{\rm tot} = X.F/W \tag{1}$$

where  $A_{tot}$  is the catalyst total activity (in mmol  $g^{-1} h^{-1}$ ), X the conversion of 2-EtPh, F the molar flow rate of 2-EtPh (in mmol  $h^{-1}$ ) and W the weight of catalyst (in g).

#### **Results and discussion**

# Effect of time on stream on the transformation of 2-EtPh over sulfided catalysts-probable causes of deactivation

The transformation of 2-EtPh over three sulfided catalysts  $(Mo/Al_2O_3, NiMo/Al_2O_3)$  and  $CoMo/Al_2O_3)$  was evaluated in the presence of 30 kPa of H<sub>2</sub>S in the feed (Fig. 1). Over these catalysts, 2-EtPh reacted according to three pathways, as already reported<sup>29</sup> and are presented in Scheme 1. The first pathway involved a direct C–O bond scission (direct deoxygenation route – DDO pathway) yielding ethylbenzene only. The second one led, after hydrogenation of the aromatic ring, to 2-ethylcyclohexanol. This alcohol was never observed



**Fig. 1** Effect of time on stream on the transformation of 2-EtPh over sulfided  $Mo/Al_2O_3$  (a),  $NiMo/Al_2O_3$  (b) and  $CoMo/Al_2O_3$  (c) at 340 °C under 7 MPa of total pressure in presence of 30 kPa of H<sub>2</sub>S in the feed. Total activity ( $\triangle$ ); HYD activity ( $\blacklozenge$ ); DDO activity ( $\square$ ); ACI activity ( $\blacksquare$ ).

in the reactional mixture owing to its high reactivity. By dehydration, it yielded a mixture of cycloalkenes (1- and 3- ethylcyclohexenes) and ethylcyclohexane as the main product (HYD pathway). As ethylbenzene was not hydrogenated into ethylcyclohexane under these conditions, these two pathways were parallel and independent. The third route (ACI pathway) mainly involving the acid properties of the catalyst support led to oxygenated products (phenol, 3-ethylphenol and diethylphenol isomers) by disproportionation and isomerization reactions.<sup>29</sup> They could be further deoxygenated following either the DDO or the HYD pathway, yielding mainly benzene, cyclohexane, diethylcyclohexanes and diethylbenzenes.

Fig. 1 shows the effect of time on stream on the activity of an unpromoted catalyst  $(Mo/Al_2O_3)$  and two promoted catalysts  $(CoMo/Al_2O_3 \text{ and NiMo}/Al_2O_3)$ . NiMo/Al<sub>2</sub>O<sub>3</sub> was



Scheme 1 Transformation pathways of 2-EtPh over sulfided Mo-based catalysts.<sup>29</sup>

the least stable of all catalysts used in the present study. Indeed, its residual total activity, calculated as the ratio between the total activity obtained after 30 h and after 1 h on stream, was 0.7 whereas it was close to 0.9 for both  $Mo/Al_2O_3$  and  $CoMo/Al_2O_3$ .

Contrary to the HYD route, the activity of the DDO pathway was quite stable for the three catalysts, since the residual activities were always close to 0.9. The difference in behavior for deactivation between these two pathways seems to indicate that the nature or the location of active sites for each pathway could be different.

The activity of the ACI pathway was also stable for all catalysts, as indicated in Fig. 1. Products formed through this pathway were mainly oxygenated and represented about 70 mol% of the products obtained by this route over both promoted catalysts and 84 mol% over the unpromoted catalyst. They were produced by disproportionation and isomerization reactions involving the acid properties of the support, as already mentioned.

The main reason for the deactivation of sulfided catalysts involves a loss of active sites that could be due to several phenomena such as coke formation and/or modification of the sulfided phase.<sup>47</sup> As shown in Table 3, all spent catalysts presented an increase in carbon content that could be contributed to coking. This amount was higher over NiMo/Al<sub>2</sub>O<sub>3</sub>, which could explain the important deactivation observed for this catalyst (Fig. 1). These results seem in contradiction with those reported by Guichard et al.48 which stated that carbon content was more important over CoMo/Al<sub>2</sub>O<sub>3</sub> than over NiMo/Al<sub>2</sub>O<sub>3</sub> after desulfurization of gas oil feedstocks. Consequently, the authors suggested that active sites on the CoMoS phase are more likely to be covered by coke than those on the NiMoS phase.48,49 The different behaviors can be explained in part by the different feedstocks used. Nevertheless, Murti et al.<sup>50</sup> observed that the carbon content was 1.3 times higher over NiMo/Al<sub>2</sub>O<sub>3</sub> than over CoMo/Al<sub>2</sub>O<sub>3</sub> after the hydrodesulfurization of straight run gas

 Table 3
 Chemical composition in carbon and sulfur of sulfided and spent catalysts

	% C	% S
Sulfided catalysts <sup>a</sup>		
Mo/Al <sub>2</sub> O <sub>3</sub>	1.3	5.3
CoMo/Al <sub>2</sub> O <sub>3</sub>	1.2	7.4
NiMo/Al <sub>2</sub> O <sub>3</sub>	0.4	7.9
Spent catalysts <sup>b</sup>		
Mo/Al <sub>2</sub> O <sub>3</sub>	3.9	5.1
CoMo/Al <sub>2</sub> O <sub>3</sub>	3.3	6.4
NiMo/Al <sub>2</sub> O <sub>3</sub>	4.7	6.1

<sup>*a*</sup> Sulfided catalysts were obtained after the sulfidation procedure described in the experimental part. <sup>*b*</sup> Spent catalysts were obtained after 30 h on stream in the transformation of 2-EtPh at 340 °C under 7 MPa of total pressure, in presence of 30 kPa of H<sub>2</sub>S.

oil, as observed in the present study. Even if carbon deposition should mainly take place on alumina,<sup>48,51</sup> it seems that the carbon content had no deactivating effect on the ACI pathway.

A second possible source of deactivation is the modification of the sulfided phases. It is now well accepted that they are made of crystallites which expose two types of edges: metallic and sulfur edges, and that active sites are coordinatively unsaturated sites (CUS) present on both edges. It has recently been proposed that coke precursors adsorb preferentially on metallic edges.<sup>52</sup> As the HYD pathway was the one showing the highest deactivation for the three catalysts, this might indicate that it probably requires active sites mainly located on the metallic edge, more sensitive to coke formation.

The sulfur content of the spent unpromoted catalyst seemed stable, as indicated in Table 3, even if it was lower than those measured for promoted catalysts. However, it is known that the presence of promoter (Ni or Co) allows a higher sulfidation level.<sup>53</sup> The loss of sulfur content for NiMo/Al<sub>2</sub>O<sub>3</sub> (about 23%) was the most significant and could also explain in part the important deactivation observed for this catalyst. The sulfur

loss over NiMo/Al<sub>2</sub>O<sub>3</sub> has actually been proposed as a main cause of deactivation during the desulfurization of thiophene.<sup>54</sup>

Another possibility is the loss of the promoted phase through the segregation of promoters.<sup>55</sup> For example, Guichard *et al.*<sup>48,49</sup> have recently reported that promoter segregation over CoMoS and NiMoS phases could be linked with sulfided catalysts deactivation. The authors suggested that Ni segregated from both the sulfur and metallic edges of crystallites, while Co might only segregate from the metallic edge. Their study<sup>49</sup> over NiMoP/Al<sub>2</sub>O<sub>3</sub> and CoMoP/Al<sub>2</sub>O<sub>3</sub> led them to conclude that with Co, deactivation was mainly due to coking, while with Ni as promoter, segregation and the MoS<sub>2</sub> phase modifications were responsible for the catalyst deactivation. In our case, as time on stream was relatively short and H<sub>2</sub>S was present in the reaction mixture, the conditions were probably insufficient to allow the segregation of the promoters (Ni or Co).

#### Effect of the promoter type-propositions of promoted active sites

Table 4 shows the activity for the three catalysts measured after 30 h on stream with 30 kPa of  $H_2S$  in the feed. The total activity was largely increased over promoted catalysts compared to the unpromoted one. The promoting effect was measured as the ratio between the activity of promoted (by Ni or Co) catalysts and the activity of the unpromoted catalyst. It ranged from 2.0 to 2.3, depending on the promoter. These results are in agreement with the fact that cobalt and nickel are known for weakening the metal-sulfur bond and therefore for increasing the number of sulfur vacancies (CUS) proposed as active sites for such a reaction.<sup>56-58</sup>

The relative importance of each pathway was very dependent on the catalyst. Over Mo/Al<sub>2</sub>O<sub>3</sub>, the contribution of both main pathways (ACI and HYD) was about the same after 30 h on stream in the presence of 30 kPa of H<sub>2</sub>S (Table 4). When Ni was present, the HYD pathway was enhanced and therefore became predominant. Indeed, the promoter effect of nickel on the HYD route was close to 3, while no promoting effect was measured on the DDO route. Over CoMo/Al<sub>2</sub>O<sub>3</sub>, both deoxygenation pathways were promoted, the DDO route in a larger extend than the HYD one. Therefore, the DDO/HYD selectivity was very dependent on the catalyst used and was always the highest over CoMo/Al<sub>2</sub>O<sub>3</sub>. These results are in line with previous studies reported with phenolic compounds.<sup>28,37</sup>

**Table 4** Activity and DDO/HYD selectivity measured after 30 h on stream in the transformation of 2-EtPh over sulfided catalysts at 340  $^{\circ}$ C under 7 MPa of total pressure in presence of 30 kPa of H<sub>2</sub>S in the feed. Promoting effects (defined as the ratio between the activity of a promoted and the unpromoted catalyst) are given in brackets for Co and Ni

	Mo/A	l <sub>2</sub> O <sub>3</sub> CoMo/Al <sub>2</sub>	O <sub>3</sub> NiMo/Al <sub>2</sub> O <sub>3</sub>
Activity (mmol g <sup>-1</sup> h <sup>-1</sup> ) Tota	al 10.5	24.6 (2.3)	21.4 (2.0)
HD	O <sup>a</sup> 6.8	20.7 (3.0)	17.3 (2.5)
HY	D 4.6	8.7 (1.9)	14.5 (3.2)
DD	O 1.5	10.4 (6.9)	1.3 (0.9)
AC	[ 4.4	5.5 (1.3)	5.6 (1.3)
DDO/HYD selectivity	0.33	1.18	0.09
" Activity in total deoxygena	ation.		

The difference in behavior between the two promoted catalysts could be explained in part by a different localisation of the promoters, Ni and Co. Based on density functional theory (DFT) calculations, it has been established that the most stable position for promoter atoms is in the substitution of molybdenum on the edges of the sulfided phase<sup>55,59-62</sup> leading to the Ni(Co)-Mo-S mixed phase model developed by Topsøe and coworkers.<sup>15,63,64</sup> For a CoMoS crystallite, close to a hexagon, the sulfur edge is supposed to be fully promoted while the metallic edge could be only partially substitued, depending on the sulfo-reductive conditions.55 As far as the NiMoS crystallite is concerned, it is close to a deformed hexagon exposing more metallic than sulfur edges. Moreover, it is proposed that Ni is preferentially located on metallic edges. As promoters are supposed to increase the number of vacancies, it is expected that the amount of active sites is more important on the sulfur edges of a CoMoS phase and on the metallic edges of a NiMoS phase. As the DDO pathway was promoted more over CoMo/Al<sub>2</sub>O<sub>3</sub>, it seems that DDO active sites could be preferentially found on the sulfur edges. On the opposite, the HYD active sites could likely be located on the metallic edges, as already proposed above to explain the deactivation of the HYD route.

It is worth mentioning that the adsorption mode of 2-EtPh is reasonably different for both pathways. Indeed, the carbonoxygen bond scission involved in the DDO pathway requires a  $\eta_1$  adsorption through the oxygen atom.<sup>65</sup> On the other hand, hydrogenation of the aromatic ring, needed in the HYD route, probably proceeds through a flat adsorption ( $\eta_5$  type).

Fig. 2 shows some representations of the promoted active sites proposed in several DFT studies<sup>44,55,57,62,66</sup> under typical hydro-treatment conditions and likely to be involved in deoxygenation



Fig. 2 Representations of probable promoted active sites from DFT studies described in the literature. NiMoS promoted metallic edge (a); CoMoS promoted metallic edge (b); CoMoS fully promoted sulfur edge (c); CoMoS fully promoted sulfur edge after S-shift (d).

reactions. Fig. 2a presents a NiMoS metallic edge where Ni has a square-planar sulfur coordination. Due to the higher density of Ni atoms on this edge and the fact that they are not covered by S atoms, the probability of the occurrence of two vacancies on two paired Ni atoms is increased, favoring a flat adsorption of 2-EtPh. Therefore, we propose that such a site could be active in the HYD pathway of 2-EtPh. In the case of the CoMoS phase, the metallic edge presents a lower promotion rate with five-fold Mo atoms and square-planar four-fold Co atoms, as depicted in Fig. 2b. Over these type of sites, the flat adsorption of 2-EtPh is probably slightly more hindered than over Ni-promoted sites presented in Fig. 2a, resulting in a higher promoting effect of Ni compared to Co for the HYD pathway, as observed in Table 4. Moreover, such sites could also allow an adsorption through the oxygen atom, contributing to the DDO activity.

On the other hand, as discussed earlier, the promotion level achieved on the sulfur edge is proposed to be more important when Co is used as promoter. Furthermore, the substitution of Mo by Co does not induce an important structural modification of the sulfur edge. As a consequence, Co is four-fold coordinated with S atoms in bridging positions as shown in Fig. 2c. On this edge, the creation of a vacancy is required to adsorb oxygenated compounds. It could be obtained by a shift of a S atom towards a neighboring Co atom, as reported recently by Badawi *et al.*<sup>67</sup> and presented in Fig. 2d. In addition, the authors proposed that the creation of such a vacancy is energy demanding contrary to the one presented in Fig. 2b. Active sites shown in Fig. 2b and 2d could be involved in the DDO pathway and therefore both the metallic and the sulfur edges could be active in the direct scission of the C–O bond. As a consequence, an important promoting

effect of Co on the DDO pathway was observed, as can be seen in Table 4. This is in accordance with results obtained by DFT calculations in the case of thiophene, which indicate that the adsorption energy through the sulfur atom is similar on both edges.<sup>45</sup> With respect to NiMo/Al<sub>2</sub>O<sub>3</sub>, due to the limited presence of Ni on the sulfur edges and the probable preference for a flat adsorption of the aromatic ring instead of an adsorption through the oxygen atom over metallic promoted edges (Fig. 2a), no promoting effect on the DDO pathway was noticed.

# Effect of $H_2S$ on the activity and selectivity of sulfided promoted and unpromoted catalysts

The effect of H<sub>2</sub>S on the activity of the three sulfided catalysts measured after 30 h on stream was studied in the range of 10-49 kPa. The three catalysts showed a different tolerance to  $H_2S$ : the activity of both Mo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> increased with the partial pressure of H<sub>2</sub>S whereas its effect on the activity of CoMo/Al<sub>2</sub>O<sub>3</sub> was more complex (Fig. 3a). Indeed,  $CoMo/Al_2O_3$  was more active in the presence of a low H<sub>2</sub>S pressure (10 kPa), whereas NiMo/Al<sub>2</sub>O<sub>3</sub> was more active when the pressure of H<sub>2</sub>S was increased. This can be explained by the fact that the main pathway over CoMo/Al<sub>2</sub>O<sub>3</sub> is the DDO route, which is strongly inhibited by H<sub>2</sub>S (Fig. 3c), while the HYD pathway, which is the main pathway observed over NiMo/Al<sub>2</sub>O<sub>3</sub>, appears to be slightly promoted by H<sub>2</sub>S (Fig. 3b). This is confirmed by negative apparent kinetic orders with respect to H<sub>2</sub>S for the DDO activity and the slightly positive ones observed for the HYD activity (Table 5). In all cases, Mo/Al<sub>2</sub>O<sub>3</sub> was roughly twice less active than the promoted catalysts. The



**Fig. 3** Influence of the partial pressure of  $H_2S$  on activities measured after 30 h on stream in the transformation of 2-EtPh over sulfided Mo/Al<sub>2</sub>O<sub>3</sub> ( $\blacklozenge$ ), NiMo/Al<sub>2</sub>O<sub>3</sub> ( $\blacksquare$ ) and CoMo/Al<sub>2</sub>O<sub>3</sub> ( $\bigtriangleup$ ) at 340 °C under 7 MPa of total pressure. Total activity (a); HYD activity (b); DDO activity (c); ACI activity (d).

Table 5 Apparent kinetic orders with respect to  $\mathrm{H_2S}$  for the transformation of 2-EtPh

	Total	HYD	DDO	ACI
Mo/Al <sub>2</sub> O <sub>3</sub> CoMo/Al <sub>2</sub> O <sub>3</sub> NiMo/Al <sub>2</sub> O <sub>3</sub>	0.77 -0.17 0.58	0.15 0.17 0.18	-0.36 -1.40 -0.54	1.48 1.20 1.70

DDO/HYD selectivity was therefore higher for a lower partial pressure of  $H_2S$ , especially in the case of CoMo/Al<sub>2</sub>O<sub>3</sub> where it was above 1 in presence of less than 30 kPa of  $H_2S$  (Fig. 4).



**Fig. 4** Influence of the partial pressure of  $H_2S$  on the DDO/HYD selectivity measured after 30 h on stream in the transformation of 2-EtPh over sulfided Mo/Al<sub>2</sub>O<sub>3</sub> ( $\blacklozenge$ ), NiMo/Al<sub>2</sub>O<sub>3</sub> ( $\blacksquare$ ) and CoMo/Al<sub>2</sub>O<sub>3</sub> ( $\bigtriangleup$ ) at 340 °C under 7 MPa of total pressure.

The difference in behavior between the DDO and HYD pathways as a function of the partial pressure of  $H_2S$  seems to confirm that the active sites involved in both deoxygenation routes are, at least in part, different. Similarly, the two parallel routes involved in the desulfurization of dibenzothiophenic compounds (namely HYD and DDS) were affected in a different way by  $H_2S$ . The DDS pathway was always more inhibited than the HYD route.<sup>68,69</sup> This is in good agreement with the proposal that sites involved in HDO and HDS reactions could be similar in nature.<sup>15</sup>

The inhibiting effect of  $H_2S$  on the DDO pathway of  $CoMo/Al_2O_3$ , as observed in Table 5, is in line with results presented in the literature.<sup>22,26,28,37</sup> It can be explained by a competitive adsorption between  $H_2S$  and 2-EtPh on the DDO active sites. After adsorption,  $H_2S$  can dissociate heterolytically on a DDO site described in Fig. 2d leading to two SH groups, as shown in Fig. 5. Such a modified active site cannot allow an adsorption through the O atom anymore, leading to a loss of the DDO activity when the partial pressure of  $H_2S$  increases.

The effect of  $H_2S$  on the DDO pathway for both  $Mo/Al_2O_3$ and  $NiMo/Al_2O_3$  was more limited since this route was less favored than over the  $CoMo/Al_2O_3$  catalyst. The absence of promoting effect of Ni and the comparable effect of  $H_2S$  on the DDO activity of both catalysts indicated that the DDO sites were similar in nature for  $Mo/Al_2O_3$  and  $NiMo/Al_2O_3$ . There could be a vacancy on a Mo atom on an unpromoted fragment. As  $H_2S$ had a limited effect over  $Mo/Al_2O_3$  and  $NiMo/Al_2O_3$  compared to  $CoMo/Al_2O_3$ , the vacancies present on an unpromoted phase seem to be less electrophilic than the vacancies involved over a CoMoS phase. Therefore the latters could favor the adsorption



Fig. 5 Saturated CoMoS fully promoted sulfur edge carrying SH groups.

and dissociation of  $H_2S$  and similarly the adsorption and the C–O bond scission involved in the DDO pathway.

Over the three catalysts,  $H_2S$  had no inhibiting effect on the HYD route indicating no competitive adsorption between  $H_2S$  and 2-EtPh over HYD sites. The same observation was made by Viljava *et al.*<sup>26</sup> for the deoxygenation of phenol over a CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. This could be explained by the fact that hydrogenation sites are proposed as less electrophilic than DDO sites<sup>32,37</sup> and could be less sensitive to the presence of  $H_2S$ .

A slight promoting effect of H<sub>2</sub>S was even noted since positive kinetic orders (close to 0.2) were calculated, as shown in Table 5. A similar promoting effect was also reported in the transformation of phenolic compounds over a NiMoP/Al<sub>2</sub>O<sub>3</sub><sup>22</sup> and a CoMo/Al<sub>2</sub>O<sub>3</sub>.<sup>37</sup> As a consequence, if the HYD active sites of the NiMoS phase are, for example, those described in Fig. 2a, they seem to be insensitive to the presence of  $H_2S$ , but cannot justify the increase of the HYD activity when the partial pressure of H<sub>2</sub>S increases. The contribution of other sites is needed to explain the positive role of  $H_2S$  in hydrogenation reactions. Accordingly, fully sulfided sites showing no vacancies could act as hydrogenation sites, as already proposed by several authors in HDS.54,69-73 Therefore, an increase of the partial pressure of H<sub>2</sub>S would result in a more important HYD activity, as observed experimentally. This saturation of vacancies could explain both the inhibition observed on the DDO pathway by loss of electrophilic active sites and the promotion of the HYD activity by an increase of hydrogenating sites. It could therefore be seen as a conversion of hydrogenolysis sites into hydrogenation sites in presence of  $H_2S$ , as proposed by several groups.37,74,75

As shown in Fig. 3d, the increase of the partial pressure of  $H_2S$  also had an influence on the ACI pathway, which mainly involves the acidic properties of the support. Indeed, the apparent kinetic orders with respect to  $H_2S$  were between 1.20 and 1.70 for this route (Table 5). It was reported that adsorption of  $H_2S$  on alumina can increase the Brønsted acidity of the support<sup>54,76</sup> and therefore ease isomerization and disproportionation reactions involved in this pathway. The presence of Co or Ni did not have any major influence on the activity of this pathway. This seems

to indicate that only the acidity of alumina is responsible for the presence of isomerization and disproportionation reactions.

#### Decomposition of DMDS in presence of carbon monoxide

Decomposition of DMDS towards  $H_2S$  and  $CH_4$  (eqn (2)) occurs over naked  $Al_2O_3$  but is twice more important over supported sulfided catalysts.

$$DMDS + 3H_2 \rightarrow 2CH_4 + 2H_2S \tag{2}$$

Table 6 summarizes the average partial pressures observed during the transformation of 2-EtPh over the three sulfided catalysts, in the presence or absence of CO. Considering that deoxygenation of 2-EtPh leads to the formation of water, two reactions can take place in the presence of CO and could modify the partial pressures in the gas phase:

$$CO + 3H_2 \leftrightarrows CH_4 + H_2O$$
 (3)

$$CO + H_2O \leftrightarrows CO_2 + H_2 \tag{4}$$

Eqn (3) and (4) being the methanation and the water-gas shift equilibria, respectively.

Nevertheless, as  $CO_2$  was never detected whatever the catalyst used, it seems that the water-gas shift reaction did not occur. Moreover, the fact that the partial pressures of H<sub>2</sub>S and CH<sub>4</sub>, in the absence and presence of CO, were comparable (Table 6) clearly outlined that no conversion of CO towards CH<sub>4</sub> was achieved. In conclusion, under our reaction conditions, CO was unreactive. The absence of Ni segregation under our experimental conditions can be highlighted since it is well **Table 6** Partial pressures of  $H_2S$  and  $CH_4$  measured in the presence and absence of CO during the transformation of 2-EtPh over sulfided catalysts

	$P_{\mathrm{H}_2\mathrm{S}}{}^a$ (kPa)	$P_{\mathrm{H}_{2}\mathrm{S}}{}^{b}$ (kPa)	$P_{\rm CH_4}$ <sup><i>a</i></sup> (kPa)	$P_{\rm CH_4}$ <sup>b</sup> (kPa)
Mo/Al <sub>2</sub> O <sub>3</sub>	29.9	29.4	29.8	29.0
CoMo/Al <sub>2</sub> O <sub>3</sub>	32.8	29.1	31.0	29.5
NiMo/Al <sub>2</sub> O <sub>3</sub>	30.7	30.9	31.6	28.8
<sup>a</sup> In absence of	CO. <sup>b</sup> In prese	nce of 30 kPa	of CO.	

known that metallic nickel catalyzes the methanation reaction. In addition, over all catalysts, the introduction of CO slightly decreased the decomposition of DMDS towards both  $H_2S$  and  $CH_4$  in similar proportions (less than 5%) as derived from Table 6.

# Impact of CO on the transformation of 2-EtPh over sulfided catalysts in presence of 30 kPa of H<sub>2</sub>S

The influence of carbon monoxide on the transformation of 2-EtPh over the three sulfided catalysts was evaluated in presence of 30 kPa of  $H_2S$  in the feed. Fig. 6 presents the activity obtained over the three sulfided catalysts as a function of the CO partial pressure. For all catalysts and whatever the partial pressure of CO applied, it was possible to fully recover the activity level obtained before exposition to CO, indicating, when observed, the totally reversible adsorption of CO on the sulfided phase.

No influence of CO was observed over  $Mo/Al_2O_3$  for both partial pressures of CO investigated (15 and 30 kPa). Consequently, the DDO/HYD selectivity was unmodified in



**Fig. 6** Effect of the CO partial pressure on activities measured after catalyst stabilization on the transformation of 2-EtPh over sulfided Mo/Al<sub>2</sub>O<sub>3</sub> ( $\blacklozenge$ ), CoMo/Al<sub>2</sub>O<sub>3</sub> ( $\bigtriangleup$ ) and NiMo/Al<sub>2</sub>O<sub>3</sub> ( $\blacksquare$ ) at 340 °C under 7 MPa of total pressure in presence of 30 kPa of H<sub>2</sub>S in the feed. Total activity (a); HYD activity (b); DDO activity (c); ACI activity (d).

the presence of CO (Fig. 7). This result clearly indicates that unpromoted sites are not affected by CO.



**Fig.** 7 DDO/HYD selectivity as a function of the CO partial pressure in the transformation of 2-EtPh over sulfided Mo/Al<sub>2</sub>O<sub>3</sub> ( $\blacklozenge$ ), CoMo/Al<sub>2</sub>O<sub>3</sub> ( $\bigtriangleup$ ) and NiMo/Al<sub>2</sub>O<sub>3</sub> ( $\blacksquare$ ) at 340 °C under 7 MPa of total pressure in presence of 30 kPa of H<sub>2</sub>S in the feed.

On the other hand, both promoted catalysts suffered from an inhibition due to CO, but in completely different proportions, as shown in Fig. 6. Over NiMo/Al<sub>2</sub>O<sub>3</sub>, the loss of total activity was practically linear and limited to less than 10% in the presence of the highest CO content studied (30 kPa). This decrease was mainly due to a slight inhibition of the HYD pathway (Fig. 6b) whereas both the DDO (Fig. 6c) and ACI (Fig. 6d) pathways were practically unaffected by CO addition. Nevertheless, the DDO/HYD selectivity was lower than 0.1 (Fig. 7), showing that the HYD route remained largely predominant over Nipromoted sulfided catalyst.

With respect to CoMo/Al<sub>2</sub>O<sub>3</sub>, the increase of CO content resulted in an increase of the inhibition level of its total activity (Fig. 6a). Indeed, it was already reduced from one third for an exposition to a low partial pressure of CO (2.5 kPa), and was halved at partial pressures above 20 kPa. As expected, a negative kinetic order with respect to CO was calculated between 2.5 and 33.5 kPa and found equal to -0.11 (Table 7). Interestingly, both deoxygenation pathways were affected at different levels. Whatever the partial pressure of CO applied, the DDO activity was the most inhibited with up to 75% of inhibition in the presence of 33.5 kPa of CO, but a low partial pressure of CO (2.5 kPa) already caused a loss of activity close to 50% (Fig. 6c). The same phenomenon was observed to a lesser extend for the HYD activity, for which the inhibition reached up to 55% in the presence of 33.5 kPa of CO (Fig. 6b). The apparent kinetic orders with respect to CO were -0.11 and -0.25 for the HYD and DDO pathways, respectively (Table 7), confirming a more significant inhibiting effect on the DDO route than on the HYD route. In fact, it seems that, in presence of a larger amount of CO,

 Table 7
 Apparent kinetic orders with respect to CO for the transformation of 2-EtPh

	Total	HYD	DDO	ACI
CoMo/Al <sub>2</sub> O <sub>3</sub> <sup><i>a</i></sup>	-0.11	-0.11	-0.25	0.01
NiMo/Al <sub>2</sub> O <sub>3</sub> <sup><i>b</i></sup>	-0.02	-0.05	-0.03	0.00

<sup>*a*</sup> Calculated between 2.5 and 33.5 kPa of CO. <sup>*b*</sup> Calculated between 6.5 and 29.7 kPa of CO.

both the HYD and DDO activities of CoMo/Al<sub>2</sub>O<sub>3</sub> would have been quite the same as the activities of the unpromoted catalyst. As shown in Fig. 7, the DDO/HYD selectivity of CoMo/Al<sub>2</sub>O<sub>3</sub> decreased with the increase of the quantity of CO introduced. The DDO route was the main transformation pathway of 2-EtPh in the absence of CO (DDO/HYD selectivity close to 1.2) while the HYD pathway became predominant for any CO partial pressure investigated (DDO/HYD selectivity near 0.5 in presence of 33.5 kPa of CO).

It is interesting to note that similar trends in terms of inhibition were obtained over the three catalysts for both the transformation of 2-EtPh and the decomposition of DMDS. Indeed, even if the latter was only scarcely inhibited, the effect was more pronounced over CoMo/Al<sub>2</sub>O<sub>3</sub>.

For all catalysts, as expected, the apparent inhibition of the ACI pathway was negligible (Fig. 6d), since CO does not modify the acidity of alumina, which is responsible for isomerisation and disproportionation reactions involved in this pathway. Nevertheless, for both promoted catalysts, the ACI product distribution revealed that oxygenated compounds accounted for 75% over NiMo/Al<sub>2</sub>O<sub>3</sub> and 90% over CoMo/Al<sub>2</sub>O<sub>3</sub>, when they represented only 70% in absence of CO for these two catalysts, confirming both the inhibition of the deoxygenation level and their different tolerance to CO.

Our results clearly show a competitive adsorption between CO and an oxygenated compound on the active sites promoted by Co, leading to a strong inhibition of the deoxygenation of 2-EtPh. Indeed, CO can be adsorbed through its carbon atom on cobalt over both edges, as depicted in Fig. 8, in accordance with DFT studies.44,45,67 Such an inhibiting effect was not observed for the unpromoted catalyst. These results are in agreement with those reported by Travert et al.,44 which indicate a considerably lower adsorption of CO over an unpromoted MoS<sub>2</sub> phase compared to any edge or promotion degree of a CoMoS phase. Similarly, the absence of inhibition by CO over Mo/Al<sub>2</sub>O<sub>3</sub> is in good agreement with the results obtained when the effect of H<sub>2</sub>S was investigated. Indeed, we propose that unpromoted vacancies involved in the DDO pathway are less electrophilic than the vacancies associated to Co and therefore the former should also be less sensitive to CO. With respect to active sites involved in the HYD pathway of the unpromoted catalyst, they



**Fig. 8** Adsorption of CO on a CoMoS fully promoted sulfur edge after S-shift (a), and on a CoMoS promoted metallic edge (b).

are likely to be fully sulfided sites and consequently unaffected by both  $H_2S$  and CO, as observed experimentally.

The differences in the inhibition of the DDO and HYD pathways observed over  $CoMo/Al_2O_3$  clearly indicate that both routes require different active sites. The levelling of the inhibition of both pathways at higher CO partial pressures towards the activity of an unpromoted catalyst might suggest that each route involves at least two distinct active sites: one involving cobalt, strongly disabled by CO and one due to molybdenum only, not affected by CO in the range of partial pressures investigated. The latter could reasonably be similar in nature to the ones present over the unpromoted catalyst and would explain why the activity of CoMo/Al<sub>2</sub>O<sub>3</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> are similar in the presence of a large amount of CO, as observed in Fig. 6.

The differences in CO inhibition between CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> confirm that different active sites are involved for both promoted catalysts in the deoxygenation of 2-EtPh. The weaker inhibiting effect of CO on the activity of NiMo/Al<sub>2</sub>O<sub>3</sub> could be explained by the lower adsorption energy of CO on Ni compared to Co, as already reported.44 In addition, since the sites involved in the DDO route of NiMo/Al<sub>2</sub>O<sub>3</sub> are not affected by the presence of CO, it is possible to confirm the hypothesis made to explain the effect of  $H_2S$ , *i.e.* that they are similar in nature to those present over Mo/Al<sub>2</sub>O<sub>3</sub>. This is in good agreement with the fact that Ni has no promoting effect on this pathway, as indicated in Table 4. On the other hand, CO slightly inhibited the HYD pathway of NiMo/Al<sub>2</sub>O<sub>3</sub>, the only Ni promoted route. In analogy with CoMo/Al<sub>2</sub>O<sub>3</sub>, we can consider that active sites of this catalyst are both unpromoted and promoted sites. As discussed above, the former are insensitive to CO. Considering that the promoted sites are mainly located on the metallic edge and are possibly described in Fig. 2a, they are scarcely affected by CO, confirming the low effect observed with H<sub>2</sub>S. This type of sites could be less electrophilic than those promoted by cobalt and described in Fig. 2b. This correlates with the difference of CO adsorption energy between Co and Ni.

## Conclusions

The present study evaluated both the influence of the hydrogen sulfide content and the impact of carbon monoxide on the hydrodeoxygenation of 2-EtPh over an unpromoted catalyst  $(Mo/Al_2O_3)$  and two promoted catalysts  $(NiMo/Al_2O_3)$  and  $CoMo/Al_2O_3$ ). Over this type of sulfided catalysts, 2-EtPh was deoxygenated *via* two parallel routes: one involving first the hydrogenation of the aromatic ring (HYD pathway) and the second consisting in a direct C–O bond scission (DDO pathway).

The global different tolerance to  $H_2S$  of CoMo/Al<sub>2</sub>O<sub>3</sub> compared to NiMo/Al<sub>2</sub>O<sub>3</sub> can be explained by the fact that  $H_2S$ strongly inhibits the DDO route, which is only promoted by Co and slightly increased the HYD route, which is mainly promoted by Ni. This clearly indicates that the sites involved in both pathway are, at least in part, different. Moreover, the strong affinity of CO for active sites present on CoMo/Al<sub>2</sub>O<sub>3</sub> compared to the weak inhibition observed over NiMo/Al<sub>2</sub>O<sub>3</sub> confirm differences between the active sites of both catalysts.

With respect to the DDO sites, they are vacancies that could be located on both edges (metallic and sulfur) of sulfided slabs. In the case of a CoMoS phase, this type of site is very sensitive to the presence of  $H_2S$  and CO due to a competitive adsorption with the oxygenated compound. In the case of NiMo/Al<sub>2</sub>O<sub>3</sub>, the DDO sites are similar to those present on the unpromoted catalyst since both DDO activities are comparable whatever the partial pressures of  $H_2S$  and CO studied. In addition as such sites are hardly affected by both  $H_2S$  and CO, they could be less electrophilic than those present over a CoMoS phase.

Concerning the HYD route, where a flat adsorption of the phenolic compound is required, the hydrogenation of the aromatic ring can take place over at least two different active sites. The first one could be two neighboring vacancies formed by two paired promoter atoms located on metallic edges. Such a site should be more present in the case of a NiMoS phase since Ni promoters are known to be more abundant on metallic edges than Co atoms. This could explain the higher promoting effect of Ni on the HYD pathway. The second type of HYD site could be a totally sulfided surface which is insensitive to  $H_2S$  and CO and could explain the HYD activity of an unpromoted catalyst.

If one aims for a lower hydrogen consumption during a sustainable HDO process, our results show that  $CoMo/Al_2O_3$  is the catalyst of choice as it is favoring the DDO pathway. Nevertheless, the probable presence of CO from deoxygenation of acid derivatives present in a large amount in bio-oils will considerably decrease its activity, whereas the one observed over a NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst should not be affected in a large extend. Similarly, H<sub>2</sub>S generated by desulfurization of fossil fuels will bring a limitation to the use of a CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst compared to NiMo/Al<sub>2</sub>O<sub>3</sub>, in the case of a co-hydro-treatment of fossil fuels and bio-oils. Consequently, despite its lower selectivity for the DDO route, a sulfided Ni-promoted catalyst seems to be the catalyst of choice for HDO reactions as it is less sensitive to inhibition by inherent by-products (CO and H<sub>2</sub>S).

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