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Effect of calcination temperature on the association between free NiO species and catalytic activity of Ni$-$Ce$_{0.6}$Zr$_{0.4}$O$_2$ deoxygenation catalysts for biodiesel production

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ABSTRACT

In this study, a series of Ni$-$Ce$_{0.6}$Zr$_{0.4}$O$_2$ catalysts, which were synthesized by co-precipitation followed by calcination at different temperatures, were applied for the deoxygenation of oleic acid. The physicochemical properties of the catalysts were characterized by N_2 adsorption-desorption, X-ray diffraction (XRD), H_2 chemisorption, H_2 temperature-programmed reduction (H_2-TPR), NH_3 temperature-programmed desorption (NH_3-TPD), and X-ray photoelectron spectroscopy (XPS). The Ni$-$Ce$_{0.6}$Zr$_{0.4}$O$_2$ catalyst calcined at 300 °C exhibited the highest conversion for oleic acid as well as selectivity for diesel-range compounds. It is predominantly related to the highest amount of free NiO species. In addition, the acidity of the catalyst significantly affected the selectivity and distribution of products.

1. Introduction

In the last few years, there has been increasing interest in the production of green fuels or chemicals; one of the main reasons for this increase is the access to energy at affordable prices because of the increasing consumption of liquid fuels with the increase in the world population. In the U.S. EIA report (IEO2016), the global transportation energy consumption increases annually at 1.4%, from 104 quadrillion Btu in 2012 to 155 quadrillion Btu in 2040. Another driving force is the threat of climate change resulting from the use of fossil fuels. The transesterification of triglycerides with methanol involves the conversion of triglycerides to fatty acid methyl esters (FAMEs) [1]. However, the application of FAMEs to existing machineries has been limited because of the undesirable fuel properties, e.g. high viscosity, thermal instability, and low heating values [1,2].

Recently, the production of diesel-like hydrocarbons, as an alternative to FAMEs, from animal or plant lipids by catalytic processes has been rapidly developed because of its similar properties to fossil-fuel-based diesel, e.g., high oxidation stability and high cetane number [3,4]. Hydrodeoxygenation (HDO), which typically proceeds by the removal of oxygen species in reactants, is a plausible pathway to produce diesel-like hydrocarbons from animal or plant lipids [4]. The NExBTL process from Neste Oil and the Ecofining process from ENI-UOP have been developed at the commercial level for producing diesel-like hydrocarbons using HDO [5]. However, these processes consume large amounts of hydrogen, 300–420 m^3_{H2}/m^3_{oil}, to produce desirable hydrocarbons [6]. Accordingly, ensuring a higher safety and reducing the production costs by avoiding the use of hydrogen, deoxygenation (DO) under an inert atmosphere (alternatively inert gas with a small amount of hydrogen) has been extensively investigated [7–10].

Murzin et al. have reported the most promising catalytic performance for DO over Pd supported on activated carbon [11,12].

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Immer et al. have reported the DO of fatty acids over Pd/C [13]. Pt-based catalysts have also been reported to effectively catalyze the HDO of FAMEs [14]. However, considering the relatively high cost and limited availability of these metals, the development of non-noble metal catalysts with similar performance is important from an industrial viewpoint. Recently, Ni-based catalysts have been employed to convert algal lipids to diesel-like hydrocarbons [15–18]. Ni-based catalysts have exhibited similar catalytic performance with the noble metal based catalysts, but these results were obtained under milder conditions (high H_2 pressure, long reaction time, etc). The catalytic performance and reaction conditions of these catalysts are summarized in Table 1. However, the research of Ni-based catalysts is still promising because the cost of Ni is approximately 1000 and 2500 times less than those of Pd and Pt, respectively. Several studies have reported that transition metals supported on CeO_2, ZrO_2, and $Ce-ZrO_2$ catalysts are active for DO or HDO. Peng et al. reported the selective cleavage of C-C and C-O bonds in C_{18} microalgae oil over ZrO_2-promoted Ni catalysts under 40 bar of pure H_2 [16]. Yakovlev et al. have reported that CeO_2 and ZrO_2 are the most effective for HDO because of the possible additional activation of oxy-compounds on the support surface [17]. In addition, Zhang et al. have reported high activity for the HDO of guaiacol over $Ni-Cu/ZrO_2-SiO_2$ catalysts at 300 °C under 50 bar of H_2 [18].

Our group has reported high oleic acid conversion, high C_9~C_{17} (diesel fuel range) selectivity, and oxygen removal efficiency for DO over a $Ni-Ce_{0.6}Zr_{0.4}O_2$ catalyst, predominantly related to the synergistic effects of Ni and $Ce_{0.6}Zr_{0.4}O_2$, presence of free Ni species, and the highest Brunauer-Emmett-Teller (BET) surface area [19]. However, issues associated with the enhancement of activity and selectivity of $Ni-Ce_{0.6}Zr_{0.4}O_2$ catalyst for DO still exist. This study investigated the effect of the calcination temperature on the performance of the $Ni-Ce_{0.6}Zr_{0.4}O_2$ (hereafter referred to as Ni−CZO) catalyst for DO. The catalysts were characterized by BET, X-ray diffraction (XRD), H_2 chemisorption, H_2 temperature-programmed reduction (H_2-TPR), X-ray photoelectron spectroscopy (XPS), NH_3 temperature-programmed desorption (NH_3-TPD), the results obtained were correlated to the catalytic activities for DO.

2. Experimental

2.1. Catalyst preparation

Ni−CZO catalysts were prepared by co-precipitation. A constant Ni loading of 20 wt% and Ce/Zr molar ratio of 6:4 were applied. Stoichiometric amounts of $Ni(NO_3)_2 \cdot 6H_2O$ (97%, Junsei), $Ce(NO_3)_3 \cdot 6H_2O$ (99%, Aldrich), and a zirconyl nitrate solution (20 wt% ZrO_2 basis, MEL Chemicals) were combined in 500 mL distilled water. To this solution, a 15% KOH solution was added drop-wise at 80 °C under constant stirring to attain a pH of 10.5. The precipitates were aged at 80 °C for 3 days. Next, the precipitates were washed 5 times with distilled water and then dried in air for 12 h. The as-prepared Ni−CZO catalysts were calcined at temperatures ranging from 250 to 700 °C for 6 h in air. The obtained catalysts will be hereafter referred to as Ni−CZO_*T*, where *T* represents the calcination temperature.

2.2. Characterization

The BET surface area was measured by nitrogen adsorption at −196 °C using an ASAP 2010 (Micromeritics) instrument. XRD patterns were recorded on a Rigaku D/MAX-IIIC diffractometer (Ni-filtered Cu-K radiation, 40 kV, 50 mA), and the crystallite size was estimated by the Scherrer equation. H_2-TPR was carried out in an Autochem 2920 (Micromeritics) instrument using 10 vol% H_2/Ar at a heating rate of 10 °C/min. H_2 chemisorption was performed by using a pulse technique to identify the metallic dispersion and metal surface area on an Autochem 2920 (Micromeritics) instrument. A 100 mg sample was reduced under 10 vol% H_2/Ar at 700 °C for 2 h. Then, the sample was cooled to 50 °C under Ar. A H_2 pulse (10% H_2/Ar) was injected into the catalyst. The adsorbed H_2 amount was used to estimate the dispersion and surface area on Ni by assuming the adsorption stoichiometry of one hydrogen atom per nickel atom on the surface ($H/Ni_{surface} = 1$). NH_3-TPD was performed on an Autochem 2920 (Micromeritics) instrument. The detailed procedure for NH_3-TPD has been reported previously [7]. XPS spectra were obtained using a $K\alpha$ spectrophotometer (Thermo-Scientific), with a high-resolution monochromator. The pressure of the analysis chamber was maintained at 6.8×10^{-9} mbar, and the detector was maintained in the constant energy mode with a pass energy of 100 eV for the survey spectrum and 50 eV for the detailed scan. The binding energy was calibrated to the C 1s peaks observed at 284.6 eV. The quantitative analysis of residual hydrocarbons and coke on the used catalysts was measured with a thermogravimetry analyzer (TGA, TA instruments SDT 2960). A 4–8 mg sample was heated from 30 to 700 °C with a heating rate of 10 °C min^{-1} in oxygen.

2.3. Catalyst activity

DO reactions were carried out in an autoclave reactor (100 mL) operating in the batch mode. All of the prepared catalysts were reduced under 10 vol% H_2/N_2 at 700 °C for 2 h and then cooled to room temperature under N_2 before the reaction. In a typical batch experiment, 27.5 g of oleic acid and 0.6875 g of the catalyst were added into the reactor. After then, the reactor was flushed with 20 vol% H_2/N_2 to remove the air and heated to 300 °C. The reaction was performed under 1 bar of 20 vol% H_2/N_2 at 300 °C for 3 h. The stirring speed was fixed at 300 rpm during the reaction. After the reaction, the liquid products were collected after the filtration of the solid-phase catalysts. The liquid products were silylated with N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA, Alfa Aesar,

Table 1
The deoxygenation performance of noble metal and Ni based catalysts (*T* is temperature; *P* is pressure; *t* is time).

Catalysts	Reactor type	Feed	Reaction conditions			Atmosphere	Conversion (%)	Selectivity (%)	Ref.
			T (°C)	*P* (bar)	*t* (min)				
4 wt% Pd/C	Semi-batch	Stearic acid	300	17	100	He	100	50	11
1 wt% Pd/C	Semi-batch	Stearic acid + Palmitic acid	300	18	300	5% H_2/Ar	100	48	12
5 wt% Pd/C	Semi-batch	Stearic acid	300	15	300	He	100	98	13
1 wt% Pt/Al_2O_3	Semi-batch	Methyl stearate	325	7	300	H_2	64	94	14
10 wt% Ni/HBeta	Batch	Stearic acid	260	40	480	H_2	98	99	15
15 wt% Ni/ZrO_2	Batch	Stearic acid	260	40	480	H_2	100	98	16
$Ni-Cu/CeO_2$	Fixed-bed	Anisole	260	10	120	50% H_2/Ar	100	100	17
10 wt% Ni−5 wt% Cu/ZrO_2-SiO_2	Batch	Guaiacol	300	50	480	H_2	100	93	18