Tailoring product distribution during upgrading of palmitic acid over bi-functional metal/zeolite catalysts

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HIGHLIGHTS

- Ni-/Co-H-ZSM-5 enhanced hydrodeoxygenation to decrease hydrodecarbonylation.
- Deoxygenation, isomerization and cracking occurred over Ni-/Co-H-ZSM-5 catalysts.
- More C_{16} and iso-products formed over Co-H-ZSM-5 catalysts.
- H-ZSM-5 favored hydrodecarbonylation and the direct cracking of palmitic acid.

GRAPHICAL ABSTRACT
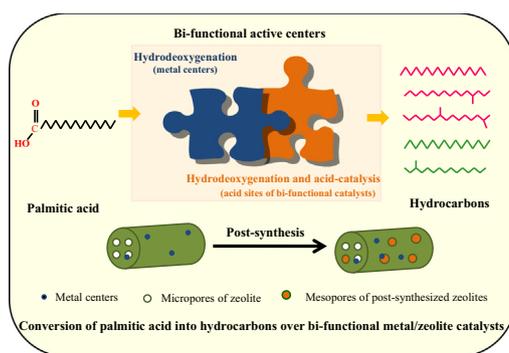
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ABSTRACT

Bi-functional metal (Ni and Co)/zeolite catalysts were designed to upgrade palmitic acid. No isomerization products were observed over parent zeolitic supports H-ZSM-5 without metal phase, but hydrodeoxygenation (minor route), hydrodecarbonylation (major route) and the direct cracking were observed. On one hand, the impregnation of Ni or Co species, enhanced hydrodeoxygenation via hydration-hygenation route and decreased hydrodecarbonylation route. On the other hand, metal phase decreased the isomerization temperature, which is consistent with enhanced the acidic strength of whole bi-functional catalysts especially for Co/zeolite catalysts. Simultaneous deoxygenation of palmitic acid, isomerization of hydrogenated products and cracking were achieved over bi-functional Ni/H-ZSM-5 and Co/H-ZSM-5 catalysts, with more C_{16} and iso-products formation. Furthermore, the introduction of mesopores obviously enhanced iso-products and C_{16} formation for Co-based catalysts.

1. Introduction

Fossil fuels have been utilized to produce transportation fuels powering the world (about 20% of total energy consumption) and petroleum chemical products consumed in our daily life. The rapid and continuous depletion of limited petroleum sources have considerably influenced the fall and rise of crude oil price. Moreover, transportation fuels emits 31% CO_2, 24% NO_x and 41% non-methane volatile organic compounds (nm VOC), which are predominant source of air pollution (Hall, 2007). Considering the limitations of transport, scholars and their industrial partners have focused on sustainable energy sources, such as wind, solar, and

biomass. Conversion of biomass, which is reproducible, universally diverse and environment friendly, is one of the most promising methods to reduce the overall carbon footprint of transport fuels (bio-gasoline, bio-diesel, and jet fuel) and chemical products (Zhao et al., 2011; Wu et al., 2014; Kasakov et al., 2015; Foo et al., 2016). In this regard, upgrading of bio-oil is a timely and interesting topic. As the primary fraction of bio-oil, long-chain fatty acids such as stearic acid (C_{18}) and palmitic acid (C_{16}), have been used as model compounds to investigate the deoxygenation of biomass materials and generate potential feedstock for bio-diesel and jet fuel (Santillan-Jimenez and Crocker, 2012; Peng et al., 2012; Wang et al., 2015). Oxygen atoms can be removed from fatty acids through three reactions, namely, decarboxylation (DCX: $R-COOH \rightarrow R-H + CO_2$), hydrodecarbonylation (HDC: $R-COOH + H_2 \rightarrow R-H + CO + H_2O$), and hydrodeoxygenation (HDO: $R-COOH + 3H_2 \rightarrow R-CH_3 + 2H_2O$).

Conventional sulfide-based NiMo/γ-Al$_2$O$_3$ and CoMo/γ-Al$_2$O$_3$, exhibit high activity but deactivate rapidly due to potential poisoning in aqueous atmosphere and coke deposition (Oyama, 1992; Sotelo-Boy et al., 2011). Noble metals (Pt, Pd, Ru, etc) are highly active and selective for fatty acid conversion, however, their exorbitant price hinders their large-scale application (Snare et al., 2006; Kon et al., 2014; Wang et al., 2012). As such, researchers have investigated non-noble metal catalysts (Ni, Co, Mo). As for Ni-based catalysts, Ni^0 metal can effectively activate C—C bond in fatty acid (C_n) deoxygenation and produce C_{n-1} alkanes with one C atom loss (Peng et al., 2012; Wang et al., 2015; Peng et al., 2012; Peng et al., 2013; Xin et al., 2016; Yang et al., 2012). According to our previous studies (Shi et al., 2016; Ding et al., 2015; Ding et al., 2016), the different states of metals show varied activity and selectivity during the hydro-conversion of bio-oil model compounds. For example, during palmitic acid upgrading over Mo/ZSM-22 catalysts, Mo^{6+} (or MoO$_3$) properly improved HDC reaction, whereas Mo^{4+} (or MoO$_2$) preferred to support HDO reaction; the Mo^{4+}/Mo^{6+} ratio significantly influenced the final HDO/HDC selectivity. Co is an excellent promoter used to enhance the catalytic performance of Mo-based catalysts. Ding et al. (2016) prepared Co-doped MoO$_2$/CNTs catalysts for catalytic hydrodeoxygenation of palmitic acid; new active sites and defects were formed with Co ions into the lattice of MoO$_2$, and the catalytic performance was improved. Hence, Co could be an effective metal catalyst for removing O atoms during deoxygenation of palmitic acid. However, few studies have investigated upgrading bio-oil or model compounds over sole metal Co catalyst.

Additionally, bulk metal catalysts, similar to catalysts with high metal loading, exhibit poor catalytic performance during chemical removal of O atoms from fatty acid (Zuo et al., 2012; Peng et al., 2012; Ma and Zhao, 2015). In this regard, supports are at least or even more important to the distribution and decrease of metal particles than the metal itself. Hence, supported metal catalysts are suitable for upgrading bio-oil to improve the distribution and decrease the particle size of the metal phase. Supports usually provide large surface area and accommodation for small particles to achieve improved distribution of metal particles, small particle sizes, minimal accumulation of metal particles, and enhanced activity and selectivity of the catalysts. Accommodation of small particles helps prevent small metal particles from sintering and improve the catalytic life of supported catalysts. Besides selective removal of O atoms over metal centers, the desired C atom arrangement should also be considered in fatty acid upgrading to improve the properties of final transport fuels and chemical raw materials. Zeolite-based catalysts have been extensively used because of their superior activity and selectivity in C management during the petroleum hydrocarbon processing. Hence, bi-functional metal/zeolite catalysts are highly recommended to tailor product distribution in one-step bio-oil upgrading (Shi et al., 2016; Peng et al., 2012; Ma and Zhao, 2015; Song et al., 2013; Liu et al., 2015; Cao et al., 2017). Introduction of zeolites (H-ZSM-22, H-ZSM-5, H-Beta), change the catalytic reaction pathway from the HDC route over Ni^0 centers into HDC and HDO over the active centers of bi-functional catalysts. Studies have mainly focused on the formation of isomerization and cracking products. Based upon mass balance, the compositions of bio-oil and its final products are carefully compared. In this paper, Ni and Co were selected as hydrogenation centers to remove O atoms from palmitic acid with lower O content than previously reported. Two ZSM-5 zeolites were also used as supports. This paper focused on points as follows: (1) the role of metal centers (Ni and Co), (2) the role of zeolites with different levels of mesoporosity, and (3) the interactivity between metals and zeolites, including their influences on metal and acid centers and compound effects in a such complicated reaction pathways consisted of parallel reactions via DCX, HDC or HDO, and its consecutive reaction toward acid-catalyzed products via cracking and isomerization.

2. Experiments

2.1. Metal/zeolite catalysts preparation

Commercial H-ZSM-5 (named HZ-5, SiO$_2$/Al$_2$O$_3$ = 225; Sinopec Research Institute of Petroleum Processing, Beijing, China) and post-synthesized H-ZSM-5 with TEAOH to introduce mesopores (named HZP-5, SiO$_2$/Al$_2$O$_3$ = 210; Sinopec Research Institute of Petroleum Processing, Beijing, China) were selected as parent zeolites to support metal hydro-active centers (5 wt% loading NiO or CoO). The pristine metal/zeolite catalysts were prepared with solid state impregnation method based upon the literatures (Cao et al., 2017; Medina-Mendoza et al., 2011; Tang et al., 2014; Zheng et al., 2009; Liu et al., 2014). The desired quantities of Ni(NO$_3$)$_2$·6H$_2$O (m.p. 56.7 °C, Guangfu Fine Chemical Research Institute, Tianjin, China) or Co(NO$_3$)$_2$·6H$_2$O (m.p. 55–56 °C, Guangfu Fine Chemical Research Institute, Tianjin, China) mixed uniformly with zeolitic supports HZ-5/HZP-5 in a closed vital at 65 °C for 24 h via solid state impregnation (or melt infiltration) method. The low melting points of Ni(NO$_3$)$_2$·6H$_2$O and Co(NO$_3$)$_2$·6H$_2$O led to molten metal salts may penetrate partially/completely into zeolitic pores via capillary forces. Clearly, there was no extra water in the solid state impregnation process, which may avoid the competitive adsorption of solvent molecules on the zeolitic surfaces to provide better dispersion of metal. The obtained products were dried at 105 °C overnight and calcined at 550 °C for 5 h in air atmosphere. Prepared catalysts were reduced at 500 °C for 4 h (ramp: 10 °C min^{-1}) in hydrogen flow (flow rate: 80 mL min^{-1}). The required reduction temperatures were determined by H$_2$-TPR. For convenience, the reduced catalysts were named as Ni/HZ-5, Ni/HZP-5, Co/HZ-5 and Co/HZP-5, respectively.

2.2. Catalysts characterization

X-ray diffraction (XRD) patterns of samples were collected on a D/MAX-III X-ray diffractometer (Rigaku Corporation, Japan) with filtered Cu Kα radiation at a tube current of 35 mA and a voltage of 35 kV. The scanning range of 2θ was 5–80°. The relative crystallinity of catalysts was calculated by the sum of the peak intensities at 2θ of 23.1, 23.3, 23.7, 24.0 and 24.4, and the crystallinity of ZSM-5 was defined as 100 %. The crystal morphology was measured on a transmission electron microscopy (TEM). The elemental analyses of the solids were performed on an X-ray fluorescence (XRF) spectrometer MagiX (Philips). Nitrogen adsorption-desorption isotherms were recorded on a Micromeritics ASAP 2010 instrument. The samples were first out-gassed under vacuum