



Transesterification of short chain esters using sulfonic acid-functionalized hybrid silicas: Effect of silica morphology



Maria Luisa Testa*, Valeria La Parola, Anna Maria Venezia

Istituto per lo Studio dei Materiali Nanostrutturati, UOS-PA CNR, via U. La Malfa 153, I-90146 Palermo, Italy

ARTICLE INFO

Article history:

Received 10 April 2013

Received in revised form 24 July 2013

Accepted 11 September 2013

Available online 15 October 2013

Keywords:

Transesterification

Acid catalyst

Sulfonic-acid silica

Mesostructured materials

ABSTRACT

Sulfonic acid-functionalized hybrid silicas with different structure (amorphous, HMS, SBA-15) were synthesized by different methodologies, with a variable amount of organic moieties (propyl-SO₃H). The obtained catalysts, characterized by X-Ray photoelectron spectroscopy, low angle X-Ray diffraction, N₂ adsorption and acid capacity measurements, were tested in the transesterification reaction of short chain esters (from hexanoic to lauric ethyl ester). The optimized reaction was carried out under mild condition in the presence of 15% mol of the corresponding organic acid in order to reproduce a typical low-grade oil. A correlation between the catalytic activity of the materials and their acid capacities was found. The propyl-sulfonic SBA-15 catalyst presented the best performance in terms of activity and structural stability with no leaching of the sulfonic groups.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

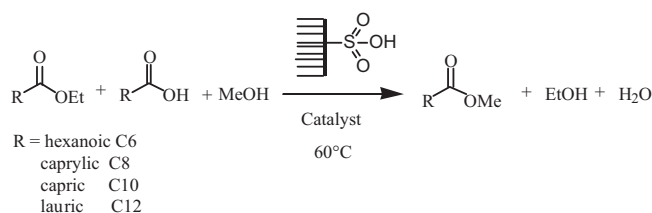
Transesterification and esterification are industrially important reactions used in several fields, among them, biodiesel production. Biodiesel is a renewable, biodegradable and non-toxic fuel. The first generation biofuels using the edible parts of food plants as feedstock are considered not fully sustainable and with a negative impact on the food supply. On the other hand, second generation biofuels using a low-grade oil feedstock, typically waste cooking oil, represent a greener alternative. However, differently from the refined oil containing less than 0.5% of free fatty acids (FFAs), the low-grade oil has an FFA contents between 0.5–15% which leads to the undesired soap formation [1]. In this case, a pretreatment, including esterification, is necessary to reduce the amount of acids. Most of the industrial processes employ homogeneous acid or basic catalysts. However, their use has several drawbacks. As concern the homogeneous basic catalysts, they must work with refined oil poor in FFA (<0.5%) to avoid soap formation and deactivation of the catalyst. As concern the homogeneous acid catalysts, they promote the esterification of FFA and transesterification simultaneously, thus avoiding soap formation, but they are very corrosive and toxic for the environment and are difficult to separate and recover. Employing new and sustainable heterogeneous solid acid catalysts for

biodiesel production facilitates the separation, regeneration and recycling of the catalyst and reduces corrosion problems [2].

A large number of heterogeneous solid acid catalysts, including modified inorganic oxide such as zirconium [3], titanium [4] and tin [5] oxides, sulfonic ion-exchange resins [6] and heteropolyacids, [7] have been reported in the literature for transesterification reactions. Special attention has been devoted to those catalysts containing sulfonic groups in particular organosulfonic-silica solids that have been proved to be active at moderate temperatures and pressure [1,8]. According to recent reports [9,10], an efficient solid acid catalyst requires large pores to minimize diffusion problems, high concentration of acid sites, high catalytic stability against leaching and poisoning and the possibility to modify the hydrophobicity of the surface to promote the preferential adsorption of substrates and the repulsion of highly polar compounds which could cause deactivation. Due to their high surface area and controlled porosity it is becoming very attractive to use ordered mesoporous silicas (e.g., MCM-41, HMS, SBA-15) as supports [11] for various catalytic applications. The pore sizes, larger than those in zeolites, can be adjusted in the nanometer range by the appropriate choice of the surfactant templates, making these systems suitable to host large molecules. Many reviews have covered several aspects of the mesoporous materials related to their synthesis, surface modification and practical applications [12–14]. The main problems associated with such materials consists in their poor hydrothermal stability and lower reactivity as compared to zeolites [15]. Among ordered mesoporous silicas HMS and SBA-15 have quite different structure: whereas the former has a wormlike porous structure the latter has an ordered close packed hexagonal arrangement of the pores forming straight channel. Moreover,

* Corresponding author at: Istituto per lo Studio dei Materiali Nanostrutturati ISMN-CNR, via U. La Malfa 153, I-90146 Palermo, Italy. Tel.: +39 0916809253; fax: +39 0916809399.

E-mail address: marialuisa.testa@ismn.cnr.it (M.L. Testa).



Scheme 1. Transesterification reaction in presence of acid on sulfonic acid-functionalized hybrid silica.

the pore size of HMS support is smaller than the pore size of SBA-15 (typically 3–4 nm vs. 6–8 nm). The reactivity of these mesoporous materials is enhanced by the addition of functional groups. In particular, organic groups with rather low reactivity, besides increasing the surface hydrophobicity and avoiding surface hydrolysis, are added to tailor the pores size. On the other hand, addition of more reactive groups such as alkylamines and alkylthiol is pursued for making innovative catalysts [16] or for environmental application. Thiol containing organic groups are certainly among the most interesting functional groups. Indeed, thiol functionalized silicas ($\text{SiO}_2\text{-SH}$) are generally oxidized to sulphonic acid silica materials ($\text{SiO}_2\text{-SO}_3\text{H}$) for being used as acid catalysts for dehydration or esterification reactions [17,18].

Sulfonic acid functionalized silicas have been recently explored as esterification catalysts [19,20]. A recent comparison of different solid acid catalysts in the acetylation of the glycerol has shown the superiority of the sulfonic-functionalized hybrid amorphous in terms of activity and stability [21].

On these premises and as a continuation of our current research on solid acid catalyst, sulfonic acid-functionalized hybrid silicas both amorphous and with ordered mesoporosity of the HMS and SBA-15 type and different loadings of organic moieties (propyl- SO_3H) were synthesized by different procedures and tested in the transesterification reaction of short chain esters (from hexanoic to lauric ethyl ester, as described in Scheme 1).

The catalytic behavior of the functionalized silicas was studied under different experimental conditions. Fresh and spent materials were analyzed by means of X-Ray photoelectron spectroscopy, X-Ray diffraction, N_2 adsorption isotherms and acid capacity measurements.

2. Experimental

2.1. Synthesis of sulfonic-acid functionalized materials

Amorphous and mesostructured (HMS and SBA-15) SiO_2 were functionalized with propyl sulfonic groups adopting two different procedures: grafting and *in situ* oxidation.

All the compounds used in the synthesis were purchased from commercial suppliers (Aldrich, Fluka) and used without further purification.

2.1.1. Grafting method

The different types of silica, the amorphous, the HMS and the SBA-15 were synthesized by sol-gel technique according to published procedures [22–24].

In a typical synthesis by grafting, a mixture of 2.00 g of calcined silica in 35 ml of dry toluene and 3-mercaptopropyltrimethoxy silane (MPTMS) (3.33 mmol) was refluxed for 24 h at 110 °C. The materials were then recovered by filtration, washed several times with toluene and dried at 120 °C overnight. Thereafter, the mercaptopropyl groups were oxidized to sulfonic groups with hydrogen peroxide (33% w/v solid:liquid ratio of 1:18) at room temperature during 24 h. After filtration the solid was dried at 120 °C overnight.

The amorphous and the mesoporous grafted silica samples are labeled as *nAm.G*, *nHMS.G* and *nSBA.G*, where *n* corresponds to the molar percentage of the $\text{-SO}_3\text{H}$ groups.

2.1.2. In situ oxidation method

2.1.2.1. Synthesis of the propyl- SO_3H amorphous SiO_2 . The propyl- SO_3H silica was synthesized by sol-gel technique according to a published procedure [19]. TEOS (7.5 ml, 0.034 mol) was dissolved in ethanol (5 ml) and stirred at 45 °C for 15 min. Then, 5 ml of aqueous solution of acetic acid at pH 5 was added to the mixture, followed by addition of MPTMS, in amounts corresponding to 2.5%, 5% and 10% mol/mol loadings, and hydrogen peroxide (33% w/v solid:liquid ratio of 1:18). The solution was heated up to 80 °C and left at this temperature until formation of the gel. The obtained wet gel was dried at 120 °C overnight.

2.1.2.2. Synthesis of the propyl- SO_3H HMS silica. The propyl- SO_3H HMS was synthesized according to a previous published procedure [25]. Typically, TEOS (6 ml, 0.027 mol), MPTMS (0.5 ml, 0.0026 mol) and hydrogen peroxide (33% w/v solid:liquid ratio of 1:18) were added to a stirred solution of ethanol (15 ml), water (15 ml), and 1-dodecylamine (1.84 ml, 0.008 mol). The mixture was stirred at room temperature for 24 h. The white precipitate obtained was filtered under vacuum and washed with de-ionized water (36 ml) and ethanol (36 ml). The organic template was extracted by suspending the solid product in ethanol and refluxing for 24 h. The final product was dried at 100 °C overnight.

2.1.2.3. Synthesis of the propyl- SO_3H SBA-15. The propyl- SO_3H SBA-15 was prepared according to the procedures described before [21,24,26]. Pluronic P123 (4.0 g) was dissolved in a solution of 2 M HCl (125 ml). To this solution TEOS (8.2 ml, 0.037 mol), MPTMS (0.69 ml, 0.0037 mol) and hydrogen peroxide (33% w/v solid:liquid ratio of 1:18) were added and stirred overnight at 40 °C in a 250 ml one neck flask. The milky suspension was aged at 100 °C for 24 h in a closed polypropylene bottle. The solid product was filtered, washed with ethanol. The surfactant was removed by ethanol washing under reflux for 24 h. The final product was dried at 120 °C overnight.

The amorphous and the mesoporous silica samples functionalized by the *in situ* oxidation method are labeled as *nAm.Ox*, *nHMS.Ox* and *nSBA.Ox*, where *n* corresponds to the molar percentage of the $\text{-SO}_3\text{H}$ groups.

2.2. Catalyst characterization

Acid capacity and concentration of sulfonic groups of samples were determined by titration with 0.01 M NaOH (aq) [27]. In a typical experiment, 0.1 g of solid was added to 10 ml of deionized water. The resulting suspension was allowed to equilibrate and thereafter was titrated by dropwise addition of 0.01 M NaOH solution using phenolphthalein as pH indicator.

The textural properties were obtained using a Carlo Erba Sorptomat 1900 instrument. The fully computerized analysis of the N_2 adsorption isotherm at 77 K allowed to obtain, through the BET method in the standard pressure range 0.05–0.3 P/P_0 , the specific surface areas of the samples. The total pore volume, V_p was evaluated on the basis of the amount of nitrogen adsorbed at a relative pressure of about 0.98 [28].

X-ray photoelectron spectroscopy analyses were performed with a VGMicrotech ESCA 3000 Multilab, equipped with a dual Mg/Al anode. The spectra were excited by the unmonochromatized Al K_{α} source (1486.6 eV) run at 14 kV and 15 mA. The analyser operated in the constant analyser energy (CAE) mode. For the individual peak energy regions, a pass energy of 20 eV set across the hemispheres was used. Survey spectra were measured at 50 eV pass

Download English Version:

<https://daneshyari.com/en/article/54735>

Download Persian Version:

<https://daneshyari.com/article/54735>

[Daneshyari.com](https://daneshyari.com)