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Synthesis of amine-functionalized mesoporous silica basic catalysts for biodiesel production

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ABSTRACT

Amine-functionalized MCM-41 were prepared for use as basic heterogeneous catalysts in trasesterification of soybean oil to produce biodiesel. The fuctionalization was obtained by reacting the silanol groups of the MCM-41 material with 3-amino-propyl-triethoxy-silane, or in two steps by firstly reacting the MCM-41 with 3-chloro-propyl-triethoxy-silane and then, undergoing nucleophilic substitution with piperazine or with a guanidine-derived compound (1,5,7-triazabicyclo [4,4,0] dec-5-ene). The introduction of the organic moieties was confirmed by ^{29}Si and ^{13}C CPMAS NMR spectroscopy, as well as by chemical analysis (CHN). The catalysts were tested in the transesterification of soybean oil with methanol. Up to 99% yield in biodiesel at 70 °C and 3 h of reaction were obtained with the guanidine-derived catalyst. The other amine-derived catalysts were less active for the production of biodiesel, presenting lower yields under more severe reaction conditions. These results can be explained by the intrinsic basicity of the amines.

1. Introduction

Biodiesel is normally produced by transesterification of vegetable oils with methanol in the presence of either acid or base catalysts [1,2]. Particularly, the homogenous acid catalysts are less active towards biodiesel production and require more drastic conditions with respect to the basic ones [3]. Industrially, biodiesel is produced using homogeneous basic catalysts, such as NaOH, KOH and $NaOCH_3$ [4]. This procedure, although efficient from a kinetic point of view, requires extensive washing of the biodiesel generating large amounts of wastes [4]. In addition, the homogeneous basic catalyst cannot be recovered from the reaction medium, being eliminated and neutralized in the glycerol fraction [4]. Finally, the sustainable production of biodiesel will require continuous flow processes that can enable the production in large scale with minimum interruption of the process. Thus, the development of heterogeneous catalysts that can minimize wastes, allow the reutilization of the catalyst and operate in continuous flow conditions is fundamental to overcome the problems related to the biodiesel commercialization. To address this issue, a high number of basic and acid heterogeneous catalysts are reported in Ref. [3], including metal oxides (CaO and MgO) [5,6], hydrotalcites [7], Keggin heteropolyacids [8], sulfonic acid-functionalized mesoporous materials [9] and polymers [10].

Due to their high basicities – with base strengths comparable to alkali hydroxides and carbonates – alkylguanidines [11] have been widely used as an efficient homogenous catalyst for many important reactions, such as methylation of phenol [12], Michael addition [13], alkylation of carboxylic acids [14] and transesterification [15]. Schuchardt and collaborators have obtained yields of methyl esters higher than 90% within 1 h of reaction at 60 °C, using 1 mol% of 1,5,7-triazabicyclo [4,4,0] dec-5-ene (or TBD), as homogenous catalyst, in the methanolysis of rapeseed oil [15]. Several approaches for immobilization of the alkylguanidines on various organic and inorganic supports, such as polymers [16,17], zeolites [17] and silica sol–gel based materials [17–19] have been reported in the literature. However, the catalytic activity of most of these systems was considerably lower than the activity observed with the alkylguanidines in solution; that means, under homogeneous catalysis conditions. The decrease in reactivity has been attributed to the leaching of the guanidines from the polymers and silica, lack of diffusion of the triglycerides through the channels of the zeolite Y and collapse of the SiO_2 sol–gel matrix. Thus, although a variety

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of heterogeneous basic catalysts have been developed for biodiesel production; new strategies for heterogenization of the amines need to be investigated.

Judicious choice of the catalyst support must take into account some requirements, such as high surface area, high mechanical, thermal and chemical stability. Mesoporous silica materials (MSM) have been widely used as catalyst support because they meet those requirements [20]. Particularly, MCM-41 possesses well-ordered mesoporous structure packed in a hexagonal symmetry, high surface area (~1000 $m^2 g^{-1}$), high pore volume (~1.07 $cm^3 g^{-1}$), regular pore size (~3 nm) and high thermal and mechanical stability [21,22]. Furthermore, various organic functional groups can be covalently bonded onto its surface either by co-condensation or post-synthetic grafting methods. In the former method, the hydrolysis of organosilanes takes place at the same time the particles are forming and in the latter method, surface functionalization with organic groups occurs after the particles are formed [23,24]. Therefore, all those properties offer the possibility to create hybrid mesoporous materials in which the reactive species will be highly distributed onto the surface and accessible for reactions. Because of these unique properties, MCM-41 has been used in a wide range of applications, such as drug delivery [25], gas sorption [26] and catalysis [27].

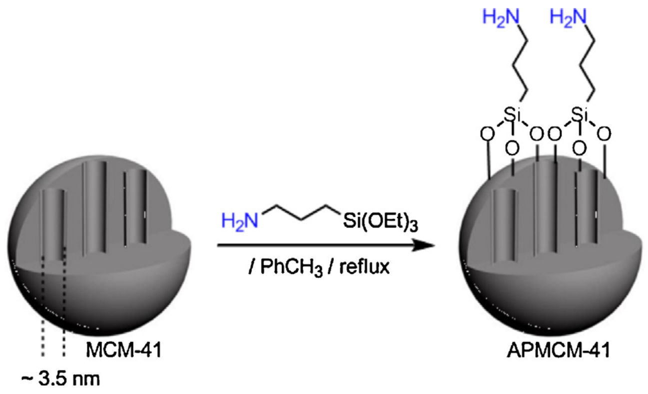
The work described herein aimed to prepare heterogeneous basic catalysts for soybean oil transesterification reaction. Commercially available MCM-41 was used as a silica support to covalently bind three different amines, piperazine, 1,5,7-triazabicyclo [4,4,0] dec-5-ene (guanidine, TBD), and 3-amino-propyl (AP), respectively, *via* post-synthesis grafting reactions. MCM-41 surface modification with amino-propyl group was carried out using a methodology described elsewhere [25,26,28]. To bind piperazine and guanidine onto MCM-41 surface, we developed the following methodology: (i) modification with 3-chloro-propyl followed by (ii) nucleophilic substitution between the chloro-propyl groups and the amines, respectively.

2. Experimental

2.1. Synthesis of the catalysts

All catalysts were synthesized using post-synthetic methods. Mesoporous MCM-41 silica nanomaterial was purchased from Sigma–Aldrich and activated prior to functionalization at 180 °C for 24 h under vacuum. This procedure removes the adsorbed water, exposing the silanol groups to react with the functionalized compounds.

The activated MCM-41 was initially reacted with 3-amino-propyl-triethoxy-silane in dry toluene (Scheme 1), as previously described in Refs. [25,26,28]. About 3.0 g of MCM-41 in 50 mL of dry toluene, under N_2 atmosphere, were reacted with 3 mL (13 mmol) of 3-amino-propyl-triethoxy-silane (3-APTS) under reflux for 90 min. After this period, the formed ethanol, together with some toluene, was distilled from the reaction vessel (about 7 mL) and an additional 3 mL of 3-amino-propyl-triethoxy-silane were introduced into the flask. This procedure was repeated three times in order to shift the equilibrium towards the product. At the end, the resulting white solid, named APMCM-41, was filtered and washed in a Soxhlet apparatus with 200 mL of diethyl ether and dichloromethane (50 vol.%) for 20 h. The resulting material was dried overnight under vacuum.



Scheme 1. Scheme showing the functionalization of the MCM-41 surface with 3-amino-propyl-triethoxy-silane.

The other catalysts were synthesized by two-step process: the first step consists in the functionalization of MCM-41 with 3-chloro-propyl-triethoxy-silane forming the MCM-41-Cl (Scheme 2). The second step involves nucleophilic substitution of the chloro-functionalized MCM-41 with different the deprotonated amines. Thus, the amino group is attached to the structure, whereas chloride is eliminated.

The MCM-41-Cl was synthesized in a similar way of APMCM-41, but using 3-chloro-propyl-triethoxy-silane as the silylating agent. The second step is the bimolecular nucleophilic substitution reaction (S_N2) between the MCM-41-Cl and an amine (piperazine or 1,5,7-triazabicyclo [4,4,0] dec-5-ene).

A solution of 6.85 g (79 mmol) of piperazine in dry toluene and propylamine was added dropwise to a suspension of 4 g of the MCM-41-Cl in toluene. The system was kept in reflux, under N_2 atmosphere and stirring, for 24 h. At the end, the solid was filtered and washed in Soxhlet with 80 mL of n-butylamine and then with 120 mL of diethyl ether and dichloromethane solution (50 vol.%). This procedure is necessary to activate the basic nanocatalysts, because upon the nucleophilic substitution, the leaving HCl remains on the catalyst surface, neutralizing the active site. After this treatment, the catalyst was dried under vacuum and named MCM-41-piperazine.

To anchor the guanidine-derived compound to the surface of the MCM-41, about 5.0 g of 1,5,7-triazabicyclo [4,4,0] dec-5-ene hydrochloride, obtained from Sigma–Aldrich, was dissolved in 70 mL of dry tetrahydrofuran (THF) and immersed in an ice bath. Then, a suspension of 1.8 g of NaH in 30 mL of dry THF was added drop wise, under N_2 atmosphere. The system was stirred for 2 h at room temperature forming a liquid phase containing the free amine, and a solid phase of NaCl. The liquid phase was carefully transferred to a dropping funnel with the aid of a syringe and then, added drop wise to a suspension of 7.5 g of MCM-41-Cl in dry THF, at 0 °C. After the complete addition of the amine solution, the system was stirred for 24 h at 70 °C. Finally, the solid was filtered and washed in a Soxhlet apparatus with 200 mL of diethyl ether and dichloromethane (50 vol.%) for 20 h. After drying overnight, the material was named MCM-41-guanidine.

Elemental analyses of the carbon, hydrogen and nitrogen contents (CHN) were carried out at the Central Analítica of the Instituto de Química, Universidade de São Paulo, Brazil. ^{13}C and ^{29}Si solid state NMR Spectroscopy were carried out on a Bruker Avance III 400 (9.4 T), operating at Larmor frequencies 100.65 and 79.51 MHz, respectively. The analyses were performed in a 3.2 ZrO_2 triple channel probe, with 3.2 rotors (Vespel caps) spinning at 10 kHz (^{13}C) and a 7.0 mm two channel broadband probe with 7.0 mm rotors (Kel-F caps) spinning at 5 kHz (^{29}Si). The spectra were obtained using magic angle spinning and cross polarization (CP ramp) with 2 ms contact time and 4 s repetition time for ^{13}C (^{13}C CPMAS); 4 ms contact time and 4 s repetition time for ^{29}Si (^{29}Si CPMAS). X-ray diffraction patterns were obtained using a Bruker D8 Advanced diffractometer (CuKα, λ = 1.5418 Å). Nitrogen physisorption measurements of the materials were performed on an ASAP 2020 V304 e-serial 1200 at 77 K.