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MgFe hydrotalcites-derived layered structure iron molybdenum sulfide catalysts for eugenol hydrodeoxygenation to produce phenolic chemicals

Q2 Xinyong Diao[a,b], Na Ji[b,*], Mingyuan Zheng[c], Qingling Liu[b], Chunfeng Song[b], Yibo Huang[b], Qing Zhang[b], Alazar Alemayehu[b], Luoyun Zhang[a], Changhai Liang[a,*]

[a] *Laboratory of Advanced Materials and Catalytic Engineering, Dalian University of Technology, Panjin 124221, Liaoning, China*
[b] *School of Environmental Science and Engineering, Key Laboratory of Biomass-Derived Gas and Oil for Chinese Petrochemical Industry, Tianjin University, Tianjin 300350, China*
[c] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*

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ABSTRACT

Hydrodeoxygenation (HDO) is an effective alternative to produce value-added chemicals and liquid fuels by removing oxygen from lignin-derived compounds. Sulfide catalysts have been proved to have good activity for the HDO and particularly high selectivity to phenolic products. Herein, we presented a novel way to prepare the layered structure sulfide catalysts (MgFeMo-S) derived from MgFe hydrotalcites via the intercalation of Mo in consideration of the memory effect of the calcined hydrotalcite. By varying the Mg/Fe mole ratio, a series of MgFeMo-S catalysts were successfully prepared and characterized by nitrogen adsorption/desorption isotherms, X-ray diffraction (XRD), transmission electron microscopy (TEM), and inductively coupled plasma optical emission spectrometer (ICP-OES). The characterization results indicated that the MgFeMo-S catalyst has retained the unique layered structure, which can facilitate uniform dispersion of the MoS_2 species on both the surface and interlayer of the catalysts. For the HDO of eugenol, the Mg_1Fe_2Mo-S catalysts exhibited the best HDO activity among all the catalysts due to its higher active metal contents and larger pore size. The HDO conversion was 99.6% and the yield of phenolics was 63.7%, under 5 MPa initial H_2 pressure (measured at RT) at 300 °C for 3 h. More importantly, MoS_2 species deposited on the interlayer galleries in the MgFeMo-S catalysts resulted in dramatically superior HDO activity to MoS_2/Mg_1Fe_2-S catalyst. Based on the mechanism investigation for eugenol, the HDO reaction route of eugenol under sulfide catalytic system has been proposed for the first time. Further applicability of the catalyst on HDO of more lignin-derived compounds was operated, which showed good HDO activity and selectivity to produce aromatic products.

1. Introduction

Fuels and chemicals derived from biomass recently have been attracted considerable interest, since biomass is a renewable resource and can be an alternative to fossil fuels [1–6]. Lignin is a primary composition of biomass which has plenty of polyaromatic units, therefore it could be possible to obtain value-added aromatic products for fine chemicals use [7–10]. However, it is challenging for direct degradation of lignin raw material due to its complicated and amorphous structure. Generally, research on the conversion of lignin model compounds is a dominant approach to investigate the transformation of lignin [11–13].

Hydrodeoxygenation (HDO) is a chemical reaction which can remove oxygen with H_2 primarily in the form of water, and it has been considered as an effective method for lignin upgrading [14–17]. Previous research found that the HDO of lignin normally possessed two main paths: direct deoxygenation (DDO) or hydrogenation–deoxygenation (HYD) [18]. The dominating divergence depends on the active site adopted in the reaction system. For the noble metal catalysts such as Pd, Pt, Ru and Rh, which are active in the hydroprocessing, prefer the HYD path which could result in full ring saturation to form cycloalkanes [19–23]. The same results were achieved using the non-noble metal Ni catalysts whereas relatively high reaction conditions are required [24]. Recently, more attentions are given to the noble metal like transition-metal nitrides, carbides, and phosphides catalysts [25–28]. Zhao et al. [25] compared the HDO activities of different transition metal phosphide catalysts using guaiacol as the substrate. The

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* Corresponding authors.
E-mail addresses: jina@tju.edu.cn (N. Ji), changhai@dlut.edu.cn (C. Liang).

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turnover frequency (TOF) based on the active sites titrated by the chemisorption of CO followed the order: $Ni_2P > Co_2P > Fe_2P$, WP, MoP, and the major products were benzene and phenol according to DDO pathway. A nitrogen-doped carbon supported cobalt nitride catalyst CoN_x@NC was used to catalyze eugenol to propyl cyclohexane by Liu et al. [28] with 99.1% total yields under 2 MPa H_2 at 200 °C for 2 h. Unfortunately, transition-metal nitrides and phosphide showed poor stability since their air sensitivity which makes them easily to be oxidized.

In order to selectively cleave the C_{Ar}-OR bonds to produce aromatic hydrocarbons, sulfide catalysts have been demonstrated to be alternatives for their relative simple preparation and DDO selectivity [29]. Historically, many works have proved the practicability of Mo-based sulfides for the HDO of lignin from early 1970 [30]. Plenty of attempts conducted to make an adjustment of Mo-based sulfides [31,32]. Wang et al. [31] explored the influence of surfactants on the synthesis of MoS_2 catalysts and their activities in the hydrodeoxygenation of 4-methylphenol. The addition of surfactant increased the surface area of MoS_2, meanwhile changed its microstructure in the stack layer, resulted in a higher activity in the HDO of 4-methylphenol. Mukundan et al. [32] had prepared highly disordered single layered MoS_2/C by a micro emulsion technique and demonstrated that the single layered MoS_2 showed superior activity than the stacked MoS_2 for the HDO of guaiacol, with a 52.0% phenol selectivity under 5 MPa H_2 at 300 °C for 5 h. In addition, other transition-metal sulfides such ReS_2 and FeS_2 also showed impressive activities for HDO reactions, but the preparation procedures were complicated [33,34]. Leiva et al. [33] examined the activity of ReS_2/SiO_2 catalyst using guaiacol as substrate. Although it showed lower selectivity towards benzene and cyclohexane than ReO_x/SiO_2 catalyst, ReS_2/SiO_2 led to more phenol products. Ji et al. [34] reported that FeS_2 on different supports could catalyze the HDO of dibenzyl ether and the FeS_2/AC catalyst exhibited high selectivity to toluene with 98% yield.

Since the layered structure has a great impact on the catalytic activity [35–37], Wang et al. [38] had prepared a layered NiAl-MoW sulfide catalyst using NiAl-layered double hydroxide (NiAl-LDHs) as the structure-directing template for hydrodesulfurization (HDS) reactions. Results showed that the layered structure actually enhanced the HDS activity, indicating a good contact between the different metal sulfide species. Recently, more works on the applications of different hydrotalcites for HDS have been reported [39–41]. But to our knowledge, no related works on layered structure sulfide catalysts designed for HDO have been reported. It is predictable that a uniform dispersion of the active sites on the catalysts could lead to the improvement of HDO activity.

Herein, we developed a novel method to prepare the layered structure sulfide catalysts (MgFeMo-S) using MgFe hydrotalcites as precursors. Unlike the method been reported [38–41], we utilized the structure recoverability of hydrotalcites to introduce Mo into the interlamination by the hydration of MgFe hydrotalcite oxides with MoO_4^{2-} solutions. In this paper, a series of MgFeMo-S catalysts with different Mg/Fe mole ratios were synthesized and characterized, and then tested in the HDO of eugenol. The influences of reaction temperature and hydrogen pressure were investigated. The possible reaction pathway was assumed according to the product distribution while prolonging the reaction time. Finally, the recyclability of the catalyst was also tested and characterized.

2. Experimental

2.1. Synthesis of catalyst

Unsupported MgFe hydrotalcite-derived sulfide catalysts were prepared by two steps. Firstly, MgFe-layered double hydroxides (LDHs) were synthesized by coprecipitation method. Here, we took Mg_3Fe_1-LDHs for example 23.1 g $Mg(NO_3)_2{\bullet}6H_2O$ and 12.1 g $Fe(NO_3)_3{\bullet}9H_2O$ (Tianjin Kemiou Chemical Reagent Co.,) were dissolved in 250 mL deionized water. In addition, 9.6 g NaOH and 5.6 g Na_2CO_3 (Tianjin Kemiou Chemical Reagent Co.,) were also dissolved in another 250 mL deionized water. Then the two settled solutions were simultaneously instilled into the 500 mL deionized water by stirring at 40 °C, and maintained pH between 9 and 10 by adjusting the rate of titration. When titration was over, stop stirring, hold it for about 40 min, then heated to 70 °C for 12 h. After filtrated and washed with distilled water and ethanol, the precipitate which was considered as Mg_3Fe_1-LDHs was dried at 70 °C for 12 h. Secondly, the LDHs were added into a quartz tube then heated to 400 °C in the air atmosphere for 5 h in order to obtain the MgFe layered double oxides (LDO). Then the LDO was hydrated with the MoO_4^{2-} solutions under sealed environment for 12 h, followed by drying at 120 °C for 12 h and sulfided at 400 °C for 4 h in the flow of 10 vol% H_2S/H_2 mixed gas to obtain the final MgFe hydrotalcites-derived MgFeMo-S catalysts. Commercial Co(Ni)Mo-S catalysts (Hhitech-Develop) and additional MgFe-S (MgFe-LDO as precursor) and MoS_2/MgFe-S (ammonium heptamolybdate as precursor and MgFe-LDO as support using impregnation method) catalysts were sulfided at the same condition for comparative HDO experiments.

2.2. Characterization of catalyst

X-ray diffraction (XRD) patterns were recorded on a D8-Focus powder diffractometer with a Ni-filtered Cu-$K\alpha$ radiation source ($\lambda = 1.54056$ Å) operated at 40 kV and 200 mA. The scan speed was 3 °/min with a scanning angle ranged from 5° to 70°.

Nitrogen adsorption measurements were performed on a Micromeritics TriStar surface area and porosity analyzer. The specific surface area of the sample was calculated using the BET method and pore size distributions were determined by BJH method from the isotherms. Before analyzing, the samples were deaerated at 100 °C for 1 h and then 300 °C for 3 h.

For determining the composition of the catalysts, inductively coupled plasma optical emission spectrometer (ICP-OES) was conducted on a Thermo 7000 series analyzer. Nitrohydrochloric acid was used to dissolve the solid samples beforehand for doing the ICP.

The morphologies of catalysts were characterized by SEM and HRTEM. SEM images were obtained on a FEI Nova NanoSEM 450 instrument, and HRTEM images were obtained on a JEM-2100F transmission electron microscope.

X-ray photoelectron spectroscopy (XPS) was measured with a ThermoFisher ESCALAB^{TM} 250Xi spectrometer for characterizing the surface chemical property.

2.3. Catalytic property tests

The catalytic property tests for the HDO were carried out in a 50 mL autoclave (Parr 4597). In a typical experiment, 2.5 mmol eugenol, and 2.5 mmol dodecane (internal standard) were dissolved in 20 mL methylcyclohexane, together with the as-prepared catalyst (0.08 g) were placed into the autoclave (catalyst: reactant mass ratio = 1:5). After purging with hydrogen for 3 times, the reactor was pressured with a certain initial pressure of H_2. The reaction was conducted at a certain temperature and reaction time with magnetic stirring. After the reaction, the products were analyzed by GC (SP-7890) and GC–MS (Agilent 6890A-5975C). Conversion and yield were determined according to the following equations

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