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Effective conversion of heteroatomic model compounds in microalgae-based bio-oils to hydrocarbons over β-Mo_2C/CNTs catalyst

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Hydrotreatment of heteroatomic model compounds in microalgae-based bio-oils into diesel-like hydrocarbons was carried out over carbon nanotubes (CNTs)-supported β-Mo_2C catalyst with superior activity and selectivity under a mild condition (≤200 °C). The results show that stearic acid and hexadecanamide can be completely converted into *n*-C_{15}–C_{18} alkanes over β-Mo_2C/CNTs catalyst. The β-Mo_2C/CNTs favors the pathway of hydrogenation–dehydration–hydrogenation to produce *n*-octadecane with an optimal yield of 91.24% at a lower temperature of 180 °C during hydrotreating process of stearic acid. The recycle tests demonstrate that the β-Mo_2C/CNTs exhibits excellent stability, and can be reused for seven times consecutively without reduction of catalytic stability. Based on the determined products, a brief reaction pathway is proposed. Therefore, a novel approach to produce diesel-like hydrocarbons via catalytic hydrotreatment of microalgae-based bio-oils over β-Mo_2C/CNTs is introduced, which provides a basic research as well as technical parameters for its further industrialization.

1. Introduction

The increasing concerns over the depletion of non-renewable fossil resources and global climate change have attracted significant attention to explore renewable and environmental friendly sources of energy [1–5]. Of all the alternatives, biomass is regarded as the only material for the production of liquid fuel, which is considered to be one of the most sustainable alternatives to petroleum because of viable means for environmental and economic sustainability [6]. Among the biomass, microalgae is considered as one of the most promising energy sources for fuel production due to superior photosynthetic efficiency, higher growth rate, area-specific yield, and higher carbon dioxide utilization capabilities compared to terrestrial plants [7–10]. However, microalgae-based bio-oils obtained from thermochemical conversion contain appreciable quantities of oxygen and nitrogen heteroatoms, which result in undesirable property including corrosiveness, thermal instability, high viscosity and low heating value [11–14]. Therefore, it is desirable to remove the heteroatoms in the bio-oils to achieve high quality transport fuel.

As reported in previous works, microalgae-based bio-oils contain a large amount of oxygen-containing compounds and nitrogen-containing compounds, especially C_{16}–C_{18} long-chain fatty acids and amide compounds [13,15]. To this end, the necessary upgrading processes must be carried out via deoxygenation and denitrification prior to actual application. Among the upgrading technologies, catalytic hydrotreatment used for processing heavy crude petroleum and shale oils, is one of the most efficient approaches for removing heteroatoms in the microalgae-based bio-oils [16,17]. However, the conventional hydrotreating catalysts, such as sulfided NiMo and CoMo [18,19], may easily lead to the generation of sulfur compounds and sulfur leaching, which result in the deactivation of catalysts. As hydrotreating catalysts, supported noble metals (Pt, Pd, Rh, etc.,) also show superior activity and selectivity [20–25]. However, the high price greatly limits their large-scale practical applications [26]. Therefore, it is urgent to develop more sulfur-free and cost-effective catalyst with high activity and stability under mild conditions (≤200 °C) for the upgrading of microalgae-based bio-oils.

Transition-metal carbides, especially nanosized molybdenum carbides (Mo_2C), have attracted considerable attention as promising alternative catalytic materials in hydrogen-involved reactions

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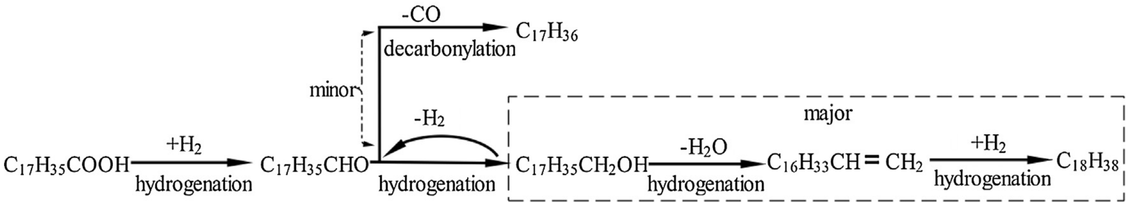

Scheme 1. Proposed reaction pathways for stearic acid conversion over β-Mo_2C/CNTs.

since the discovery of their "platinum-like" behavior, preferable resistance to poisoning of carbon monoxide and better anti-sintering characteristics [27–29]. Ren et al. [30] demonstrated that the Mo_2C exhibited high hydrodeoxygenation (HDO) activity with propanal as a model compound. Han et al. [31] reported that carbon nanotubes (CNTs)-supported Mo_2C could efficiently transform esters into diesel-like hydrocarbons in the presence of hydrogen. These papers clearly indicate the potential application of Mo_2C as a selective catalyst for hydrotreating of oxygen-containing compounds. As mentioned above, long-chain fatty acids and amide compounds are main components of the microalgae-based bio-oil [13], and it is necessary to convert these heteroatomic compounds into chain hydrocarbons. However, few papers have reported the conversion of long-chain fatty acids and amide compounds into hydrocarbons over Mo_2C catalyst. Although Stellwagen and Bitter [32] has researched the catalytic conversion of stearic acid over pre-treated carbon nanofibers (CNFs)-supported Mo_2C, the yield of alkanes is relatively low of 80% at 300 °C. In addition, the catalytic conversion of a mixture of long-chain fatty acid and amide compound in microalgae-based bio-oils over Mo_2C catalyst has not been reported. Herein we describe for the first time that Mo_2C/CNTs can efficiently catalyze the conversion of stearic acid and a mixture of stearic acid and nitrogen-containing compound to diesel-like hydrocarbons at a lower temperature ($\leq$ 200 °C).

In this work, catalytic hydrotreatment of stearic acid and hexadecanamide as the oxygen-containing, nitrogen-containing model compound in microalgae-based bio-oils, respectively, was carried out over the β-Mo_2C/CNTs catalyst, which was synthesized by the carbothermal hydrogen reduction (CHR) method. The aim of the present work is to evaluate catalytic performance of β-Mo_2C/CNTs catalyst in multi-aspect including HDO and hydrodenitrogeneration (HDN) process under mild conditions ($\leq$200 °C). Reaction parameters optimization and a brief pathway based on the experimental results had been investigated in the HDO process. This work will develop a foundation on industrial production of liquid hydrocarbons via hydrotreating process over inexpensive transition metal catalysts with the economic value and strategic significance.

2. Experimental

2.1. Materials

Stearic acid (98%), octadecane ($\geq$99.5%), heptadecane ($\geq$99.5%), hexadecane ($\geq$99%), pentadecane ($\geq$99%) and octadecanol ($\geq$99.5%) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Hexadecanamide was provided from Tokyo Chemical Industry Co., Ltd., Decane (>99%) and ammonium molybdate (99.0%) were purchased by Guangfu Technology Development Co., Ltd. (Tianjin, China). Multi-walled CNTs (>95%) were generously provided from XFNANO Materials Tech., Co., Ltd. (Nanjing, China). All reagents were used as-received without further purification.

2.2. Catalyst preparation

The β-Mo_2C supported CNTs (BET specific surface area: 178 $m^2\,g^{-1}$) catalyst was synthesized by the CHR method described as follows: in a typical run, β-Mo_2C/CNTs catalyst was prepared by first dissolving ammonium molybdate (1.36 g) in deionized water (15 mL) and then slowly dropping this solution onto CNTs (2 g) with continuously stirring in a 100 mL beaker. After allowing the metal to permeate into the support for 12 h at ambient temperature, the catalyst was first dried at 105 °C for 3 h. The dried sample was then calcined in air at 500 °C with a heating rate of 10 °C min^{-1}, and maintained at that temperature for 3 h. Thereafter, it was disposed by reduction in a H_2 flow of 80 mL min^{-1} from room temperature to 700 °C with 10 °C min^{-1} and reduced at 700 °C for 4 h. The theoretical β-Mo_2C loading was approximately 5% based on CNTs support.

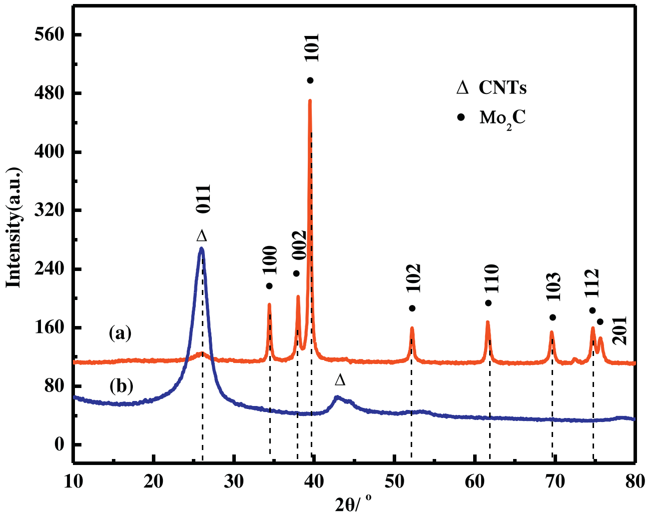

Fig. 1. XRD patterns of the catalyst: (a) β-Mo_2C/CNTs; (b) CNTs.