Hydrodeoxygenation of 2-ethylphenol as a model compound of bio-crude over sulfided Mo-based catalysts: Promoting effect and reaction mechanism

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ABSTRACT

The hydrodeoxygenation of 2-ethylphenol was carried out under 7 MPa of total pressure and at 340 °C in a fixed-bed reactor over unpromoted Mo/Al_2O_3 catalyst and over two promoted catalysts ($CoMo/Al_2O_3$ and $NiMo/Al_2O_3$). For all experiments, dimethyldisulfide was added to the feed to maintain the sulfidation state of the catalysts. On these sulfided catalysts, the transformation of 2-ethylphenol is considered to proceed by three pathways: (1) prehydrogenation of the aromatic ring followed by a dehydration reaction leading to a mixture of alkenes (1-ethylcyclohexene and 3-ethylcyclohexene) and after hydrogenation leading to ethylcyclohexane (HYD pathway); (2) direct cleavage of the C_{sp2}–O bond leading to ethylbenzene (DDO pathway); (3) disproportionation and isomerization reactions leading to oxygenated products (phenol, isomers of 2-ethylphenol and diethylphenols) and their deoxygenated products (ACI pathway). The production of those oxygenated compounds mainly involved the support acidity. The presence of nickel and cobalt allowed an increase of the deoxygenation rate. Nickel only promoted the HYD pathway whereas cobalt promoted both the HYD and DDO pathways. Consequently, the DDO/HYD selectivity was very dependent on the catalyst used. The highest DDO/HYD selectivity was obtained for $CoMo/Al_2O_3$. Sulfur vacancies are proposed as active sites for both deoxygenation pathways of 2-ethylphenol, although other active sites (e.g. brim sites) could be involved to explain that the HYD pathway was always predominant. For both deoxygenation pathways, two probable mechanisms are described. The adsorption mode of the molecule most likely determines the deoxygenation route.

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1. Introduction

The worldwide energy demand continues to rise because of two main reasons: (1) the ongoing increase in world population, and (2) the growing demand by the developing countries to improve their standards of living. In addition, the fossil fuels, which meet most of the world's energy demand today, are being depleted fast [1]. Under this scenario the development of new liquid fuels coming from biomass is an attractive alternative [2]. The European Union is committed to use non-food cellulosic and ligno-cellulosic biomass as a sustainable alternative for bio-fuel production [3]. This kind of feedstock, unlike those from fossil fuels, has a high oxygen content (between 20 and 55 wt%) depending on the biomass source and the transformation process used [4–10]. A lot of oxygenated functions are observed in these oils such as acid, aldehyde, alcohol and phenolic groups [10–12]. For example, Marsman et al. [12] gave the composition of a beech pyrolysis oil which contained about 20 wt% of acids, 35 wt% of aromatic compounds (such as guaiacols and phe-

nolic compounds), 15 wt% of alcohols and 20 wt% of sugars. These oxygenated compounds are responsible for some detrimental properties of bio-oil such as high viscosity, low volatility, corrosiveness, immiscibility with fossil fuels, thermal instability and tendency to polymerize under exposure to air. Therefore, bio-oil upgrading to liquid fuel requires oxygen removal by a catalytic hydrodeoxygenation (HDO) in which oxygen is taken out in the form of water and/or carbon oxides under a high pressure of hydrogen [13]. To upgrade these bio-fuels without changing drastically the processing conditions, the use of sulfided Mo/Al_2O_3 catalysts, promoted by sulfides of group VIII (Co, Ni), is required. The presence of cobalt or nickel is known to increase the activity of molybdenum sulfide catalysts for hydrotreating reactions [14]. The model based on the so-called "Co(Ni)–Mo–S" structure proposed by Topsøe and coworkers [15–17] is most widely accepted nowadays to explain this promoting effect. It was proposed that the promoter (Ni or Co) donates electrons to molybdenum and leads to a weakening of the metal–sulfur bond [18,19]. The active site in these catalysts is accepted to be a sulfur vacancy (coordinatively unsaturated site: CUS) present on the edges of the MoS_2 slabs.

In most of the studies on hydrodeoxygenation reactions, phenolic compounds were used as model molecules [20–32]. Over

sulfided catalysts, it is generally accepted that phenolic compounds react through two pathways: one involving direct C–O bond scission (direct deoxygenation route – DDO) yielding aromatic products, and the other via prehydrogenation of the aromatic ring leading to cycloalkenes and cycloalkanes (HYD pathway) [20,22–25,27–29,32]. The latter pathway involves an alcohol as intermediate. When 2-ethylphenol (2-EtPh) was used as reactant, a third pathway was observed over a NiMoP/Al$_2$O$_3$ catalyst, leading to oxygenated products which involved the acid properties of the catalyst [32]. These oxygenated products were obtained by disproportionation and isomerization reactions. In the presence of cobalt as promoter, the DDO pathway was the main route of hydrodeoxygenation of phenolic compounds [20,22,24,27], whereas in the presence of nickel as promoter, the HYD pathway was always the more prominent [23,24,29,31,32]. For example, Laurent and Delmon [24] studied the transformation of 4-methylphenol in a batch reactor at 340 °C under 7 MPa of total pressure over sulfided NiMo and CoMo catalysts. In the presence of CS$_2$ as sulfiding agent in the feed to maintain the sulfided form of the catalyst, the authors reported that NiMo/Al$_2$O$_3$ was about twice as active as CoMo/Al$_2$O$_3$ in hydrodeoxygenation. In addition, the HYD/DDO ratio was 0.9 when cobalt was used as promoter and 20 in the presence of nickel. Under 1.5 MPa of total pressure at 250 °C in a flow reactor, Senol et al. [29] observed that CoMo/Al$_2$O$_3$ was more active than NiMo/Al$_2$O$_3$ for the hydrodeoxygenation of phenol. Benzene, obtained by the DDO pathway, was the major product over CoMo, whereas cyclohexane (the main HYD product) was the major product over NiMo. It was also reported that the DDO pathway is predominantly affected by steric hindrance of alkyl groups adjacent to the OH group [20,22,25]. Furthermore, 2-ethylphenol was the main oxygenated product observed during the transformation of benzofuran over sulfided catalysts [32–38]. It was also observed an inhibiting effect of benzofuranic compounds on the hydrodeoxygenation of 2-ethylphenol due to a competitive adsorption between these two types of compounds on the deoxygenation active sites [32,34].

As indicated above, nearly all the results reported on the hydrodeoxygenation of model oxygenated molecules over sulfided catalysts were obtained with NiMo/Al$_2$O$_3$ and/or CoMo/Al$_2$O$_3$. While the importance of the promoting effect is well quantified for hydrodesulfurization and hydrodenitrogenation [14], it appears that such data are not available for hydrodeoxygenation reactions. The aim of this paper is to evaluate the promoting effect of nickel and cobalt and to determine their influence on the two main hydrodeoxygenation pathways of phenolic compounds.

In this paper we examined the effect of cobalt and nickel promoters on the activity of a Mo/Al$_2$O$_3$-based catalyst in the hydrodeoxygenation of 2-ethylphenol used as an oxygenated model molecule. Its transformation was carried out in a fixed-bed reactor under conditions close to hydrotreatment process conditions (7 MPa and 340 °C) in the presence of H$_2$S to maintain the sulfidation level of the catalyst during the hydrodeoxygenation process. In order to evaluate the influence of the support, the activity and selectivity of γ-Al$_2$O$_3$ was studied under the same experimental conditions. Our aim is to discuss the nature of the catalytic active sites and the mechanisms involved during the hydrodeoxygenation over typical hydrotreating catalysts, and more particularly to iden-

tify if the DDO and HYD pathways occur on the same or on distinct catalytic centers.

2. Experimental

2.1. Chemical materials

2-Ethylphenol (2-EtPh, 99%), dimethyldisulfide (DMDS, 98%) and toluene (99%) were purchased from Aldrich and used without further purification.

2.2. Catalysts

All the catalysts (γ-Al$_2$O$_3$, Mo/γ-Al$_2$O$_3$, NiMo/γ-Al$_2$O$_3$, CoMo/γ-Al$_2$O$_3$) were supplied by TOTAL. Textural properties of catalysts and supports were determined by nitrogen physisorption on an ASAP 2000 Micromeritics instrument. The specific surface area was calculated from the linear portion of BET plots (P/P_0 = 0.05–0.30) and the pore volume at P/P_0 = 0.99. The cobalt and nickel composition was measured by XRF and the molybdenum content by ICP. The catalyst composition and the textural properties of the support (γ-Al$_2$O$_3$) and catalysts in the oxidic form are given in Table 1. For all catalysts, the same alumina was used. All catalysts have comparable textural properties and/or Mo and promoter content.

The acidity of the support was measured in absence of H$_2$S by IR spectroscopy of adsorbed pyridine (Nicolet Magna IR 550 Fourier transform spectrometer). The concentration of the Lewis acid sites (258 μmol g^{-1}) able to retain pyridine at 150 °C was determined by using the band at 1450 cm^{-1} with the extinction coefficient of 1.28 cm μmol^{-1}. No Brønsted acid sites were observed.

TEM analysis was performed on a Philips CM 120 instrument operating at 120 kV. Samples were dispersed in ethanol and deposited on a Cu grid previously covered with a thin layer of carbon. At least 25 micrographs (each corresponding to about 2700 nm^2) were evaluated, corresponding to about 200 particles, for each sulfided catalyst (Mo/Al$_2$O$_3$, CoMo/Al$_2$O$_3$ and NiMo/Al$_2$O$_3$). Particle sizes were similar for sulfided Mo/Al$_2$O$_3$ and CoMo/Al$_2$O$_3$ (near 3.2 nm) and were lower for sulfided NiMo/Al$_2$O$_3$ (Table 2). The stacking was also lower for NiMo compared to the two other catalysts. The presence of Ni$_3$S$_2$ or Co$_9$S$_8$ crystallites was not observed.

The percentages of carbon and sulfur present on the catalysts after the sulfidation step and after reaction were obtained by using an elementary analyzer (NA2100 analyzer, CE instruments). Before these analyses, the weakly adsorbed organic compounds over spent catalysts were eliminated by a Soxhlet extraction with dichloromethane.

Table 2
Average stacking and particle size of sulfided catalysts measured by TEM analysis.

Catalyst	Size (nm)	Stacking
MoS$_2$/γ-Al$_2$O$_3$	3.3	2.0
CoMoS/γ-Al$_2$O$_3$	3.1	1.6
NiMoS/γ-Al$_2$O$_3$	2.2	1.2

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

	γ-Al$_2$O$_3$	Mo/γ-Al$_2$O$_3$	CoMo/γ-Al$_2$O$_3$	NiMo/γ-Al$_2$O$_3$
BET area (m^2/g)	252	251	255	257
Pore volume (cm^3/g)	0.85	0.70	0.64	0.66
Mo (wt%)	–	9.9	9.2	9.3
Co (wt%)	–	–	4.2	–
Ni (wt%)	–	–	–	3.9