Catalytic study in the HDO-HDT reaction of guaiacyl model compound for the direct valorization of biomasses pyrolysis oil

Lorenzo Spadaro, Alessandra Palella, Francesco Arena.

Abstract— **A catalytic study in the HDO-HDT reaction of biomass pyrolysis product derivates, as guaiacyls species (2-methoxyphenol) have been carried out by using refinery commercial catalysts timely sulfided in flowing H_2S at 400°C. Reaction kinetic studies were performed at high pressure (20 bar), and temperature (250°C). The reaction pathway in the hydrogenation process, approaching industrial conditions, has been assessed.**

Keywords— **biofuels production, bio-refinery, biomass valorization, catalysis, HDO-HDS processes.**

I. Introduction

The instability of energy market, the limited availability of fossil fuels and the development of more efficient vehicles call for the development of innovative fuels, timely "designed" to achieve the required industrial targets in terms of thermal efficiency, engine performance, low pollutant in exhaust gas emission, supplying, safety and manufacturing. Moreover, the implications in the actual climate change deeply regard the automotive sector, prompting the rise of "hybrid" or "bi-fuel" vehicles. On this address, TAR bio-oils [1] represent one of the most suitable and renewable "bio-fuel" for stationary and mobile application. In particular, the bio-oil for its easily availability, insensitivity to market fluctuations, low sulfur and metal content, CO_2 neutrality and low exploitation is strongly promoted by European Community [2], although its use is still under target. In spite of the considerable progresses done, the bio-oils from the pyrolysis of biomasses still suffer of several drawbacks, that strongly limit their use in large scale [2-6]. In particular, the characteristics of the pyrolysis bio-oils are very different from that of fossil petroleum. The sulfur content is negligible while they are rich in oxygenated molecules which are responsible for several deleterious properties of these crudes as high viscosity, low volatility, corrosiveness, thermal instability and tendency to polymerize under exposure to oxygen [1,2].

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Then, the large amount of refractory compounds, as the Guaiacyl species, and the unsaturated hydrocarbons chains, must be converted to be useful as alternative fuel or as liquid and easily storable hydrogen source for mobile applications [1,2,8]. One of the most widely studied route for the pyrolysis oil upgrading is represented by the catalytic hydrodeoxygenation (HDO), where oxygen is removed by utilizing high pressure hydrogen and heterogeneous catalysts [9-13]. Many model compounds, as phenols, esters, ethers and organic acids, were used to prove the performance of catalysts in the HDO process of bio-oils from wood pyrolysis [9-14], among the different model compounds, Guaiacyl species deserve of special consideration in reason of two factors: first, the huge content into the crude woody TAR and second the complexity of reactions and phenomena occurring during the catalytic HDO [11,15]. Recently, Mochizuki et al. [11] have analyzed the effect of catalyst reduction in the Guaiacol HDO reactions for Ni/SiO_2, Co/SiO_2, Pt/SiO_2 and Pd/SiO_2 catalysts, while Pinheiro et al. [18] have performed HDO/HDT process over sulfided $CoMo/Al_2O_3$ catalyst by co-feeding Straight-Run-Gas-Oil (SRGO) and Guaiacol as pyrolysis model compounds, ascertaining the feasibility of simultaneous treating oxygenates and hydrocarbons. In spite of the extensive work carried out, the influence of the chemical composition of bio-oils in the reactivity of molybdenum base catalyst in the HDO/HDT processes is still under debate [11]. Therefore, this work is aimed to disclose the potential use of TAR oil as alternative fuel and hydrogen source/vector by catalytic hydrogenation upgrading. Namely, a systematic study in the HDO of 2-methoxyphenol (Guaiacol) as model compound, approaching industrial condition, have been carried out by using alumina supported $CoMoS_2$ based catalysts.

II. Experimental

Commercial CoMo based catalysts, supported on alumina, with different chemical-physical properties, as summarized in Tab. 1, were in-situ sulfided at 400°C under flowing 60 stp cm^3min^{-1} H_2S (GHSV= 0.9 Nl $g^{-1}h^{-1}$) for 6 hours [1]. $CoMo/Al_2O_3$ catalysts were characterized by the means of XRD and XRF analysis, physisorptions and chemisorptions measurements and temperature programmed reduction (TPR).

Table 1. List of the catalysts with the chemical and physical properties

Catalysts	Chemical composition wt. %			Physical properties		
	CoO	MoO$_3$	Al$_2$O$_3$	S.A.$_{BET}$ (m^2/g)	A.P.D. (Å)	P.V. (cm^3/g)
HR-144	7.0	22.0	71.0	215	80	0.33
HR-145	7.1	22.3	70.6	163	50	0.16

Catalytic tests were performed by using a laboratory micro-plant equipped with a AISI 316 stain steel Plug Flow Reactor (i.d., 10 mm; o.d., 12 mm; l. 250 mm), loaded with 1.0 g of catalyst samples diluted (1/1, wt/wt) with inert 2 mm quartz spheres, reacting 30 stp cm^{3}min^{-1} of hydrogen gas mixture (i.e. H$_2$/H$_2$S/N$_2$ = 90/2/8) with 0.02 stp cm^{3}min^{-1} of liquid reactants mixture, using nitrogen as internal standard. Catalytic tests were carried out at 20 bar and 250°C, while the composition of reactants and products were online monitored by using a GC model Agilent 7890A, equipped with a triple-column analytical system connected to FID and TCD detectors [1].

Conversion values were calculated either by the internal N$_2$ standard (1) or mass-balance (2) methods:

$$\chi_{H2} = 1-[(H_{2,out}/H_{2,in})\cdot(N_{2,in}/N_{2,out})] \quad (1)$$
$$\chi_{Pi} = P_{i,out}/(\Sigma_{prod.} + P_{i,out}) \quad (2),$$

Selectivity data were obtained from the following standard formulae:

$$S_{Pi} = P_{i,out}/(1- P_{i,out}) \quad (3)$$
$$S_{Pi} = P_{i,out}/\Sigma_{prod} \quad (4),$$

while global hydrogenation rate and specific reaction rate were calculated as follow:

$$rate_{H2} = F_{H2}\cdot\chi_{H2}/g_{cat} \quad (5)$$
$$rate_{Pi} = F_{Pi}\cdot\chi_{Pi}\cdot S_{Pi}/g_{cat} \quad (6).$$

each data set being obtained from the average of three independent measurements.

III. Results

A. Characterization

As reported in Tab. 1, in spite of almost similar mesopore structure, the results of N$_2$ physisorption prove that the catalyst HR-144 is characterized by a larger total surface area (ca. 220 m^2/g) than HR-145 sample (ca. 160 m^2/g). Thereafter, XRD analysis clearly confirms the nearly identical crystalline structure of the catalysts, characterized by almost similar XRD patterns, as shown in Fig. 1A, in which very sharp diffraction lines of the orthorhombic MoO$_3$ phase (Molybdite; s.g. PBNM) and of the tetragonal γ-alumina crystalline structure (s.g. 141/AMDZ) are mainly detected in the whole 2θ range of 10-80 degrees, along quite less intense reflections of defective Mo$_4$O$_{11}$. While, the presence of crystalline phases related to cobalt oxides is hard to ascribe in both catalysts. Instead, the reflection peaks in the region of 35-45 degrees point out the presence of small crystallites of CoMoO$_4$ phase. Therefore, as proof of the effectiveness of H$_2$S sulfiding treatment, the Fig. 1B shows the XRD patterns of sulfided catalysts, in which besides the broad reflection peaks of tetragonal γ-alumina support, the convoluted diffraction lines of MoS$_2$ phase were recorded in the region of 26-44 degrees [1,17].
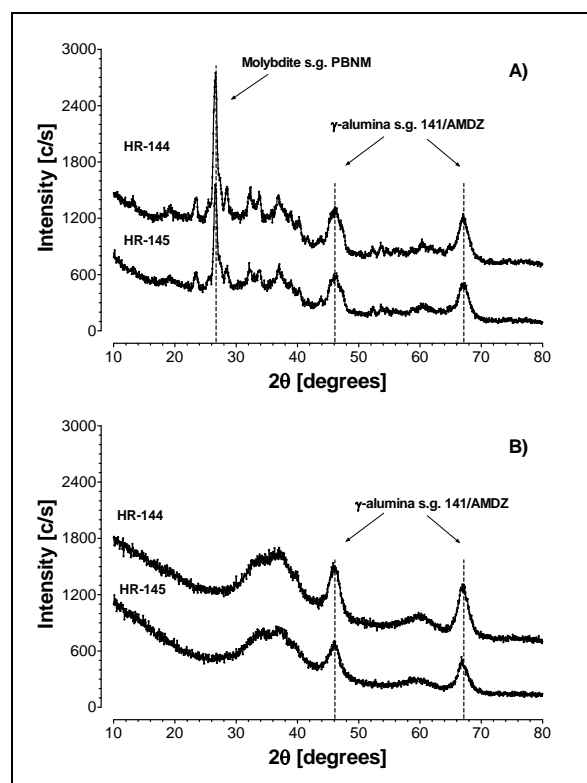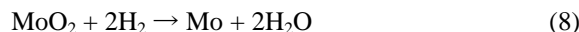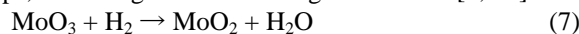

Figure 1. XRD patterns of CoMo/Al$_2$O$_3$ catalysts before (A) and after (B) sulfiding treatment.

In Fig. 2 are shown the TPR profiles of studied catalysts. Namely, the two samples exhibit an almost similar reduction pathway, mainly characterized by the reduction of molybdenum oxides, which takes place in more consecutive steps, according to the following mechanism [1, 19]:

$$MoO_3 + H_2 \rightarrow MoO_2 + H_2O \quad (7)$$
$$MoO_2 + 2H_2 \rightarrow Mo + 2H_2O \quad (8)$$
$$CoMoO_4 + 4H_2 \rightarrow Co + Mo + 4H_2O \quad (9)$$

The first step (7) involves the reduction of isolate MoO$_3$ to MoO$_2$ phase, which can be subsequently reduced into molybdenum at higher temperature (8), also promoting the reduction of spinel-type CoMoO$_4$ phase (9). In particular, both TPR profiles show two main peaks placed at 475°C and 590°C, which monitor the reduction of isolate MoO$_3$ (7) and the occurring of the concomitant reduction of MoO$_2$ (8) and CoMoO$_4$ (9), respectively. Then, the larger reduction zone observed at higher temperature (>600°C) refers to bulk reduction of species in strong interaction with γ-alumina support. The wide area of the negative signal, observed in the range of temperature between 100°C and 300°C, is due to the decomposition phenomena of matrix (i.e. citric acid, PEG and others precursors) and relative gas evolution/desorption, Fig. 2.
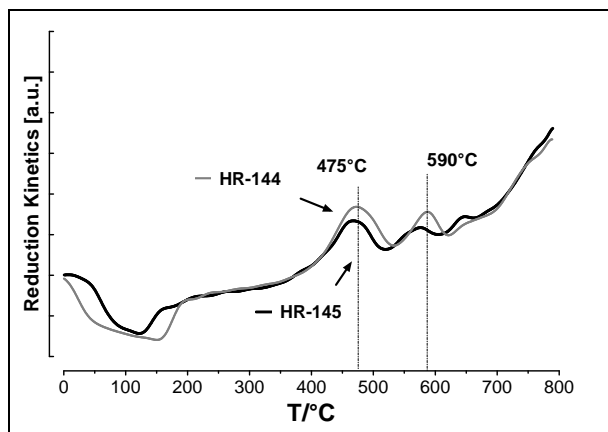
Figure 2. H_2-TPR profiles of CoMo/Al$_2$O$_3$ catalysts

The hydrogen chemisorptions capacity of studied catalysts after reduction was assessed by measures of H_2 programmed temperature desorption (TPD), as described in Fig. 3. Indeed, the TPD profile of catalyst HR-145 shows two spanned and partially convoluted desorption peaks, placed at about 400°C and 600°C, respectively. Diversely, the H_2 desorption process on catalyst HR-144 takes place almost essentially in a single kinetic act, which has the maximum development at a temperature of approximately 560°C. Then, catalyst HR-144 exhibits a larger desorption of H2 (ca. 0.63 mmol/g) than sample HR-145 (ca. 0.41 mmol/g), mirroring an higher metal dispersion.
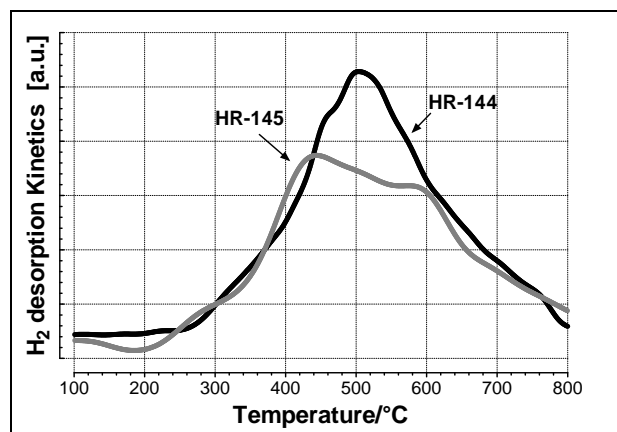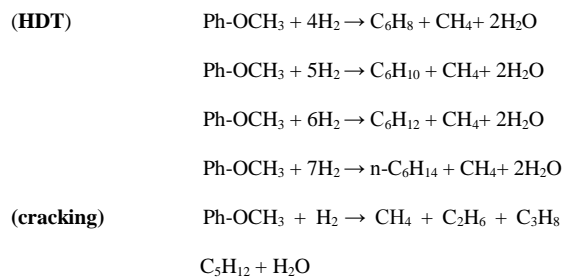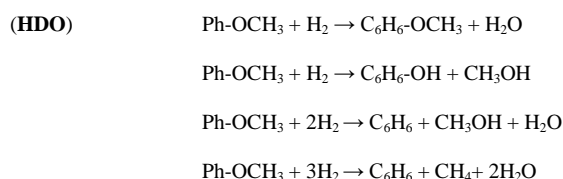

Figure 3. H_2-TPD profiles of CoMo/Al$_2$O$_3$ catalysts.

B. *Catalytic activity Measurements*

Kinetic studies in the hydrogenation reactions were carried out by using 2-methoxyphenol (98%, Sigma-Aldrich) as model molecule. The reaction monitored in the hydrogenation process of Guaiacol are the follow:

(**HDO**) $Ph\text{-}OCH_3 + H_2 \rightarrow C_6H_6\text{-}OCH_3 + H_2O$

                     $Ph\text{-}OCH_3 + H_2 \rightarrow C_6H_6\text{-}OH + CH_3OH$

                     $Ph\text{-}OCH_3 + 2H_2 \rightarrow C_6H_6 + CH_3OH + H_2O$

                     $Ph\text{-}OCH_3 + 3H_2 \rightarrow C_6H_6 + CH_4 + 2H_2O$

(**HDT**) $Ph\text{-}OCH_3 + 4H_2 \rightarrow C_6H_8 + CH_4 + 2H_2O$

                     $Ph\text{-}OCH_3 + 5H_2 \rightarrow C_6H_{10} + CH_4 + 2H_2O$

                     $Ph\text{-}OCH_3 + 6H_2 \rightarrow C_6H_{12} + CH_4 + 2H_2O$

                     $Ph\text{-}OCH_3 + 7H_2 \rightarrow n\text{-}C_6H_{14} + CH_4 + 2H_2O$

(**cracking**) $Ph\text{-}OCH_3 + H_2 \rightarrow CH_4 + C_2H_6 + C_3H_8 + C_4H_{10} + C_5H_{12} + H_2O$

The catalytic tests in the hydrogenation of 2-methoxyphenol (Guaiacol) were conducted using a 80% mixture in normal pentane. In Table 2 are summarized the results of catalytic hydrogenation of Guaiacol, obtained through the use of HR-144 and HR-145 catalytic systems. HR-145 catalyst exhibits a larger activity and selectivity in the hydrogenation of guaiacol, resulting also less subject to deactivation phenomena. As a proof, HR-145 catalyst achieves almost 39% in 2-methoxyphenol conversion while the hydrogen consumption is about 29% of the reactant stream. Those findings overcome the rough 20% and 12% of conversion of guaiacol and hydrogen, respectively, reported by HR-144 catalyst.

On the other hand, reaching the steady-state-condition the two catalysts exhibit an almost similar reaction pathway, which sees methane, catechol and methoxybenzene as the main products of hydrogenation reactions, resulting slightly higher the methane formation on HR-145 catalyst, due probably to its larger activity, as shown in Fig. 3-4. Therefore, side reactions promote majorly the selective formation of phenol under both catalysts, although the full hydrogenation of guaiacol is reached only for HR-145 catalyst, by forming cyclohexane, most likely for its greater activity. Then, methanol was not detected, agreeing with the increased formation of Catechol and methoxybenzene, Fig 4-5.

Table 2. Results of catalytic tests.

Catalyst	X_i	$S_{(HDO)}$	$S_{(HDT)}$	$S_{(PCP)}$	rate$_{HDO/HDT}$	X_{H2}	rate$_{H2}$	$R_{H2/HDO\text{-}HDT}$
	(%)	(%)	(%)	(%)	mol·h^{-1}·g^{-1}	(%)	mol·h^{-1}·g^{-1}	
HR-144	20.2	67.0	5.0	28.0	1.27E-03	12.3	7.97E-03	6.3
HR-145	39.0	70.0	15.0	15.0	2.90E-03	28.9	1.88E-02	6.5

X_i = Conversion of model compound; $S_{(HDO)}$ = Selectivity to HDO reactions; $S_{(HDT)}$ = Selectivity to HDT reactions; $S_{(PCP)}$ = Selectivity to poly-condensation-products; rate$_{HDO-/HDT}$ = global rate of HDO-HDT processes; X_{H2} = Conversion of hydrogen; rate$_{H2}$ = rate of hydrogen consumption; $R_{H2/HDO\text{-}HDT}$ = ratio between rate of rate of hydrogen consumption and of HDO-HDT global rate
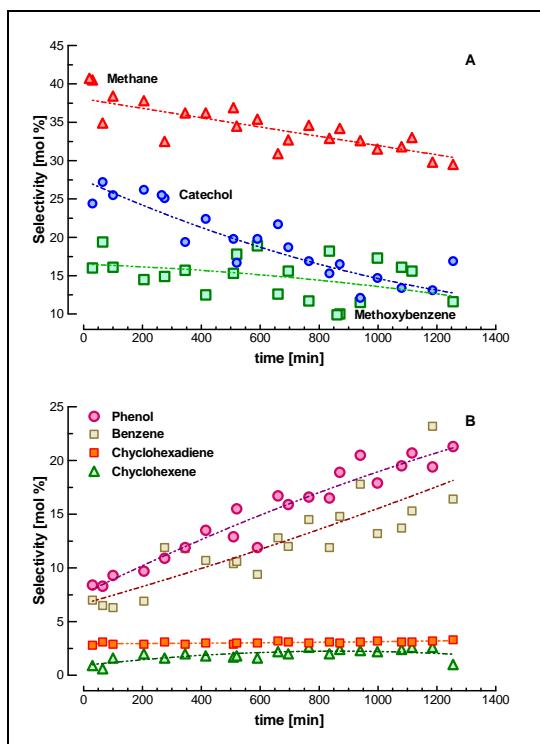
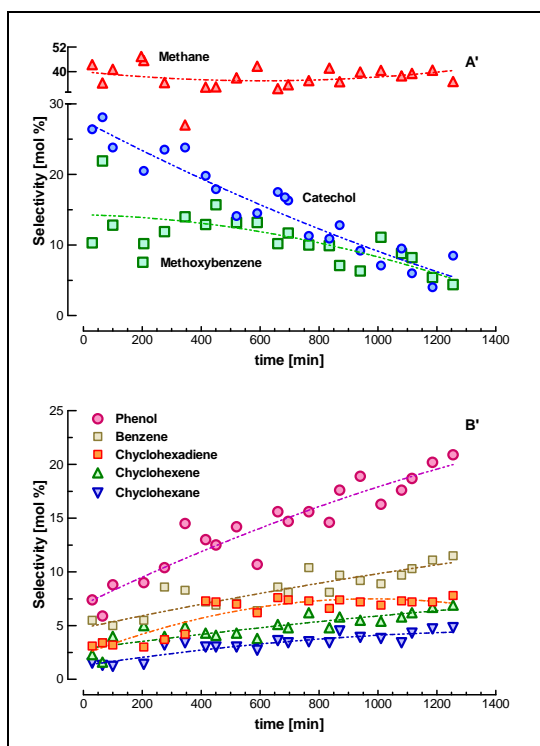Figure 4. Selectivity data to "primary" (A) and "secondary" products (B) for HR-144 catalyst.

Figure 5. Selectivity data to "primary" (A') and "secondary" products (B') for HR-145 catalyst.

Fig. 6 shows the proposed reaction pathway of the guaiacol HDO reaction based on our results. Laurent and Delmon [19] reported the HDO of guaiacol over $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts, showing that guaiacol is first transformed into catechol via the demethylation(DME)

reaction, followed by the elimination of a catechol hydroxyl group, forming phenol.

Accordingly to what reported, phenol is mainly formed through the hydrogenation of "secondary" products (i.e. catechol and methoxybenzene), while benzene derive mostly from phenol hydrogenation rather than from methoxybenzene transformation, as proved by the absence of some products (as methanol) in the out-stream, Fig. 6.
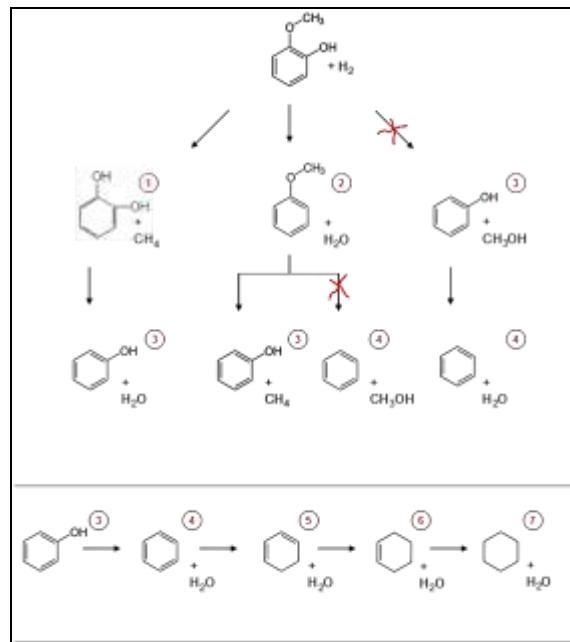

Figure 6. Reaction scheme for guaiacol HDO.

IV.   Conclusion

The best catalytic performance has been achieved by using HR-145 catalyst Then, sulfided $CoMo/Al_2O_3$ catalysts promote majorly the direct hydrogenation of model compounds than hydrodeoxygenation, cracking, isomerization, decarbonylation and decarboxylation reactions, assessing the effectiveness of the upgrading process for the employment of upgraded bio-oil as transportation fuels [9,14].

Acknowledgment

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