



Catalytic performance and deactivation of sulfonated hydrothermal carbon in the esterification of fatty acids: Comparison with sulfonic solids of different nature



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ABSTRACT

Sulfonated hydrothermal carbon is able to catalyze the esterification of palmitic acid with methanol at a higher initial rate per site than other well-known sulfonic solids, including stronger acids such as Nafion–silica. Although the origin of this higher rate per site is not clear, it seems to be related to high surface density of acid groups (both carboxylic and sulfonic). At the same time, their close proximity makes possible the mutual activation of the surface groups for esterification with methanol. The formation of sulfonate esters on the surface produces irreversible partial deactivation of the solid for a second reaction. Other solids able to bring sulfonic groups close, such as Dowex, show the same deactivation pattern, but their sites are less active than those in sulfonated hydrothermal carbon. As an additional advantage, this solid displays enhanced stability against the presence of water, which enables improvement of the behavior after recovery by minimization of the esterification of the surface acid sites.

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1. Introduction

Acidic solids are among the most useful heterogeneous catalysts for both bulk [1,2] and fine chemicals [3] synthesis. Sulfonic acids supported on inert matrixes have been envisaged as interesting alternatives to classical inorganic acid solids. Polystyrene-supported sulfonic acids are commonly applied as catalysts [4], even in industrial processes, but new developments are still being produced to optimize their performance [5,6]. Perfluorinated sulfonic polymers constitute a special type of solids with enhanced acidity [7]. The development of sulfonic organic–inorganic hybrid materials tried to overcome the possible problems of lack of thermal and mechanical resistance of the polymeric materials. Propylsulfonic and arylsulfonic groups have been incorporated onto amorphous silica [8] and more recently onto siliceous mesostructured materials [9,10], whereas Nafion–silica nanocomposites have been developed by entrapment of Nafion chains in the silica structure [11]. One alternative to both organic and hybrid materials is the family of sulfonated carbons [12].

Esterification of carboxylic acids is an important industrial acid-catalyzed reaction [13]; one example is the synthesis of fatty acid methyl esters [14]. All types of sulfonic heterogeneous catalysts

have been used for this kind of reaction, including sulfonated polystyrene [5,15], organosulfonic mesoporous silica [16,17], Nafion–silica nanocomposites [18], and sulfonated carbon prepared by thermal [19] or hydrothermal carbonization [20], as well as ordered mesoporous carbon [21]. Our group has described the esterification of palmitic acid with methanol catalyzed by a sulfonated hydrothermal carbon prepared from glucose, either in bulk [22] or supported on graphite felt [23].

Generally, in the literature, the performance of catalysts of similar nature is compared, whereas comparisons of sulfonic solids of different natures are scarce and not directly related to esterification reactions [24,25]. Additionally, the question of deactivation of solid acids is of great interest in connection with their practical application. Whereas some authors have described an almost full recovery of sulfonic acids after esterification reactions [19,26], in other cases partial deactivation has been observed. This has been attributed to different causes, such as leaching of sulfonated material [27] or pore blocking with fatty acid derivatives [18,28]. In our previous work [22], the deactivation of sulfonated hydrothermal carbon by methanol was described as a consequence of methyl sulfonate ester formation.

The objective of the present work is to compare the catalytic performance of sulfonic solids of different nature in the esterification of fatty acids, taking palmitic acid as a model, as well as their

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behavior with respect to deactivation with methanol, and to correlate both aspects with the properties of the solids.

2. Experimental section

2.1. Materials

Dowex 50W×2 (D50, sulfonated polystyrene gel-type resin, 2% divinylbenzene, 50–100 mesh) and Dowex CCR-2 (CCR, carboxylic polyacrylic gel-type resin, 20–50 mesh) were purchased from Fluka. Amberlyst 15 (A15, sulfonated polystyrene macroreticular resin, 20% divinylbenzene) was purchased from Alfa Aesar. Propylsulfonic silica (PSS, ≈0.74 mmol/g loading) was purchased from Aldrich. Deloxan ASP I/9 (DI9, particle size 0.1–0.4 mm) was a gift from Degussa. SAC-13 (Nafion–silica composite, 13 wt% Nafion content) was a gift from Dupont. All the solids were dried at 120 °C overnight prior to use as catalysts. Norit SX Ultra Cat 8020-1 and Elorit 8042-1 were a gift from CABOT.

2.2. Preparation of sulfonic carbons

2.2.1. Sulfonated hydrothermal carbon (SHTC)

The solid was prepared from glucose in two steps, hydrothermal synthesis in water and sulfonation with concentrated sulfuric acid, as described previously [22].

2.2.2. Sulfonated carbon nanofibers (SCNF)

For the growth of carbon nanofibers (CNF), a catalyst with 20% Ni was prepared by incipient wetness impregnation on γ -alumina (Pural, Sasol). After calcination in N_2 for 2 h at 600 °C, heating rate 1 °C/min, and reduction in H_2 for 1 h at 550 °C in a quartz reactor, the carbon nanofiber growth was carried out by hydrocarbon decomposition. To this end, a gas mixture of $C_2H_6:H_2$ 50:50 (v/v) was fed to the reactor containing the growth catalyst at 600 °C for 3 h. After the CNF growth, the catalyst was removed by purification first with NaOH (5 M) at 80 °C and subsequently with concentrated HNO_3 (65%) at 80 °C. The thermogravimetric oxidation of the solid up to 700 °C shows less than 2 wt% of residue. Sulfonation was carried out under the same conditions used for hydrothermal carbon.

2.2.3. Sulfonated activated carbons (SNor and SElor)

Norit SX Ultra Cat 8020-1 and Elorit 8042-1, were sulfonated under the same conditions (concentrated sulfuric acid, 150 °C, 15 h) as the other carbons to give SNor and SElor, respectively.

2.3. Characterization

Surface areas were determined by N_2 adsorption (BET) using a Micromeritics ASAP 2020 apparatus after outgassing for 4 h at 423 K. C, H, S elemental analyses were carried out by combustion in a ThermoFlash 1112 elemental analyzer equipped with a TCD detector. Oxygen analysis was performed by direct assay, which involves pyrolysis of the sample at 1070 °C in a nickel/carbon bed under a controlled He flow. The outlet flow, after passing a separation column, ends in a TCD detector. The oxygen content of the sample is quantified on the basis of the amount of CO analyzed. The IR spectrum was recorded with a Nicolet Avatar 360 spectrometer.

The total number of acid sites on each catalyst was determined by back titration. The solid (30–100 mg, depending on the catalyst acidity) was added to 25 ml of 0.01 M NaOH solution (0.0025 M in the cases of SAC-13 and sulfonated carbon nanofibers) and allowed to equilibrate under stirring for 1 h. Thereafter, it was titrated with 0.05 M potassium hydrogen phthalate solution (0.01 M in the cases

of SAC-13 and sulfonated carbon nanofibers) using a Crison pH Burette 24.

MAS NMR spectra were recorded in a Bruker Avance III WB400 spectrometer with 4 mm zirconia rotors spun at magic angle in N_2 at 10 kHz (12 kHz in the case of D50, A15, and CCR). 1H - ^{13}C CP spectra (up to 10,000 scans) were measured using a 1H $\pi/2$ pulse length of 2.45 μs , with a contact time of 2 ms, and a spin-64 proton decoupling sequence of 4.6 μs pulse length. ^{31}P NMR spectra of adsorbed triethylphosphine oxide (TEPO) were recorded using a ^{31}P $\pi/2$ pulse length of 4.3 μs without proton decoupling, with a 30 s recycle delay.

Ex situ XPS spectra were recorded with a Kratos Analytical Limited AXIS ultra DLD system equipped with Al $K\alpha$ radiation source to excite the sample. Calibration of the instrument was done with the $Ag3d_{5/2}$ line at 368.27 eV. All measurements were performed under UHV at less than 10^{-10} Torr. Internal referencing of spectrometer energies was made using the dominating C1s peak of the carbon catalyst at 284.6 eV. The program used to do curve fitting of the spectra was CasaXPS after the Shirley baseline method.

2.4. Catalytic tests

A mixture of 7.5 mmol of palmitic acid (1.92 g), 75.0 mmol of methanol (3.04 ml), the catalyst (10 mg of D50; 100 mg of A15, DI9, PSS, HTC, SHTC; 200 mg of SAC-13; 300 mg of SCNF, CCR, SNor, and SElor), and 2.1 mmol of 1-methylnaphthalene (0.30 g) as internal standard was stirred (≈ 1000 rpm) in a round flask immersed in a silicone bath at 85 °C. The reaction was monitored by gas chromatography (HP-5890-II). The catalyst was filtered, washed with CH_2Cl_2 and a small amount of methanol, dried under vacuum, and reused under the same conditions.

The kinetic studies were carried out at 7.5 ml scale in 25 ml round-bottom flasks immersed in silicone baths at 85 °C. The reactions were started by addition of the required amount of methanol to the preheated mixture of catalyst, internal standard, palmitic acid, and dioxane to prevent the possible deactivation of the catalyst in the presence of methanol. In this way, the volume of dioxane was calculated by assuming $V_{MeOH} + V_{dioxane} + V_{palmitic} + V_{1-methylnaphthalene} = 7.5$ ml, as the possible error was less important than that produced for the other possible alternatives (starting the reaction by addition of palmitic acid or catalyst).

2.5. Deactivation tests

The catalyst (150 mg) was stirred under reflux in methanol (40 ml) for 72 h. The solid was filtered at the same temperature and dried under vacuum at 105 °C. In some cases, the catalyst was then thoroughly washed with dichloromethane at room temperature. For NMR characterization, some solids were treated for longer times (72 h periods) at 50 °C under vacuum. The solid was used in esterification of palmitic acid with methanol under the standard conditions.

DI9, SHTC, SElor, and D50 were treated with benzyl alcohol. The catalyst (200 mg) was stirred at 100 °C with benzyl alcohol (1.4 ml) in toluene (1.4 ml) for 96 h. The solid was filtered at the same temperature, washed with toluene, and dried at 120 °C.

3. Results and discussion

3.1. Types of catalysts used

Several sulfonic solids of different natures (Fig. 1) were tested in an attempt to compare the performance of groups attached to chains of different chemical natures. SAC-13 Nafion–silica

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