



Nb₂O₅/SBA-15 catalyzed propanoic acid esterification



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ABSTRACT

A family of niobia (Nb₂O₅) functionalized SBA-15 solid catalysts have been prepared via wet impregnation with NbCl₅ (2–32 wt% Nb) and subsequent thermal processing, for application in the acid catalyzed esterification of propanoic acid with methanol. Bulk and surface physicochemical characterization revealed that highly dispersed niobia species present at low loadings when calcined at 500 °C exhibit strong Brønsted acid character and associated activity for esterification. Increased calcination temperatures are found to result in a decrease in Brønsted:Lewis acid ratio associated with recrystallization of the niobia phase leading to a loss of catalyst activity. Esterification activity is found to be directly proportional to Brønsted:Lewis acid ratio, with the 2 wt% Nb/SBA-15 catalyst pre-calcined at 500 °C found to exhibit highest activity and excellent reusability without deactivation.

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1. Introduction

Humanity faces unprecedented environmental, social, and economic challenges in the 21st century due to population growth, with an associated *per capita* increase in the consumption of natural resources and a continued reliance on fossil fuels for both energy and chemicals production [1]. The search for alternative renewable energy sources has attracted attention in large part due to anthropogenic climate change, with biomass emerging as a frontrunner for provision of liquid transportation fuels [1–5]. Biodiesel is the best established and commercially most widely available biomass derived fuel that has been introduced in the energy matrix of various countries (notably Brazil), with the goal of reducing air pollution and increasing both energy security and economic benefits [6,7]. Biodiesel is a good substitute for conventional diesel and can be obtained from vegetable oils, animal fats, fatty acids or waste fatty materials from residual cooking oils [7–10]. Waste raw materials are advantageous for biodiesel production since they do not compete with food applications or require land use change and offer lower cost production [11]. Biodiesel is conventionally synthesized

through the transesterification of triacylglyceride components and esterification of fatty acid components, of vegetable oils and fats with light alcohols; excess alcohol is usually employed in order to drive the equilibrium towards the desired fatty acid alkyl ester (biodiesel) product [6,7]. Although transesterification is more rapid when catalyzed by base than by acid catalysts, the presence of free fatty acid (FFA) impurities in most oil/fat feedstocks hinders the use of the former due to soap formation and attendant energy intensive biodiesel separation [7]. Fatty acid esterification may be catalyzed by mineral or organic acids, such as sulfuric or *p*-toluenesulfonic acid [7,8], however the corrosive and toxic nature of these liquid acids and the requirement for their neutralization and separation increases process costs and lowers the green credentials of biodiesel [7,8].

Solid acid catalysts offer economic and process benefits, especially so for low cost feedstocks with high FFA content, enabling one-pot esterification and transesterification of bio-oils [12]. A wide range of solid acids [13], including heteropolyacids [14,15], sulfonated metal oxides [16,17] and carbons [18], and zeolites [19] have been applied to biodiesel production, however new materials with improved solvothermal stability and recyclability are still sought. Aranda et al. reported on the application of bulk niobia for biodiesel production from the esterification of palm oil which is high in FFAs, including palmitic (46.4%), oleic (41.2%) and linoleic

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(11.1%) acids [20]; a net FFA conversion of around 80% was achieved with methanol at 130 °C. Niobic acid and niobium phosphate have also been applied for the esterification of C₁₂ and C₁₈ FFAs with methanol, ethanol and butanol. Amorphous niobium phosphate exhibited strong Brønsted acidity comparable to niobic acid, proving efficacious for lauric acid esterification with butanol [21].

Mesoporous materials are attractive in heterogeneous catalysis due to their high surface areas, tunable pore architectures and associated improved mass-transport, and ability to generate highly dispersed and active sites [22]. For example, SBA-15 mesoporous silica was recently used to stabilize dispersed conformal zirconia and sulfated zirconia monolayers for the synthesis of either ethyl levulinate or 5-hydroxymethylfurfural from glucose [23,24], and alkali-free hydrotalcite nanocrystals for biodiesel production from triacylglycerides [25]. Nb/SBA-15 has been explored by Calvino-Casilda et al. who studied the impact of Zr, Nb and Mo modified SBA-15 in Knoevenagel condensation, along with a series of bifunctional materials based on modified SBA-15 co-functionalized by aminopropyl groups. Nb/SBA-15 co-functionalised with propylamine groups showed the highest activity, which was attributed to a strong interaction between Nb cations and the silica support generating Lewis acidity [26,27]. Nb/SBA-15 has also been prepared in the presence of grafted propylsulfonic acid groups for use in glycerol esterification with acetic acid, in which Nb appeared to improve the stability of sulfonic acid functions, resulting in 66% glycerol conversion and 35% selectivity to triacetyl glycerol [28,29]. Sumiya et al. also prepared Nb/SBA-15 comprising hydrated niobia (niobic acid) through treatment of a colloidal niobium oxide solution in the presence of the silica support. The resulting material exhibited high thermal stability and was more active for sucrose hydrolysis than bulk niobic acid [30].

Surprisingly despite the interest in niobia based catalysts and importance of esterification reactions for both chemical and bio-fuels production, a systematic study of the structure activity relationships in Nb/SBA-15 materials has not yet been reported for esterification reactions. Here we explore the potential of SBA-15 supported niobium for the esterification of propanoic acid as a model reaction to assess its potential for biodiesel production, and associated structure–function relations, notably the significance of Brønsted:Lewis character in dictating activity.

2. Experimental

2.1. Preparation of SBA-15

Mesoporous SBA-15 was synthesized following the method reported by Zhao and co-workers [31,32]. In a typical procedure, 16 g of Pluronic P123 (Aldrich, 96%) were dissolved in 500 mL of aqueous hydrochloric acid (1.9 mol/L) in a round bottom flask at room temperature. After complete dissolution, the mixture was warmed up to 35 °C and 28 g of TEOS (Aldrich) were added dropwise in a single step. The solution was then vigorously stirred for 24 h at 35 °C and hydrothermally aged at 80 °C for another 48 h. The solid product was then recovered by filtration and air-dried. Finally, surfactant was removed from inside the porous structure by calcination in static air at 550 °C for 5 h to give the product as a white powder.

2.2. Preparation of xNb/SBA-15(y) materials

Mesoporous silica supported niobium species were prepared by impregnation of SBA-15 with NbCl₅ in an isopropanol solvent, following the procedure of Chae et al. [33]. 3 g of SBA-15 was added to 30 mL of deionized water, 20 mL of isopropanol (Fisher Scientific) and an appropriate mass of niobium pentachloride (NbCl₅) (Aldrich,

99%) to obtain solids with niobium loadings spanning 2–32 wt% (theoretical loadings). The reaction mixture was stirred at room temperature for 24 h, and the liquid phase subsequently evaporated at 80 °C. The resulting solid was calcined subsequently at 500, 600 or 800 °C for 5 h (ramp rate 1 °C min⁻¹). The final materials are designated xNb/SBA-15(y), where *x* is the theoretical Nb loading and *y* is the solid calcination temperatures in Celsius degree (°C). Actual Nb loadings were obtained by XPS.

2.3. Materials characterisation

Nitrogen adsorption isotherms were obtained on a Quanchrome NOVA 4000e gas sorption analyzer using NovaWin software. Samples were degassed at 120 °C in vacuo overnight. Analyses were carried out under liquid nitrogen (−196 °C) and adsorption/desorption isotherms for N₂ were obtained over the relative pressure range 0.01–0.99. Specific surface areas were calculated using the multi-point Brunauer–Emmet–Teller (BET) method over the relative pressure range 0.01–0.3. Pore sizes were calculated from analysis of the desorption branch using the Barrett–Joyner–Halenda model (BJH) or Horvath–Kawazoe (HK) model with relative pressures >0.35 and <0.02 respectively. Powder XRD patterns were recorded on a PANalytical X'pertPro diffractometer fitted with an X'celerator detector and Cu-K α source for 2θ = 0 to 5° (small angle) and 2θ = 10 to 80° (wide angle) with a step size of 0.02°. The Scherrer equation was used to calculate Nb crystallite sizes. XPS analysis was performed on a Kratos Axis HSi X-ray photoelectron spectrometer fitted with a charge neutralizer and magnetic focusing lens employing Al Kα monochromated radiation (1486.7 eV). Spectral fitting was performed using CasaXPS version 2.3.15. Binding energies were corrected to the C 1s peak at 284.5 eV. HRTEM analysis was carried out on a JEOL/JEM instrument operating at 100–120 kV (dispersed in ethanol and dropped onto a grid). Dark-field images obtained in STEM mode. Diffuse reflectance UV–vis analyses (DRUV) were made using a Thermo Scientific™ Evolution 201/220 spectrophotometer, for wavelengths between 190 and 800 nm. Acid properties were determined by DRIFTS on a Nicolet IS50FT-IR Thermo Scientific™ spectrometer, through pyridine adsorption at room temperature. Approximately 1 mL of pyridine (Aldrich, 99.8%) was adsorbed on 200 mg of sample, which was dried overnight in a vacuum oven prior to analysis in order to remove physisorbed pyridine.

2.4. Catalytic activity

Esterification was performed in a Radley's Carousel reaction station under reflux using a 50 mL double neck round-bottomed flask. Reactions were conducted using 10 mmol of propanoic acid in 12.5 mL of methanol (molar ratio MeOH:acid = 30), at 60 °C, using 50 mg of catalyst and 0.12 mL of dihexylether as an internal standard. Reactions were periodically sampled for kinetic analysis using a Varian450 GC equipped with Phenomenex ZB-5HT Inferno wide bore capillary column (15 m × 0.32 mm × 0.10 μm), with analysis performed in triplicate. Recycle experiments were also conducted with the most active 2Nb/SBA-15(500) sample under solvothermal conditions, in which 50 mg of catalyst was placed inside a 15 mL Teflon liner with 10 mmol of propionic acid and 6.25 mL of methanol (molar ratio MeOH/acid = 15). The liner was then placed inside a stainless steel autoclave and put in a silicone oil bath and heated to 120 °C for 4 h under magnetic stirring at 800 rpm. After cooling to room temperature, excess alcohol in the supernatant solution was removed by vacuum evaporation, and fatty acid conversion to the corresponding propyl ester assayed by titration of the remaining acidity with NaOH (0.01 mol/L). The spent catalyst

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