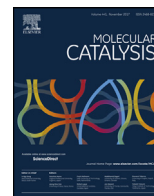




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Tailored hybrid materials for biodiesel production: Tuning the base type, support and preparation method for the best catalytic performance

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ABSTRACT

Hybrid materials were prepared by the functionalization of mesoporous silica MCM-41 with 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) and 3-aminoquinuclidine (3AQ) by the co-condensation method, resulting in the heterogeneous catalysts **MCM-41-TBD**, **MCM-41-3AQ**. Silica gel was also functionalized with TBD and 3AQ using post-synthetic method upon the reaction with 3-chloro-propyl-triethoxy-silane and then, undergoing nucleophilic substitution with TBD or 3AQ, resulting in **SG-TBD** and **SG-3 AQ**, respectively. The successful anchoring of the organic bases on the silica supports has been shown by ²⁹Si MAS/NMR and elemental analysis (CNH). The ordered structure of the MCM-41 support was damaged upon base functionalization. The heterogeneous catalysts were tested in the transesterification of soybean oil to produce biodiesel. **MCM-41-TBD** catalyst converted 100% of the soybean oil to biodiesel within 2 h at 70 °C, whereas the other catalysts required more severe reaction conditions to achieve conversion in the range of 24–98%. The catalysts based on grafted TBD, regardless of the type of silica used, were more active than those based on 3AQ, because of the higher basicity of the former amine. The **MCM-41-TBD** presented slower deactivation rate, upon reuse, compared with the same material prepared by post-synthetic methods. The possible explanation is related with the higher incorporation of the base on the silica support by the co-condensation synthetic method as well as its more uniform distribution on the catalyst surface.

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1. Introduction

In the face of global warming and consensus for the use of clean energy sources, biodiesel has emerged as a promising alternative to fossil diesel. It is usually obtained by transesterification of oils and fats with short chain alcohols in the presence of basic or acid catalysts. Biodiesel can be used in diesel engines without requiring significant modifications [1–4]. In addition, there are advantages, such as biodegradability, absence of sulfur and aromatics compounds and the carbon dioxide released in the combustion can be absorbed by the plants [5–7]. However, the costs of production depends on the raw material used [8,9].

Typically, homogeneous catalysts, such as NaOH and NaOCH₃, are used in biodiesel production. They are highly active under mild reaction conditions, but cannot be reused. In addition, expeditious washing procedures are necessary to remove catalyst residues [10,11]. Heterogeneous catalysts, on one hand, can be easily separated from the medium and reused, but on the other hand, usually require more drastic reaction conditions to achieve satisfactory conversion [12]. The advantages and disadvantages of heterogeneous basic catalysis for biodiesel production were recently addressed [13].

The incorporation of the organic compounds on mesoporous silica to generate hybrid materials has been widely reported in the literature. MCM-41 mesoporous silica has high surface area and their mesopores are arranged in a hexagonal shape. Silica gel, otherwise, has no organized structure, but present high surface area and thermal stability. These different types of silica-based materials

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are extensively used in catalysis, drug delivery systems, adsorbents and biosensors [14–20].

Guanidine derivatives, such as 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD), are known for their strong basicity ($pK_a = 25.9$). TBD, as homogeneous catalyst, has catalytic activity comparable to NaOH and KOH in the transesterification of soybean oil [21]. In a previous report [22], we have shown that TBD anchored on the surface of MCM-41, prepared by post-synthetic method, showed excellent catalytic performance for soybean transesterification with methanol. Notwithstanding, the catalyst showed strong deactivation upon reuse, mostly due to neutralization by the free fatty acids present in the oil.

Quinuclidine is a strong base ($pK_a = 11$) formed by a bicyclic system with a bridgehead nitrogen atom [23]. Quinuclidine derivatives with different basicities have been used as homogeneous and heterogeneous catalysts in the Baylis-Hillman reaction [24,25]. The products were obtained in moderate to high yields, indicating that quinuclidine derivatives are promising compounds for basic catalysis. To the best of our knowledge quinuclidine, or its derivatives, has not been used as catalyst in the transesterification of vegetable oils to produce biodiesel.

In this work we describe the synthesis of silica-based heterogeneous basic catalysts grafted with 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) and 3-aminoquinuclidine (3AQ), for the transesterification of soybean oil with methanol. The catalysts based on MCM-41 were obtained using the co-condensation method, whereas the catalysts based on commercial silica gel were synthesized in two steps using the post-synthetic method. Grafting of the organic bases on the mesoporous material by the post-synthetic method mainly occurs on the external surface of the solid, and may lead to pore blockage and lower incorporation of the organic moiety on the silica support. On the other hand, in the co-condensation method the functionalization occurs inside and outside the pores, resulting in a material in which the catalytic sites are more homogeneously distributed and with higher incorporation of the organic moiety [26]. Thus, it would be expected that MCM-41-TBD synthesized by co-condensation could be more resistant toward deactivation than the same catalyst prepared by post-synthetic methods.

2. Experimental section

2.1. Materials and characterization methods

The following reagents were purchased from Sigma-Aldrich and used without any prior treatment: (3-chloropropyl)trimethoxysilane (CPTES) 95%, tetraethyl orthosilicate (TEOS) 98%, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 3-aminoquinuclidine (3AQ) dihydrochloride, hexadecyltrimethylammonium bromide (CTAB) and sodium hydride (NaH). Ammonium hydroxide, anhydrous toluene, anhydrous tetrahydrofuran (THF) and methanol (MeOH) were acquired from Vetec, whereas a commercial silica gel was purchased from Merck. Commercial refined soybean oil was used in the transesterification reactions.

Fourier-transform infrared (FTIR) spectra were recorded in the range from 400 to 4000 cm^{-1} on a Varian 660-IR FTIR spectrophotometer using KBr pellets. Elemental analyses (CHN) were carried out on a Perkin-Elmer CHN 240C analyser at the Analytical Center of the Institute of Chemistry of the University of São Paulo, Brazil. ^{13}C and ^{29}Si solid-state NMR 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 nm ZrO_2 triple channel probe, spinning at 10 kHz (^{13}C NMR) and in a 7.0 mm two channel broad band probe with 7.0 mm rotors (Kel-Fcaps) spinning

at 5k Hz (^{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 were carried out at the State University of Santa Cruz (UESC), Bahia, Brazil, using a RIGAKU diffractometer model Miniflex 600, operating with Cu $K\alpha$ radiation generated about 40 KV and 30 mA. The analyses of the samples were carried out scanning from 1.5° to 10° (2 theta) with an interval of 0.02° and scan of 1 min^{-1} . Textural analyses were carried out by N_2 adsorption/desorption isotherms on an ASAP 2020 V304 e-serial 1200 at 77 K. The samples were pretreated at 120°C for 10 h.

2.2. Synthesis of the silylating agents modified with TBD and 3AQ

A solution of TBD (3.20 g, 22.9 mmol) or 3-aminoquinuclidine (3AQ) dihydrochloride (3.57 g, 17.9 mmol) in THF was added dropwise to a suspension of NaH (0.88 g, 22.0 mmol for TBD or 2.55 g, 63.75 mmol for 3AQ) in THF under nitrogen atmosphere at 0°C . The suspension was stirred for 2 h at room temperature. Then, a solution of CPTES in THF was added to the mixture at 0°C and stirred for 24 h at 70°C . The resulting products were filtered and used in the co-condensation synthesis of the hybrid catalysts.

2.3. Preparation of the functionalized MCM-41

The CTAB surfactant (1.0 g, 2.7 mmol), 3.5 mL of 2 mol L^{-1} solution of NaOH and 240 mL of deionized water were heated at 80°C for 30 min 5 mL of TEOS was added together with the amino-functionalized silylating agents, previously synthesized as described in Section 2.2. The reaction mixture was vigorously stirred at 80°C for 2 h. The materials were filtered, washed with water and then with methanol and dried under vacuum; the materials were named **MCM-41-TBD** and **MCM-41-3AQ**.

The CTAB surfactant was removed by acid extraction at 60°C for 3 h with 50 mL of MeOH and 0.3 mL of HCl. Dispersions of the products (**MCM-41-TBD** and **MCM-41-3AQ**) in methanolic solutions of sodium carbonate were stirred at room temperature for 3 h to neutralize any remaining HCl. The resulting materials were filtered, firstly washed with water and then methanol and dried under vacuum.

2.4. Functionalization of the silica gel with (3-chloropropyl)trimethoxysilane (CPTES)

9.0 g of commercial silica gel were dried at 150°C for 10 h under vacuum. Then, the silica gel was dispersed in 150 mL of dried toluene. To the dispersion, under reflux and N_2 atmosphere, 9.0 mL of CPTES were added. After 1.5 h, 21 mL of the solvent was withdrawn and further 9 mL of CPTES were added to the reaction mixture. This procedure was repeated twice. After washing the material in a Soxhlet with a mixture of 200 mL of diethyl ether and 200 mL of dichloromethane for 20 h, the solid was dried resulting in a material named **SG-Cl**, which was subsequently used to anchor the bases.

2.5. Preparation of the SG-TBD and SG-3AQ

A solution of TBD (2.50 g, 17.9 mmol) or 3-aminoquinuclidine (3AQ) dihydrochloride (2.86 g, 14.3 mmol) in THF was added dropwise to a suspension of NaH (0.68 g, 28.3 mmol for TBD or 2.61 g, 65.3 mmol for 3AQ) in 15 mL of THF under N_2 atmosphere and 0°C . The suspension was stirred for 2 h at room temperature. Then, 3.0 g of the synthesized **SG-Cl**, as described in section 2.4, in THF was added to the suspension at 0°C . The dispersion was stirred for 24 h at 70°C . Subsequently, the suspension was filtered and the solid

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