



Biodiesel production from hempseed oil using alkaline earth metal oxides supporting copper oxide as bi-functional catalysts for transesterification and selective hydrogenation

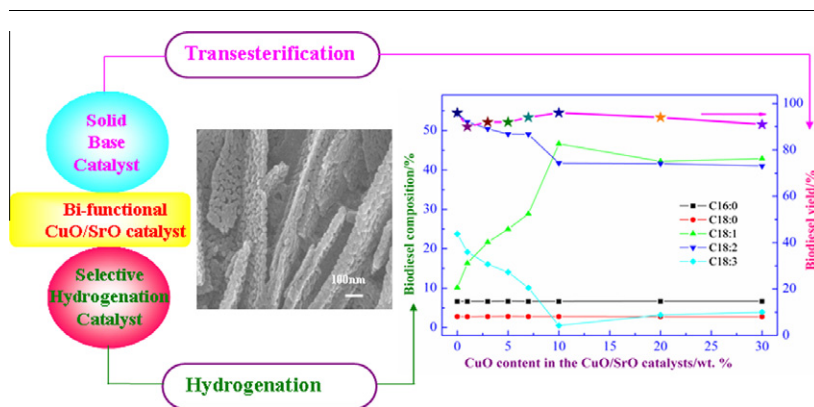
Mengxing Su, Ru Yang*, Min Li

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

HIGHLIGHTS

- ▶ Highly unsaturated hempseed oil was converted into high quality biodiesel.
- ▶ Cu/SrO is an effective catalyst for transesterification and hydrogenation.
- ▶ Increasing hydrogen pressure and reaction temperature favor selective hydrogenation.
- ▶ Basic strength and basicity affected catalytic activity for transesterification.
- ▶ Surface copper species determined catalytic activity for selective hydrogenation.

GRAPHICAL ABSTRACT



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ABSTRACT

Alkaline earth metal oxides supporting copper oxide (Cu/AMO) were used as bi-functional catalysts for transesterification and selective hydrogenation to produce biodiesel from highly unsaturated hempseed oil. Cu/AMO catalysts were characterized by XRD, SEM, N₂ adsorption, CO₂-TPD, H₂-TPR, and XPS to reveal the crystal structure, morphology, texture properties, basicity, reducibility, and surface chemical states. The bi-functional catalysts formed alkaline earth metal cuprates and showed strong basic strengths. Cu/SrO catalyst presented much surface copper species, which were reduced to metallic copper after reactions. The effect of the molar ratio of methanol to oil, copper oxide content, hydrogen pressure, and reaction temperature on the catalytic performance was further investigated. Cu/SrO catalyst showed superior catalytic activity for transesterification and selective hydrogenation. Catalytic activity for transesterification is strongly dependant on basic strength and the amount of basic sites of the bi-functional catalysts. The amount of reduced surface copper species of Cu/SrO catalysts made a large contribution to catalytic activity for selective hydrogenation.

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1. Introduction

Biodiesel, a biodegradable and renewable form of energy, emitting less carbon monoxide, sulfur compounds, particulate matter and unburned hydrocarbons than traditional diesel [1], is usually

* Corresponding author. Tel./fax: +86 10 64436736.
 E-mail address: yangru@bncn.cn (R. Yang).

composed of fatty acid methyl esters formed by transesterification of renewable triglycerides such as vegetable oils and animal fats with methanol. The vegetable oils being exploited for biodiesel production constitute the edible oils like rapeseed, soybean, palm, and sunflower, of which there is a big gap in the demand and supply. An increase in the production of biodiesel will only be possible by making available new feedstock apart from these edible fatty oils, for both economic and ethical reasons [2]. More than 350

oil-bearing crops have been identified [3]; oils from 75 plant species have been converted to biodiesel and the iodine value (IV) and cetane number (CN) varied from 4.8 to 212 and 20.56 to 67.47, respectively [4]. Many of them are highly unsaturated oils, which are unsuitable as starting materials for direct transesterification to produce biodiesel since their IVs and CNs do not meet the specifications of EN14214 that contains a specification for IV (120, maximum) and CN (51, minimum) [5]. Hempseed oil obtained by expression of hempseed which is a waste of hemp planting is such a typical highly poly-unsaturated vegetable oil with an iodine value of 164 g I₂/100 g. To use the highly un-saturated oils as raw materials for biodiesel production, selective hydrogenation is essential and practical to reduce the degree of un-saturation without increasing the totally saturated components [2]. It is difficult to get the selectivity with the conventional nickel [6] and noble metal-based catalysts like platinum [7] and palladium [8] since these catalysts resulted in the formation of significant quantities of saturated components with high melting points, which compromised the cold-weather behavior of the product obtained [2]. Fortunately, supported copper catalysts possess high selectivity for hydrogenating linolenate (C18:3) to oleate (C18:1) with oleate C18:1 unreduced, therefore, the percentage of saturated is scarcely changed during the hydrogenation process.

Acidic oxides like SiO₂, Al₂O₃, TiO₂, ZnO, and sepiolite have been widely employed as support for copper catalysts in the hydrogenation [2,9]. Ravasio et al. [10] investigated catalytic performances of copper catalysts on different acidic supports and the effect of catalyst preparation method on the catalytic activity. Cu/SiO₂ prepared by chemisorption–hydrolysis (CH) method had a good copper dispersion over supports, and it exhibited high activity and promising selectivity for hydrogenating C18:3 to C18:1 with C18:1 unreduced. Copper catalyst on the less acidic supports like alumina and sepiolite presented less activity but very high selectivity, whereas Cu/TiO₂ and Cu/ZnO catalysts with much less acidic supports gave poor results of both activity and selectivity. Copper catalyst prepared by the conventional incipient wetness technique did not show any activity even after very long reaction time. Basic oxides, such as MgO, CaO, SrO, and BaO, have been rarely reported as support for copper catalysts in the hydrogenation except MgO. Derouane et al. [11] used a Cu/MgO catalyst for the hydrogenation of ethylene and they proposed that surface Cu²⁺ ions were the active species. Okkerse et al. [12] studied a similar catalyst (Cu–Mg–SiO₂) for soybean oil hydrogenation and they found that the active center consisted of copper metal crystallites. However, little attention has been focused on the acidity and basicity of the Cu supported catalysts and its effect on catalytic activity toward hydrogenation.

Alkaline earth metal oxides (AMOs) including MgO, CaO, SrO, and BaO, have been intensively studied as heterogeneous basic catalysts for transesterification of triglycerides with methanol. AMO became active for transesterification after a thermal pretreatment and the catalytic activities were predominant upon their alkalinities [13]. As the basic strength increased in the order of MgO < CaO < SrO < BaO, which was attributed to the decrease of electro-negativity of the conjugated metal cation of AMO, the catalytic activities of transesterification exhibited in the same sequence. SrO had basic sites stronger than H₊ = 26.5 and gave a biodiesel yield in excess of 95% at 65 °C within 30 min in the transesterification of soybean oil to biodiesel [14]. Taking into account that AMO presented high catalytic activity for transesterification and copper supported catalyst showed promising hydrogenation selectivity, we developed Cu/AMO as a bi-functional catalyst for transesterification and selective hydrogenation [15]. In the previous work, we explored the catalytic performances of Cu/AMO catalysts for one-pot process combining transesterification and selective hydrogenation under hydrogen pressure conditions and tested the hydrogenated biodiesels obtained.

The present study aimed to give a detailed study of the effects of reaction conditions on the transesterification and selective hydrogenation over Cu/AMO catalysts and to give a detailed characterization of Cu/AMO catalysts using X-ray diffraction (XRD), scanning electron microscope (SEM), N₂ adsorption, CO₂-Temperature programmed desorption (CO₂-TPD), H₂-Temperature programmed reduction (H₂-TPR), and X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Materials

Refined hempseed oil, obtained from Xishuangbanna Dai autonomous prefecture, Yunnan province, China, was used as the starting material since it had an IV of 164 g I₂/100 g which was higher than 120 g I₂/100 g required by EN 14214. The acid value was less than 0.1 mg KOH/g. According to GC analysis, the fatty acid consisted of palmitic acid 6.64%, stearic acid 2.76%, oleic acid 10.12%, linoleic acid 54.31%, linolenic acid 23.76%, and traces of other acids. All chemicals used were of analytical grade, which were purchased from Beijing Chemical Co. Ltd., China.

2.2. Catalyst preparation

MgO, CaO, SrO, BaO, and CuO samples were prepared by the conventional precipitation method from metal nitrates using ammonium bicarbonate as precipitate [15]. Cu/AMO were prepared by the CH method [10]. The support was added to a (Cu(NH₃)₄)²⁺ solution prepared by adding NH₄OH to 100 mL Cu(NO₃)₂·3H₂O solution (0.2 mol/L) until pH was 9. After 20 min under stirring, the slurry was slowly diluted in order to allow hydrolysis of the copper complex and deposition of the finely dispersed product to occur. After that, the solids were separated by filtration, dried overnight at 120 °C. Prior to each reaction, the as-prepared catalysts were calcined at 1000 °C in vacuum for 5 h. The loading amounts of copper oxide were calculated on the basis of the amounts of the initial materials.

2.3. Catalyst characterization

Phase identification of calcined Cu/AMO catalysts was performed by powder XRD patterns on a Japan Rigaku D/Max-2500 diffractometer, operated at 28 kV and 40 mA. The powders were ground and then loaded in sample holders for data collection, using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) and a scanning speed of 10° min⁻¹ over a 2 θ range of 5–90°. The phases of the as-prepared catalysts were identified by comparing their peak positions and relative intensities with standard JCPDS files.

The texture properties of calcined Cu/AMO were determined from nitrogen adsorption isotherms measured at liquid nitrogen temperature (–196 °C) using a Micromeritics Instrument Corp. ASAP 2020. Prior to any adsorption measurement each sample was degassed at 250 °C for 8 h to eliminate air and water vapor from the capillaries of the pore structure of the solids. Specific surface areas and pore size distributions of the samples were obtained using the BET and BJH calculation methods, respectively.

The morphology of calcined Cu/AMO was investigated by SEM, and the images were obtained using a HITACHI S-4700 SEM working at 20 kV, and the samples were gold coated prior to analysis. The size of used Cu/SrO catalyst was investigated using a HITACHI H-800 transmission electron operated at 200 kV.

The basicity of Cu/AMO catalysts was investigated by CO₂-TPD, which was performed in a straight quartz tube in Ar flow, using a thermal conductivity detector (TCD). The standard procedure consisted of pretreatment, saturation, and desorption steps. For each

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