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High *iso*-alkanes production from palmitic acid over bi-functional Ni/H-ZSM-22 catalysts

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ABSTRACT

Bi-functional Ni/H-ZSM-22 catalysts with melt infiltration, incipient wetness impregnation and wet impregnation methods, were used to catalyze palmitic acid. Compared to parent zeolite, there were decrease of relative crystallinity, some blockage effects of micro pores and less strong acid sites after Ni loading. The complete conversion of palmitic acid and 100% alkanes selectivity were achieved at lower temperature (200 °C). No deactivation was observed in five recycle reaction, indicating the excellent catalytic performance and stability of Ni/H-ZSM-22 catalysts. Higher reaction temperature (240–260 °C), more *iso*-alkanes/*n*-alkanes formed, while less C_{16}/C_{15} produced. Additionally, the catalysts prepared by melt infiltration were more inclined to HDO routes and produced more *iso*-alkanes (0.8 mol ratio of *iso*-alkanes/*n*-alkanes) than their counterparts prepared by conventional impregnation methods.

1. Introduction

Increasing concerns about the consumption of non-renewable fossil resources and environmental challenges have urged the exploitation of environmentally friendly and sustainable renewable energies (Wu et al., 2015). Bio-oil from converted biomass has attracted extensive attention as an alternative energy source and is considered as the most potential replacement for fossil fuels (Aysu and Sanna, 2015; Li et al., 2015; Zhang et al., 2014). However, bio-oil, which consists of hundreds of compositions, cannot be directly used as a high-grade fuel because of its relatively high oxygen content, which leads to poor calorific value, corrosiveness, thermal instability, and high viscosity (Ding et al., 2015). Deoxygenation methods for upgrading bio-oil have attracted increasing attention in recent years. Among deoxygenation methods, hydrodeoxygenation (HDO: $R\text{-}COOH+3H_2 \rightarrow R\text{-}CH_3+2H_2O$) has been extensively studied as a method for the direct conversion of bio-oil into hydrocarbon products (Ding et al., 2016; Yoosuk et al., 2012; Zhang et al., 2014). Meanwhile, regardless of the loss of one carbon atom, decarboxylation (DCX: $R\text{-}COOH \rightarrow R\text{-}H+CO_2$) and hydrodecarbonylation (HDC: $R\text{-}COOH+H_2 \rightarrow R\text{-}H+CO+H_2O$) have also been regarded as alternative approaches for deoxygenation because they can occur under relatively low hydrogen pressures or even without H_2 (Morgan et al., 2012; Srifa et al., 2014). Fatty acids and their derivatives are the major oxygenated compounds of bio-oil (Sugami et al., 2016); therefore, the deoxygenation of fatty acids is crucial in upgrading bio-oil. As typical long-chain fatty acids, stearic acid (C_{18}) and palmitic acid (C_{16}) are the major fatty acids obtained from the thermochemical conversion of algal biomass (Srifa et al., 2015; Zou et al., 2010). Thus, these two fatty acids are usually selected as model compounds of bio-oil. The present study selected palmitic acid (C_{16}) as the model compound for investigation.

Several catalysts for the catalytic hydro-treatment of fatty acids have been investigated. In particular, Ni-based catalysts have been exploited by many researchers because of their high hydrogenation activity (Santillan-Jimenez et al., 2015; Veses et al., 2016). Conventional sulfide catalysts, such as NiMo and NiW (Yang et al., 2013; Zhou and Lawal, 2016), show complete conversion of fatty acids. The major products of Ni-based catalysts are *n*-C_{17} alkanes from C_{18} fatty acids with the loss of one carbon atom. Although sulfide NiMo or NiW catalysts can catalyze fatty acids to alkanes, the deactivation of catalysts and the formation of undesirable S-containing products may cause environmental problems. Therefore, the development of sulfur-free catalysts must be investigated further. Metal Ni catalysts support

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on metal oxides for fatty acid deoxygenation; for instance, 5 wt% Ni/ZrO_2 could completely catalyze fatty acids to hydrocarbons via DCX (–CO_2) and/or HDC (–CO) routes at 260 °C under 4 MPa H_2 (Peng et al., 2012). Previous studies (Santillan-Jimenez et al., 2015; Peng et al., 2012; Zhou and Lawal, 2016; Veses et al., 2016; Yang et al., 2013) reported that the main products of bio-oil upgrading are *n*-C_{17} hydrocarbons via DCX and/or HDC routes, which limit the application of upgraded bio-oil as transportation fuels, especially as jet fuels. *Iso*-hydrocarbons are more desirable than *n*-hydrocarbons because of the former's better combustion properties. Importantly, jet fuels require low freezing points at low temperatures (−55 °C) (Cheng et al., 2014; Robota and Alger, 2015). Therefore, acid-catalyzed isomerization coupled with deoxygenation is desired in the catalytic upgrading of bio-oils. Introducing Ni into acid-support zeolites may achieve the desired synergistic effects on the catalysis of long-chain bio-oil to light hydrocarbons and isomerization. Peng et al. (2012) conducted detailed studies on fatty acid deoxygenation catalyzed by Ni/H-ZSM-5 (10 wt% Ni loading, Si/Al=45) and Ni/H-beta (5 wt% Ni loading, Si/Al=75) at 260 °C under 4 MPa H_2 for 8 h. Their results showed a high cracking amount of 42.7% with Ni/H-ZSM-5 and a selectivity of 18.8% for isomerization with Ni/H-beta. Ma and Zhao. (2015) demonstrated that the HDO of stearic acid with Ni-incorporated untreated and treated H-beta catalysts at 260 °C and 4 MPa H_2 (35 wt% Ni loading, Si/Al=9.5) achieves the maximum isomerization yield of C_{17} and C_{18} at 11.2%. Metal-catalyzed hydrogenation and acid-catalyzed reactions (isomerization, cracking, and dehydration) were separately conducted and analyzed on the basis of the above-mentioned studies. A series of reactions is required in the catalytic upgrading of bio-oil, and the interaction between metal centers and acid sites is a significant issue for reactions with bi-functional catalysts. Our recent study has realized selective HDO and isomerization using bi-functional Mo/ZSM-22 catalysts during palmitic acid upgrading (Shi et al., 2016). The two active centers show an obvious interactivity and influence the reactions with bi-functional Mo/ZSM-22 catalysts. Improving hydrogenation by metal active centers would increase *n*-alkane concentration and drive isomerization over acid sites to form more *iso*-alkanes. Improving isomerization would decrease *n*-alkanes concentration and drive hydrogenation forward. According to our previous work, H-ZSM-22 possesses several acid sites, which promote isomerization reactions. In addition, H^+(ionic radius, 0.29 Å) exerts less hindering effect on the distribution of metal oxides because of its smaller ionic radius than K^+(ionic radius 1.33 Å), leading to the severe blockage of micro-pores and better distribution of metal oxides. Therefore, we selected H-ZSM-22 as the acidic metal support for loading Ni in the hydro-active centers.

The efficient preparation of catalysts is highly important. Methods for loading a metal onto the support are dominated by impregnation with water as the solvent. Compared with wet impregnation, incipient wetness impregnation is a simpler, less expensive way to prepare supported-metal catalysts. Zhu et al. (2013) proved that incipient wetness impregnation dramatically improves metal dispersion in loading a metal onto the support. As a relatively solvent-free method, melt infiltration is energy efficient and recyclable, thereby avoiding the problems of impregnation solutions (Li et al., 2012). Liu et al. (2014) demonstrated that melt infiltration adjusts metal distribution by controlling infiltration time. Wong et al. (2000) demonstrated that melt infiltration-prepared catalysts for ethylbenzene dehydrogenation display lower deactivation rates and higher catalytic activities compared with impregnated-prepared catalysts. Generally hydrated transition metal nitrates are suitable to melt infiltration approach based upon their low melting points; in which process, molten metal salts would penetrate inside of zeolitic pores through capillary forces. The temperature of this process must be carefully controlled to avoid the decomposition of hydrated metal nitrates. Clearly it is unnecessary to add extra water in the whole process, which may prevent the competitive adsorption of solvent molecules on the zeolitic supports surface to provide better dispersion of metal (Liu et al., 2014). In the present study, bi-functional Ni/H-ZSM-22 catalysts were prepared by melt infiltration, incipient wetness impregnation, and wet impregnation to evaluate the HDO and acid-catalyzed performance of palmitic acid. This study analyzed the adjusted distribution of final products at different reaction temperatures and explored the differences in physicochemical properties and catalytic performance among the three methods. It also investigated the interactivity between hydrogenation centers and acid centers of bi-functional catalysts to promote HDO and isomerization.

2. Experiments

2.1. Catalysts preparation

Zeolite HZSM-22 (Si/Al=37.5, Sinopec Research Institute of Petroleum Processing, Beijing, China) was chosen to support hydro-active centers (Ni particles), and Ni/H-ZSM-22 (NiO loading 5 wt%) catalysts investigated in this study were prepared by melt infiltration, incipient wetness impregnation and wet impregnation methods.

2.1.1. Melt infiltration method

Zeolitic support (H-ZSM-22) preheated at 150 °C for 24 h for removing its moisture; and then a certain amount of $Ni(NO_3)_2{\cdot}6H_2O$ (m.p.56.7 °C, purchased from Guangfu Fine Chemical Research Institute, Tianjin, China) and H-ZSM-22 were mixed uniformly in a closed vial at 65 °C for 24 h via melt infiltration method (Li et al., 2012; Liu et al., 2014). As well known $Ni(NO_3)_2{\cdot}6H_2O$ would be completely molten in a few minutes at 65 °C, and then impregnated into zeolitic pores via capillary forces in this process.

2.1.2. Incipient wetness impregnation and wet impregnation methods

$Ni(NO_3)_2{\cdot}6H_2O$ were dissolved in these two kinds of distilled water and then slowly dropped this solution onto calcined zeolitic supports H-ZSM-22. As for wetness impregnation, the mixed compounds should stir for 4 h to make sure the metal precursor was dispersed on the supports. The obtained samples prepared by melt infiltration, incipient wetness impregnation and wetness impregnation, were dried at 105 °C overnight.

Three methods prepared Ni/H-ZSM-22 catalysts were followed by calcination up to 550 °C for 6 h in air atmosphere. These calcined catalysts were reduced at 500 °C for 4 h (ramp: 10 °C min^{-1}) with a hydrogen gas (flow rate: 50 mL min^{-1}), which the H_2-TPR was used to determine the required reduction temperatures. For convenience, the reduced catalysts were named as Ni/HZ-1 (melt infiltration), Ni/HZ-2 (incipient wetness impregnation) and Ni/HZ-3 (wetness impregnation), respectively.

2.2. Catalysts characterization

X-ray diffraction (XRD) crystal phases of samples were collected on a D/MAX-III instrument (Rigaku Corporation, Japan) with filtered Cu Kα (35 mA, 35 kV). The samples were scanned in the 2θ range of 5–80°. The surface morphologies and particle sizes of Ni/HZ-n catalysts were examined by transmission electron microscopy (TEM) images taken with a Model FEI Quanta. X-ray fluorescence (XRF) spectrometer MagiX (Philips) measurement was used to evaluate the elemental analyses of the solids. The BET equation (relative pressure range: 0.05–0.16) was performed in the nitrogen adsorption isotherm as range of linearity to obtain the total surface area of Ni/HZ-n using a molecular cross-sectional area for N_2 of 0.162 nm^2. The prepared catalysts were first out-gassed under vacuum at 90 °C for 1 h and then at 350 °C for 15 h. The micro pore volume was obtained by the t-plot method. The acidity of H-type zeolites was measured by Ammonia – temperature programmed desorption (NH_3-TPD), which was recorded