



Hydrodeoxygenation of guaiacol

Part II: Support effect for CoMoS catalysts on HDO activity and selectivity

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ABSTRACT

Bio-oils coming from ligno-cellulosic biomass are suitable material for the production of second generation biofuels. The oxygenated compounds have to be eliminated to confer good properties to these bio-oils and to permit their addition to traditional fuels. Hydrodeoxygenation (HDO) process which allows O-elimination by C–O bond cleavage under H₂ can be realized with the same type of catalysts as those used in HDS, supported CoMoS or NiMoS phases. In this work, the support effect associated with CoMoS catalysts has been investigated in guaiacol HDO reaction. Zirconia and titania supports have been compared with the traditional industrially used γ -alumina and it appeared that zirconia as support gave very efficient conversion of guaiacol into deoxygenated hydrocarbons with a totally different selectivity. The difference in selectivity allowed us to propose a different reaction scheme compared to γ -alumina and titania supported CoMoS.

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1. Introduction

The limited resources of crude oil, the increasing demand on fuel during these last years and the new environmental standards on the greenhouse gas emissions arouse a strong interest to develop the use of the biomass as new base for the fuels and petrochemistry. The liquid products of biomass resulting from pyrolysis or high pressure liquefaction, so-called bio-oils, contain less sulfur than classic fuels, but high oxygen proportion (about 15–40% mass) [1,2]. This characteristic confers on these bio-oils some deleterious properties like: high viscosity, corrosiveness, thermal instability and tendency to polymerize under exposure to air [3]. Thus, their practical use, asks for a treatment called hydrodeoxygenation (HDO) which consists in breaking the C–O bond of oxygenated molecules under hydrogen pressure. By comparison with other hydrotreating processes (HDS, HDN and HYD), HDO was not much studied by researchers because the oxygenated compounds are present in very low amount (less than 2%) in conventional crude. Academic research in the field of HDO calls up to now, the same types of catalysts as those used for the hydrodesulfurization (HDS) process: sulfided CoMo/Al₂O₃ or NiMo/Al₂O₃. In this way, if bio-oils are added to traditional fuels, the

whole feed can be hydrotreated (HDO and HDS) in the same process [4]. In previous studies, catalysts based on Mo supported on Al₂O₃ showed higher activity compared to potential other supports but they were rapidly deactivated by coke deposition due to the acidity of the alumina support [5,6]. To avoid this problem, some authors like Centeno et al. [5], Ferrari et al. [7,8] have used activated carbon like a “neutral” support to study the HDO reaction. They found that catalysts on the base of carbon support were more selective to deoxygenated products despite a lower activity. By modification of carbon surface sites by oxidative treatment, Grange et al. found that the selectivity in ester decarboxylation was dependant of the oxidation state of the carbon support before adding CoMo [9]. In which concerns some other supports potentially utilizable in HDO, it has been well established from HDS studies that TiO₂ and ZrO₂ supports presented very interesting properties for MoS₂ phase dispersion [10,11]. For dibenzothiophenic molecules conversion, MoS₂/TiO₂ allowed higher catalytic activity compared to traditional γ -alumina [12]. Several possible explanations have been given for the higher activity obtained with TiO₂ support like a favorable morphology, the formation of small crystallites of MoS₂, the reducibility or a higher sulfidability. ZrO₂ was also considered like an appropriate support for MoS₂ and good dispersion of the active phase can be obtained according to the preparation method leading to high hydroconversion of sulfur molecules [13–15]. Beside a high specific mass and an extreme hardness, it has both acidic and basic properties which could limit the coke deposition which would be a great advantage in HDO reaction. Recently, zirconia and sulfated zirconia

Abbreviations: DME, demethylation; DMO, demethoxylation; GUA, guaiacol; CAT, catechol; PHE, phenol; Me-CAT, methyl-catechol; Me-PHE, methyl-phenol.

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Table 1
Catalysts and supports textural properties.

	BET (m ² g ⁻¹)	wt% Co	wt% Mo	Mo at nm ⁻²
γ-Al ₂ O ₃	260	–	–	–
TiO ₂	120	–	–	–
ZrO ₂	96	–	–	–
MoS ₂ /γ-Al ₂ O ₃	230	–	7.8	2.1
MoS ₂ /TiO ₂	120	–	7.7	4.0
MoS ₂ /ZrO ₂	94	–	5.6	3.8
CoMo/γ-Al ₂ O ₃	190	2.1	8.3	2.7
CoMo/TiO ₂	112	2.0	7.4	4.1
CoMo/ZrO ₂	90	1.3	5.2	3.7

have been used as support for ReS₂ catalysts [16]. Nevertheless, the promotion of MoS₂ phase with cobalt or nickel on titania or zirconia has never reached the level of promotion obtained on γ-alumina in HDS reactions. This phenomenon has been tentatively explained by the morphology, the strength of interaction between the promoted phase and the support or an electronic effect but these hypotheses are still under debates and the catalytic activity of CoMoS phase supported on titania or zirconia is now investigated using different approaches and techniques [17–19].

Up to now, there are few researches devoted to the promoting effect in HDO reaction. In the first part of this work [20], we showed that promotion of the molybdenum sulfide phase by cobalt allowed a change in selectivity during HDO reaction. It has been clearly observed that CoMoS phase enhanced the C_(sp²)-O bond cleavage via a direct deoxygenation (DDO) pathway. The object of the present paper was to evaluate the support effect for promoted CoMoS catalysts in hydrodeoxygenation (HDO) reaction of guaia-col (GUA) or 2-methoxyphenol used as model compound as it is a typical phenolic compound present in pyrolytic oils. With this aim, MoS₂ and CoMoS phases supported on titania, zirconia and γ-alumina were prepared, characterized and have been tested in a continuous reactor. Catalytic activities and selectivities obtained for supports, unpromoted and promoted supported systems are reported and fully discussed.

2. Experimental

2.1. Preparation of catalysts

The catalysts were prepared by incipient wetness co-impregnation method with aqueous solutions of ammonium heptamolybdate and cobalt nitrate. The prepared catalysts contained about 3–4 Mo at nm⁻² with the atomic ratio Co/Co + Mo = 0.3 (Table 1). γ-Alumina, zirconia and titania were commercial supports (Norpro, Saint-Gobain) with initial surface areas of 260, 120 and 96 m²/g respectively. The supports were crushed and sieved to 80–120 μm size before impregnation. After impregnation and maturation overnight, the solids were dried at 383 K under vacuum condition for 10 h and calcined at 773 K for 3 h under air flow (4 L/h). Before each catalytic experiment, the catalysts were sulfided *ex situ* under H₂S/H₂ 15% (v/v) flow at 673 K for 4 h (rate: 10 K/min, flow rate: 4 L/h). At the end of the sulfidation step, the catalysts were cooled down under nitrogen flow and stored under argon.

2.2. Catalytic evaluation in GUA HDO

The catalytic equipment to perform GUA HDO experiments and the analytic conditions has been previously described [20]. In brief, a continuous fixed-bed reactor has been used under 4 MPa of H₂ at 573 K and with a partial pressure of GUA of 2.7 kPa. Hydrogen sulfide (H₂S) was added to reach a partial pressure of 400 Pa (100 ppm). The flow rate and mass of catalyst have been varied to

obtain contact times between 0.3 and 8 s. As the main objective of this study was to identify the primary products of the HDO reaction, the parameters of the reaction have been chosen to get the lower conversion as possible and the total flow rate has been varied during the experiment. The contact times which have been used to obtain these conditions were in the range 0.3–1 s. Catalytic activities measurements have been done at steady state after 12 h on stream at least. The selectivity was always compared at the same conversion.

The products were analyzed online by gas chromatography with a HP 5890 equipped with a flame ionization detector (FID) with CP-Sil5 capillary column (50 m × 0.32 mm × 5 μm). The condensed products trapped in liquid nitrogen were also analyzed by gas chromatography coupled with mass spectrometry (GC-MS Agilent 5975B) and the product identification was confirmed by manual injection of pure compounds on the same column. Response factors were determined experimentally using pure compounds and they served as a basis for the determination of the molar balance and the selectivity. The molar balance has been checked closed to 98% for each experiment.

According to the integral reactor model, and assuming a first-order reaction, the rate constant of reaction can be expressed according to the following equation:

$$k = -\frac{F_0}{wC_0} \ln(1 - \tau)$$

where τ is the total conversion, w is the catalyst weight (g), F_0 is the molar flow of reactant (mol s⁻¹), and C_0 is the initial concentration of reactant (mol L⁻¹).

The specific reaction rate (r , mol g⁻¹ s⁻¹) can be expressed by the following equation:

$$r = kC_0 = -\frac{F_0}{w} \ln(1 - \tau)$$

and the intrinsic reaction rate r_i (molec. Mo at⁻¹ s⁻¹) is expressed by

$$r_i = \frac{r}{n} * N$$

with n is the number of Mo atoms per g of catalyst and N is Avogadro number.

2.3. Acido-basic properties of the catalysts

The acidity of the supports used in this study was evaluated by the dehydration reaction of isopropanol in a flow reactor at atmospheric pressure under helium [21]. The partial pressure of isopropanol was maintained at 2.0 kPa in the reactor. The reaction was carried out at 473 K for alumina and titania and at 523 K for titania and zirconia because the catalytic activities were very different and it was not possible to compare the solids in the same conditions. The weight of catalysts varied between 80 mg and 200 mg, thus the GHSV was varying in the range 0.1–5 h⁻¹.

Supported CoMoS catalysts were evaluated in the transformation of *o*-xylene as it was already described in Part I for unsupported MoS₂ and CoMoS, in the same conditions than those used in GUA HDO (P(H₂) = 4 MPa, 573K, P(*o*-xylene) = 2.7 kPa) in a continuous flow reactor.

2.4. Raman spectroscopy

Raman spectroscopy has been used to optimize the loading of Mo onto TiO₂ and ZrO₂. The appropriate surface loading was chosen in order limit the formation of MoO₃ and CoMoO₄ undesirable species. Raman spectra were recorded with a LabRamHR spectrometer (Jobin Yvon) equipped an exciting line at 514 nm of an

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