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HDO activity of carbon-supported Rh, Ni and Mo-Ni catalysts

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ABSTRACT

This work reports the performance of low metal loading (about 3 wt.%) Rh, Ni and Mo-Ni catalysts supported on carbon in the hydrodeoxygenation (HDO) of phenol. The catalytic tests were carried out in a flow microreactor at 310 °C and at a total hydrogen pressure of 3 MPa. A commercial NiMoP/γ-Al_2O_3 sulfided catalyst was used as reference. The effect of catalyst pre-treatment (reduction against sulfidation) was investigated in the case of the noble metal catalyst. The thermally treated in inert atmosphere, fresh reduced and spent catalysts have been characterized by several physicochemical techniques: chemical analysis, N_2 adsorption-desorption isotherms, Raman spectroscopy, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and High Resolution Transmission Electron Microscopy (HRTEM).

The HDO of phenol was found to be favored on the bifunctional Rh/C and Ni/AC catalysts which exhibit a large amount of well dispersed metallic species (from HRTEM). Contrary to a commercial sulfided NiMo/Al_2O_3 catalyst, the hydrogenation of aromatic ring of phenol was favored being the C—O bond hydrogenolysis a minor reaction route. Catalytic HDO of phenol over Rh/C reveal that the catalyst activation by reduction is advantageous compared to that by sulfidation. The partial substitution of Ni by Mo in the Mo-Ni/AC catalyst led to enhance of the catalyst stability but decrease of overall activity occurs due to the decrease of amount of metallic nickel species. The role of the MoO_3 species in the inhibition of deactivation by coke is discussed.

1. Introduction

The demand for energy worldwide is predicted to double before 2050 [1] as a result of population growth. Currently, fossil fuels account for over 85% of energy production. The combustion of fossil fuels produces CO_2 emissions. CO_2 emissions lead to environmental problems, including global warming. Thus, the global energy crisis [2] coupled with current environmental issues generates a serious problem.

To overcome these challenges, renewable energy sources such as wind, solar, biomass, and hydroelectricity are being used increasingly. Biofuels are sustainable and have net zero carbon emissions. As a result, they appear to be a promising replacement for fossil fuels. However, the biofuel liquid produced from fast pyrolysis of biomass is rich in oxygen-containing compounds. Oxygen-containing compounds show the following negative properties: non-volatility, high viscosity, corrosiveness, poor heating value, thermal instability, and immiscibility with fossil fuels. To improve the properties of the biofuel liquid, oxygen can be removed using hydrodeoxygenation processes (HDO) [3]. Catalytic biomass conversion is developing extremely fast in recent years. Recent laboratory and commercial findings in the field of catalytic hydroprocessing of biomass liquefaction products are presented in a few excellent reviews [4–12]. A detailed survey of recent publications on Ni-based heterogeneous catalysts for energy and environmental applications was reported by De et al. [10] whereas recent advances in the design of metal-based nano-catalysts for de-functionalization of different biomass components was revised by Wang et al. [11]. For the Ni-based bimetallic systems, it was concluded that some reactions were favored and proceed on specific surfaces of the bimetallic catalysts, thus, the continued efforts on the rational design of surface of specific bimetallic catalysts

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are critical to achieve superior catalytic performances [10]. In this sense, the study of Zhang et al. [12] demonstrated that the bimetallic NiRu, NiRh and NiPd catalysts exhibited superior activity than corresponding monometallic counterparts in the hydrogenolysis of lignin C—O bonds under low temperature (100 °C) and low H_2 pressure (1 bar). However, although the conversion of lignocellulose, lipids, and chitin can be effectively catalyzed by well-defined nanocatalysts, it has been proposed that more studies are required to improve the synthesis procedure in order to extent their application from model reactions to real biomass conversion [11,12].

To perform HDO, a catalyst with high activity and stability is desired. Up to now, sulfided catalysts have been the main focus of biofuel HDO research. Published reports have shown that sulfided catalysts are not ideal for biofuel HDO because of their instability in the presence of H_2O, contamination of product, and poor cost-effectiveness. As a result, current research has been redirected towards investigating sulfur-free catalysts. Noble metal catalysts offer exciting potential [4–10 and references within]. Under mild conditions noble metals are especially effective catalysts in the activation of molecular hydrogen. This is because without difficulty hydrogen can be activated and cleaved at the interface or surface to react with other reactants. Among the noble metals Rh is quite promising.

The effect of support acidity on HDO activity of supported Rh-based catalysts was investigated using acidic substrates such as ZrO_2 [13–17], Al_2O_3 [13,17], SiO_2-Al_2O_3 [17]. The critical role of the support for the HDO of O-containing compounds is largely documented [4,18]. Alumina supports have been reported to produce large coke formations due to weak Lewis type acidic sites on the surface of the support [5]. In addition, the instability of the alumina support in the presence of the high levels of water was recognized as a serious shortcoming [19,20]. Thus, to prevent coke formation, a support of lower acidity and higher stability is necessary. In this sense, mesoporous carbon (C) and activated carbon (AC) are of interest because they possess these characteristics [5–13].

A very interesting study on the Rh/C catalyst was reported by Zhao et al. [21]. The catalyst activity of dual Rh/C and H_3PO_4 systems was evaluated in aqueous-phase hydrodeoxygenation of bio-derived phenols to cycloalkanes performed in a batch reactor at 200 °C with a H_2 pressure of 5 MPa. In such conditions, hydrodeoxygenation of phenol proceeds via stepwise hydrogenation of the aromatic ring, transformation of the cyclic enol to the corresponding ketone, hydrogenation of the cycloalkanone to the cycloalkanol and its subsequent dehydration as well as the hydrogenation of the formed cycloalkene. The phenol conversion was 100% and the catalyst showed 92% selectivity toward cylohexane and 7% selectivity toward cylohexanone [21]. A comparison of the activity results of the Rh/C sample with Ru/C, Pt/C and Pd/C catalysts demonstrated that these four catalysts exhibited similar high activities (cyclohexane yields in the range 84–92%) in phenol conversion with H_3PO_4 at 200 °C [21].

Studies concerning the use of carbon supports for HDO catalysts have been also reported for non-noble metals (e.g. Co, Ni, Mo). In this context, no coke formation during the HDO over sulfided CoMo/AC catalysts has been reported [5]. However, the extensive microporosity of active carbon is a drawback because part of the metals located in micropores is not accessible to large molecules involved in the reactants [22]. The influence of the active phase loading on the hydrodeoxygenation (HDO) activity of carbon-suported catalysts was investigated by Ferrari et al. [23]. It was found that the most important parameter for liquid phase HDO reaction of a mixture of model compounds (guaiacol, ethyldecanoate, 4-methylacetophenone) over sulfided CoMo/AC catalysts was the dispersion of the active phase. The use of carbon as support was evaluated also by Centeno et al. [24] and Mortensen et al. [25]. In the latter study, carbon-supported nickel catalyst was found to be practically inactive for HDO of phenol suggesting that the nickel based catalysts require a metal oxide as carrier on which the activation of the phenol for the hydrogenation might take place through heterolytic dissociation of the O—H bond to facilitate the reaction. Ni-based bimetallic catalysts have been proved very active for C—O bond hydrogenolysis [10,11], which is crucial for the title reaction.

The aim of the present work is (i) to investigate the effect of pre-treatment conditions (reduction against sulfidation) on the behavior of carbon supported Rh catalysts for HDO of phenol (ii) to compare the catalytic performance of a carbon supported Rh catalyst with that of a Ni one (iii) to examine the promoting action of Mo on a carbon supported Ni catalyst. The catalytic activity was evaluated in the HDO of phenol because the phenolic compounds represent approx. 25% of oxygenates present in bio-oils produced by pyrolysis of lignocellulosic biomass and it is known that those compounds have shown low reactivity in hydrotreating.

2. Experimental methods

2.1. Catalyst preparation

The mesoporous carbon (C; nanopowder) and a Norit RX 3-extra commercial active carbon (AC; cylindrical pellets) used as supports were supplied by Sigma–Aldrich and NORIT Americas Inc. D, respectively. Their specific surface area, total pore volume and average pore diameter of pure supports are listed in Table 1.

The Rh/C sample was prepared by the wet impregnation of mesoporous carbon (C) with $Rh(NO_3)_3$ aqueous solution. After adsorption equilibrium had been reached, the excess of water was removed until dryness in a rotary evaporator. Catalyst drying was performed in air at 60 °C overnight, followed by decomposition of the $Rh(NO_3)_3$ salt under He stream 30 mL/min at 400 °C for 2 h.

Ni/AC and Mo-Ni/AC samples were prepared by impregnation of active carbon (AC). Before impregnation, carbon pellets were crushed and sieved to a particle size fraction 0.25–0.35 mm, purified consecutively by refluxing several times with distilled water and dried. The Ni/AC and Mo-Ni/AC samples were prepared at 100 °C by deposition-precipitation of active components on AC surface using aqueous solution containing $Ni(NO_3)_2$ or $Ni(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$ as well as aqueous ammonia as precipitating agent. Considering our previous study [26], the value of $\frac{Ni}{Ni+Mo} = 0.77$ atomic ratio was adopted for the preparation of Mo-Ni/AC catalyst. After filtration, the solids were dried and decomposed as previously.

2.2. Catalyst characterization

2.2.1. Chemical analysis

The chemical analysis of the C- and AC-supported samples was performed, respectively, by atomic absorption spectrophotometry conducted on a Perkin-Elmer Optima 3310 DV inductively coupled plasma atomic emission spectrometer (ICP-AES) and by T-XRF spectrometry using TXRF S2 PicoFox (Bruker) apparatus.

2.2.2. X-ray diffraction

The crystal phases of the fresh reduced samples were investigated by power X-ray diffraction employing a Brucker D8 Advance diffractometer equipped with nickel-filtered CuKα (1.5418 Å) radiation source. The step size and the time per step were respectively fixed at 0.02° and 0.5 s in the range of $10° \leq 2\theta \leq 80°$. The mean crystallite size was estimated using the Scherrer's equation.

2.2.3. Raman spectroscopy

Raman spectra were recorded with a Renishaw in Via Raman Microscope spectrometer equipped with a laser beam emitting at 785 nm, at 310 mW output power. The photons scattered by the