



Synthesis and characterization of the acidic properties and pore texture of Al-SBA-15 supports for the canola oil transesterification



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HIGHLIGHTS

- Mesopore and surface acidity of Na/SBA-15 improve the transesterification activity.
- Pore structure of Na/SBA-15 were altered using different aging temperature.
- Surface acidity of Na/SBA-15 were modified by incorporation of heteroatom Al.
- The FAME yield of Na/Al-SBA-15 was comparability with commercial support.

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ABSTRACT

Ordered mesoporous SBA-15 was used as a support for the transesterification of canola oil to produce biodiesel. The pore size and surface acidity of SBA-15 were modified by synthesis conditions using different aging temperatures and the addition of heterogeneous Al atoms. The results of the characterization study indicated that a large amount of mesopore and surface acidity can greatly improve the transesterification reaction at a high aging temperature and with the incorporation of aluminum into the SBA-15 framework. This improvement in transesterification activity is due to the formation of more stable $\equiv\text{Si}-\text{O}-\text{Al}\equiv$ bonds on the surface of the framework. The transesterification reaction was also compared with synthesis involving traditional supports such as acidic and basic $\gamma\text{-Al}_2\text{O}_3$, hydrotalcite, and SiO_2 . The activities of the catalysts were related to their acidic strength.

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1. Introduction

The biodiesel fatty acid methyl ester (FAME) is a renewable and clean energy source that can replace oil and has the potential to help reduce oil dependence and global warming [1]. Biodiesel is synthesized by the transesterification of vegetable oils or animal fats with a short-chain alcohol in the presence of catalysts. In the synthesis, the exchange of the organic group R' of an ester with the organic group R of an alcohol occurs [2,3]. Transesterification is usually catalyzed by acid or base catalysts that donate a proton to the carbonyl group or remove a proton from the alcohol, thereby making them both more reactive [4,5]. Most biodiesels are currently produced in the presence of homogeneous basic catalysts, which offer advantages such as higher reaction rates and a low

temperature requirement to obtain high biodiesel yields in a short period of time [6]. However, the main drawback of using homogeneous basic catalysts is the occurrence of saponification as a side reaction (i.e., $\text{R}-\text{COOH} + \text{NaOH} \rightarrow \text{R}-\text{COONa} + \text{H}_2\text{O}$), thereby making the process inefficient [7].

Although the reaction rate of syntheses that involve the use of heterogeneous catalysts is slower compared to the reaction rate of syntheses that involve homogeneous catalysts, the heterogeneous catalysts still offer several advantages, which include being noncorrosive, able to regenerate, and causing fewer disposal problems [8]. The process is thus continuous. Heterogeneous catalysts can be designed to exhibit higher activity, selectivity, and longer lifetimes by modifying the characterization of the catalysts.

Several types of heterogeneous catalysts have been investigated for transesterification. These catalysts include alkaline earth metal oxides [4,8,9] or metal oxides supported on alumina [2,5,10], zeolite [1], or hydrotalcite [11,12]. Zeolites were initially considered as a promising material because of their unique porous structure, high surface area, and high thermal stability. However, reactions

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involving zeolites were unsuccessful because larger reactive molecules are involved [7]. The acidity of the support is also essential in transesterification because solid acid catalysts can simultaneously catalyze the transesterification of triglycerides and the esterification of free fatty acids when waste cooking oil is used to produce second-generation biofuels [13]. Therefore, aside from the physical texture, the surface acidity of the support is also essential in improving the biodiesel yield rate. Based on previous studies, the following strategies have been recommended to improve the catalyst performance: (i) developing the pore structure with a large pore diameter and surface area to improve the mass transfer and metallic dispersion; and (ii) increasing the support surface acid/basic strength for proton donation/removal [14]. These strategies may be accomplished by using supports with appropriate morphologies and acidic surface properties.

Amorphous silicas with ordered mesoporous structures (like MCM-41 and SBA-15) have been widely used as supports for various metals [15–18] because of their controllable molecular-sized pores, strong surface acidity and large number of active sites [17]. These supports are particularly attractive applied in heterogeneous reactions involving large organic molecules where microporous zeolites cannot be used [19]. Among different supports with an ordered mesopore structure, SBA-15 seem to be more suited to react in transesterification because SBA-15 has larger pore sizes (4.6–30 nm), thicker pore walls (3.1–6.4 nm) and higher surface area (up to 1000 m²/g). SBA-15 also shows a greater opportunity to improve the hydrothermal stability [17] than the conventional MCM-41 support. Samart et al. [1] applied mesoporous silica as a support in transesterification, and they evaluated the reaction conditions for the reaction of soybean oil with methanol. They showed that the methyl ester yield was close to the yield produced by the conventional homogeneous catalysis method. However, the characteristics of the silica, which are important in determining the activity of the catalysts, were not evaluated. Saravanamurugan et al. [20] controlled the SBA-15 morphology with an amino group and applied this support to the transesterification of diethyl malonate with various aliphatic and aromatic alcohols. They found that functionalized catalysts exhibited enhanced catalytic activity strongly dependent on the morphologies of the support.

However, the electrically neutral framework of silica provides SBA-15 materials with a weak acidity due to the silanol groups located on the pore walls. Several efforts have been made to synthesize SBA-15 with various heteroatoms such as aluminum [15,17,18,21], iron [15], and zirconium [16,22] to enhance its acidity by creating Lewis acid sites. Al-SBA-15 materials with a large number of moderately acidic sites are one kind of very promising catalysts and supports involving catalytic reaction. Li et al. [17] have showed that Al-SBA-15 materials exhibit high hydrothermal stability due to the formation of more stable $\equiv\text{Si}-\text{O}-\text{Al}\equiv$ bonds on the surface of the framework. Szczodrowski et al. [23] also indicated that the doping procedure enhanced SBA-15 acidity, especially as observed with Al-SBA-15 compared to Zr-SBA-15 or Ti-SBA-15.

This study aims to improve the activity of NaOH/SBA-15 catalysts by altering the physicochemical properties of the support. The properties of the support can be altered by changing its pore structure and surface acidity. The introduction of Al into the silica framework to improve the acidity and to modify the pore texture by changing the aging temperature was systematically investigated.

2. Experimental

2.1. Materials

Commercial chemicals with the highest purity available (>98%), namely, NaOH (RDH, Germany), aluminum oxide (Sigma–Aldrich,

France), hydrotalcites (Sigma–Aldrich, France), silicon dioxide (Sigma–Aldrich, France), and methanol (Fluka, France) were used without further purification. Canola oil (purity >99.9%) was obtained from Tatung Chang Chi Food Stuff Factory Co., Ltd. (Taiwan).

Tetraethyl orthosilicate (TEOS), non-ionic triblock copolymer PEO–PPO–PEO ((poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide)) (pluronic P123, MW: 5800 g/mol), hydrochloric acid (HCl, 37%), and aluminum isopropoxide (AIP) were purchased from Sigma–Aldrich (France). All chemicals were used for the preparation of pure or Al-doped SBA-15 mesoporous materials.

2.2. SBA-15 and Al-SBA-15 synthesis

The SBA-15 support was synthesized using pluronics P123 as a structure-directing agent and TEOS as a silica source. In this typical process, 4 g of P123 was dissolved in 150 mL of aqueous HCl at pH 1.5. Subsequently, 5 mL of TEOS was added dropwise to the solution. After stirring at 40 °C for 24 h, the mixture was aged at 90 °C, 100 °C, 110 °C, or 120 °C for 24 h. The white precipitate was then collected by filtration and dried at 110 °C overnight. The product was obtained by removing the template at 550 °C for 6 h at a heating rate of 1 °C/min. The samples obtained were designated as S90, S100, S110, and S120.

Al-SBA-15 was synthesized through a “direct synthesis” method [24] by using the same procedure and by using AIP as an Al source. In a typical synthesis, 5 mL of TEOS and a calculated amount of AIP were added to 10 mol of aqueous HCl at pH 1.5 to obtain Si/Al molar ratios of 10, 30, and 50. The solution was stirred for 3 h and then added to a second solution containing 4 g of P123 in 140 mL of 2 M HCl solution at 40 °C. The mixture was stirred for 24 h at the same temperature and then aged at 110 °C for 24 h in closed Teflon bottles. The solid product obtained was filtered, dried at 110 °C and finally calcined in air at 550 °C for 6 h at a heating rate of 1 °C/min. The sample was designated as Al-S110(X), where X is the theoretical Si/Al molar ratio.

Catalyst preparation

The impregnation of the supports with the Na precursor salts was conducted using a pore volume impregnation technique. An appropriate concentration of NaOH ethanol solution (20 g support/150 mL ethanol) was used to impregnate the support with 5 wt% loading weight of Na. After 24 h, the solution was heated and constantly stirred until the liquid was entirely evaporated. NaOH loaded on basic $\gamma\text{-Al}_2\text{O}_3$, acid $\gamma\text{-Al}_2\text{O}_3$, silica dioxide, and hydrotalcite was also prepared for comparison with other catalysts using the impregnation method from an aqueous solution. The prepared catalysts were dried in an oven at 105 °C for 2 h and calcined at 400 °C for 5 h in air.

2.3. Catalyst characterization

The crystal structure of the catalyst was determined by a small angle X-ray diffraction system (SAXRD; Mac Science Co., M18XHF), with a Cu K α X-ray source. The diffraction patterns were acquired with a 2θ angle, which ranged from 0.5° to 8° and a scanning step of 0.02°.

The morphology of the supporting materials and the supported catalysts was examined using a field emission scanning electron microscope (FESEM, JEOL JSM-6700F).

Fourier transform infrared (FT-IR) spectra were obtained in the 4000–400 cm⁻¹ region with a PerkinElmer 1730 FT-IR spectrometer.

High-resolution transmission electron micrograph (HRTEM) images were obtained using a JEOL 2010 microscope. The solids were ultrasonically dispersed in heptane, and the suspension was collected on carbon-coated grids.

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