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Hydrodeoxygenation of 2-methoxyphenol over Mo_2N catalysts supported on activated carbons

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ABSTRACT

The hydrodeoxygenation (HDO) of 2-methoxyphenol using Mo_2N supported on three commercial activated carbons (Pica, Norit and Cudu) with different textural and chemical properties was studied. The reaction was carried out in a batch reactor at 50 bar of H_2 and 300 °C. The catalysts were prepared by wetness impregnation and nitrided with ammonia at 700 °C. The supports and catalysts were characterized by N_2 adsorption–desorption, thermal programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence and X-ray diffraction (XRD). The Mo_2N/Norit catalyst displayed higher HDO activity compared to the Mo_2N/Cudu and Mo_2N/Pica catalysts. HDO conversion increased when the Mo_2N/Norit catalysts were activated with hydrogen for 6 h at 400 °C due to increased surface nitridation. The Mo_2N/Norit catalyst displayed a higher phenol/catechol ratio relative to the Mo_2N/Pica and Mo_2N/Cudu catalysts, which displayed similar (phenol/catechol) ratios. The phenol/catechol ratio was unaffected by the H_2 activation time.

1. Introduction

The transportation sector accounts for more than 30% of the energy consumption in the European Union, and consumption is continuously increasing [1]. Currently, the price of oil and natural gas is highly volatile, with a clear upward trend due to the demand of rapidly developing countries such as China, India and Brazil. This, combined with CO_2 emissions from fossil fuels, has attracted renewed interest in the development of new, renewable energy technologies. Many researchers have focused their attention on the transformation of biomass to transportation fuels and chemicals because biomass is both a renewable resource and inert with respect to CO_2 emissions [2–8].

Biomass may be gasified to biosyngas and then converted to liquid fuels and/or gases by Fischer Tropsch Synthesis (FTS) [9–13]. Biomass can also by pyrolyzed and converted to primarily liquid and solid products. The liquid is called pyrolysis oil or bio-oil. It is brown and viscous with a high oxygen content due to the presence of large quantities of oxygenates. These are reactive and can polymerize, resulting in a product that is unstable. In addition, bio-oil is not miscible with diesel and has a low heating value. Efforts at developing catalytic hydrotreating processes to remove oxygen (hydrodeoxygenation or HDO) and improve the chemical and fuel properties of bio-oil are critical to its eventual use as a transportation fuel [14,15].

Laurent and Delmon [16,17] reported the HDO of a model compound mixture representing bio-oil over CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 catalysts. In particular, 2-methoxyphenol (guaiacol) is an excellent model compound for bio-oil that contains two oxygen functionalities (–OH and –OCH_3) [3–6]. They found that guaiacol first underwent a demethylation (DME) forming catechol. Catechol was subsequently deoxygenated by a combination of C–O bond breaking (DDO) and hydrogenation (HYD). The final products were benzene and cyclohexane, as shown in Fig. 1. Sulfided CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts used in these HDO experiments were industrial hydrodesulfurization (HDS) catalysts and have been reported to be useful also for HDO [18–20]. As an example of alternative HDO catalysts, Ruiz et al. [21] recently studied rhenium sulfides supported on zirconia and sulfided zirconia. They found that guaiacol HDO activity of ReS_2/ZrO_2 increased 6.4 times when sulphided in a H_2S/N_2 mixture. Similar behavior has been observed in the HDS of thiophene [22].

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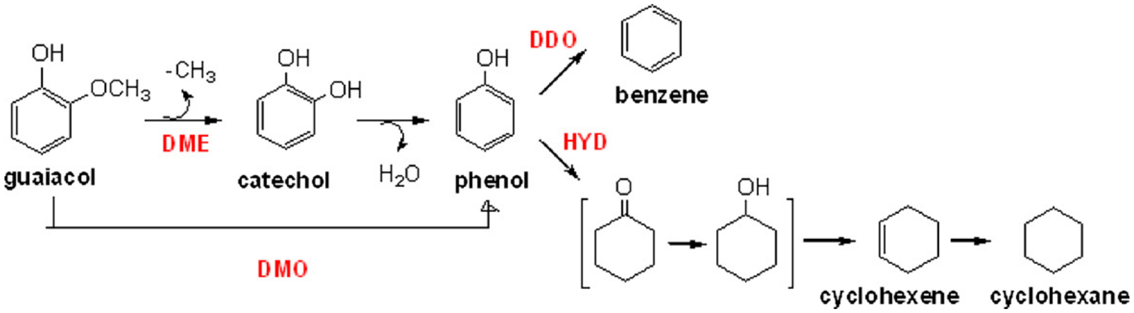

Fig. 1. HDO reaction scheme for guaiacol conversion.

Although transition metal sulfide catalysts have been effective for HDO of bio-oil, they suffer from deactivation during reaction processing [23–26]. In order to maintain active sulfided catalysts, small amounts of H_2S must be added to the feed. Alternatively, Bui et al. [20] have shown a new and interesting method for co-processing bio-oil with gas-oil, simultaneously performing HDS and HDO to maintain a stable active catalyst phase for HDO.

In addition to metal sulfides, metal nitrides have shown to be stable and active for HDS [27,28]. Considering that HDS catalysts are suitable for HDO, it is expected that metal nitride/support phases would also display a high activity for HDO. Recently, Monnier et al. [29] studied the HDO of oleic acid and canola oil over alumina-supported metal nitrides. They found that activated phases of WN, VN and Mo_2N displayed a high activity, with Mo_2N achieving the highest formation of alkanes. In this study, we report the synthesis and characterization of molybdenum nitride catalysts supported on activated carbons; the potential advantages of carbon as a support are well known [30]: (i) in HDS reactions its acidity can be tailored to minimize cracking [31]; (ii) it can be produced inexpensively from the solid product of biomass pyrolysis; and (iii) its surface physical and chemical properties can be tailored over wide ranges in this process [32]. The effects of the support and of the catalyst activation conditions were evaluated in the HDO of guaiacol.

2. Experimental

2.1. Preparation of catalysts

The supported molybdenum oxide catalysts were prepared by wetness impregnation using aqueous solutions of ammonium heptamolybdate [$(NH_4)6Mo_7O_{24}\cdot 4H_2O$, Fisher Scientific] as a precursor salt. Three commercial activated carbons (Pica PICATAL, Norit Darco® MRX and Cudu PETROCHIL), whose textural properties are summarized in Table 1, were used as supports. After impregnation, the samples were dried at 110 °C for 12 h and calcined at 500 °C for 4 h. The catalysts were prepared to obtain a nominal loading of 10 wt% Mo. An unsupported molybdenum oxide precursor was prepared by thermal decomposition of ammonium heptamolybdate at 500 °C for 4 h. The nitrides were prepared following the procedure described by Volpe and Boudart [33]. This procedure involved a temperature-programmed reaction of the molybdenum oxide precursor with ammonia (100 mL min^{-1}). The temperature was linearly increased from room temperature to 300 °C in 30 min, 300–500 °C in 330 min, and 500 to 700 °C in 100 min. It was maintained at 700 °C for 2 h. The samples were then cooled under ammonia flow to room temperature and passivated with O_2/N_2 1% for 12 h. Prior to reaction, the catalysts were activated in hydrogen at various temperatures and times. The catalysts were stored in nitrogen prior to use.

2.2. Reaction conditions

HDO of guaiacol was carried out using a batch reactor (model Parr 4841). The feed contained 0.232 mol L^{-1} guaiacol, hexadecane as internal standard (0.0341 mol L^{-1}) and 100 mL of decalin as solvent. Prior to reaction the catalysts (0.2 g) were reduced ex-situ at 400 °C for 4 h with a flow of H_2 (4 L h^{-1}). To avoid air contamination, N_2 was bubbled through the solution for 1 h. The reactor was then heated under N_2 up to the reaction temperature, 300 °C, under continuous stirring. N_2 was then replaced by H_2 and the reactor was pressurized to 5 MPa, which was kept at constant during the course of the experiment. Samples were taken periodically during the reaction and analyzed by gas chromatography (GC) in a Perkin Elmer Autoystem XL. The reaction rates were calculated from the initial slopes of the conversion data. The phenol/cathecol ratio was determined at 3% conversion of guaiacol.

2.3. Characterization of supports and catalysts

The "apparent" surface area, micropore and mesopore volume and average pore diameter of the supports and catalysts were determined from nitrogen isotherms at −196 °C using a Micromeritics ASAP-2020 instrument. Prior to the measurements, the samples were degassed at 200 °C for 12 h. The total micro-plus mesopore volumes of the materials were calculated from the amount adsorbed at a relative pressure of 0.99 on the desorption branch of the corresponding isotherms, equivalent to the filling of all pores below 50 nm diameter. The contribution of micropores was calculated from a *t-plot* analysis of these isotherms, where the intercept of the linear portion was equivalent to the micropore volume and the slope proportional to the external surface area. The mesopore volume was obtained by subtracting the *t-plot* micropore volume

Table 1
Specific surface (S_{BET}), micropore volume (V_o), mesopore volume (V_m) and average pore diameter of the catalysts and supports, and zero point charge (pH) of the activated carbon supports.

Sample	S_{BET} ($m^2\,g^{-1}$)	V_o ($cm^3\,g^{-1}$)	V_m ($cm^3\,g^{-1}$)	Pore diameter (nm)	Zero point charge (pH)
Norit	612	0.12	0.50	7.9	6.88
MoO_3/Norit	479	0.08	0.46	8.2	
Mo_2N/Norit	752	0.14	0.58	7.9	
Pica	1181	0.41	0.16	4.3	6.81
MoO_3/Pica	1072	0.31	0.2	4.4	
Mo_2N/Pica	1213	0.31	0.32	5.0	
Cudu	1057	0.33	0.18	5.0	7.81
MoO_3/Cudu	741	0.23	0.12	4.8	
Mo_2N/Cudu	811	0.23	0.19	4.9	
Unsupported			–		–
MoO_3	3.0	–		–	
Mo_2N	1.6	–	–	–	