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Efficient magnetic recoverable acid-functionalized-carbon catalysts for starch valorization to multiple bio-chemicals

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ABSTRACT

A series of solid acid catalysts were prepared by functionalization of graphene-oxide (GO) and MWCNT-oxide (MWCNTO) with triflic and sulfonic acids affording a triflate-functionalized graphene oxide ($GO@SO_3CF_3$), and a sulfonated MWCNT (μ-CNT-SO_3H). To facilitate the separation of the catalysts from the reaction mixture MWCNTs were modified by incorporating magnetic nanoparticles. For comparison, the composites of MWCNTO with magnetic nanoparticles were further modified by deposition of niobia in two loadings, *e.g.* 30 and 60 wt.%. Depending of the functionality the catalysts exposed preponderantly either Brønsted (μ-CNT-SO_3H) or Lewis ($GO@SO_3CF_3$) acid sites. Deposition of niobia also led to catalysts with acid properties, but as a function of the precursor nature and loading, they exposed niobia phases with either Brønsted (*e.g.*, Nb-O units) or Lewis acid sites (*e.g.*, –Nb = O units) in excess. Catalytic performances, in terms of the yields in one of the platform molecule (*ie*, levulinic acid *versus* lactic acid) were directly correlated with the nature of these acid sites. Interestingly enough, the catalysts showing high efficiency for lactic acid led also to high efficiency for the synthesis of succinic acid under pressure of molecular oxygen.

1. Introduction

Research devoted to the chemicals, materials and ecologic fuels synthesis from renewable materials, as an alternative to the fossil resources, received a special attention in the past decades [1–3]. Part of this research was focused to the identification of new active catalytic systems adapted to the biomass particularities (*e.g.*, the special nature of the bio-polymer raw material and low solubility in most of organic solvents) [2–5].

Former studies conducted in the cellulose and starch valorization, in the presence of homogeneous acid catalysts (19–35%, in HCl or H_2SO_4), showed that the yields in levulinic acid (one of the most important platform molecules) are relatively low [6,7]. In addition, the use of mineral acids presented a series of drawbacks due to the corrosive nature of the catalyst, the difficulty of separation at the end of reaction and hazardous waste generated. Since the separation processes represent more than half of the total investment in equipment for the chemical and fuel industries, obviously industry prefer solid catalysts to homogeneous ones. However, these catalysts should be stable, should exhibit a water tolerant behavior and should be highly selective to guarantee the cost-effectiveness of the process [8]. In this context, many reports shown that grafted sulfonic groups on inorganic or organic polymers, as solid carriers, are hydrolyzed and leached into water at elevated temperatures [9]. Therefore, new active and selective solid catalyst systems are waiting to be discovered and developed.

In recent years, niobia as well as modified niobia have been intensively investigated in a variety of important acid-catalyzed reactions, as dehydration, hydration, etherification, hydrolysis, and condensation, in which water molecules are directly involved as reactant or as reaction product [10–12]. One of the reasons of this high interest for niobia is its remarkable high acidity ($H_o = -8.2$) which is also maintained in water [13–15]. Due to these characteristics, niobia-based catalysts were investigated by different research groups, in different transformations of biomass derivatives [16–19]. However, commercial bulk niobia suffers from poor hydrothermal stability resulting in a low catalytic stability under a high-water environment and temperatures higher than 200 °C [20]. However, the deposition of niobia on oxide supports (*e.g.*, silica, titania,

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alumina) is somehow improving both the hydrothermal stability and the acidity in aqueous phase reactions [21].

Other types of catalysts that may potentially be considered for such processes are those incorporating triflic groups, like metal triflates or organic-triflate derivatives. To date, in spite of the remarkable acidity of triflic acid (it is one of the strongest Brønsted acids, with a pK_a of −12 [22], of the very strong Lewis acidity of triflates, and of a very high tolerance towards water of both triflic acid and triflates, only scarce reports on their use in the direct valorization of biomass were published in literature [23]. Obviously, the functionalization of solid carriers with triflates is expected to provide environmentally friendly stable catalysts. However, there are also reports claiming that grafting with triflic acid is a matter of leaching if not stable bonds, on covalent nature, are formed between triflate species and carrier during impregnation process [24].

On the other side, nano-supported catalysts may bridge the gap between homogeneous and heterogeneous catalysis, preserving the desirable attributes of both systems [25]. In addition, the use of magnetically active nanoparticles like magnetite (Fe_3O_4) may generate a more efficient separation of the catalyst simply by applying an external magnetic field. An example is the hydrolysis of cellulose to glucose with a solid acid Fe_3O_4–SBA–SO_3H with ordered mesopores and MNPs [26]. Likewise, not long ago, our group also demonstrated the efficiency of Fe_3O_4@SiO_2-Ru(III) catalysts, able to directly convert the cellulose into sorbitol and glycerol through three successive steps (ie, dehydration, formic acid decomposition, glucose hydrogenation with *in situ* produced hydrogen) [27] and levulinic acid into succinic acid through its oxidation with molecular oxygen [28]. In both cases the catalyst was easily recovered by simple applying a magnetic field on the external wall of the reactor. The developed nano-structured system also offers an excellent example on how the same catalyst can generate different active species able to produce multiple important platform molecules. Although not demonstrated, the SiO_2 shell may be the subject of the hydrothermal degradation during the harsh reactions conditions.

Based on this state of the art, in this study we explored novel heterogeneous catalytic systems, developed by functionalization of carriers with high mechanical strength properties (*ie*, graphene and MWCNT) with water tolerant acid species (*ie*, triflic acid, sulfonic acid and niobia). Very important, for an efficient separation of the catalyst, magnetic materials produced by incorporating superparamagnetic Fe_3O_4 nanoparticles into remarkable mechanical stable MWCNTs were also investigated. The new designed catalysts were tested in starch valorization affording biomass-derived platform molecules like levulinic, lactic and succinic acids.

2. Experimental section

All the chemicals and reagents were of analytical purity grade, purchased from Sigma-Aldrich and used without any further purification. Multiwalled carbon nanotubes (MWCNTs) were purchased from Sigma-Aldrich with following features: armchair configuration; preparation method Catalytic Chemical Vapor Deposition (CVD) (CoMoCAT®), over 98% carbon, O.D. × L/6–9 nm × 5 μm.

2.1. Catalyst preparation

Graphene-oxide (GO) and MWCNT-oxide (MWCNTO) were prepared by treating the pristine graphene and MWCNT with concentrated HNO_3 following the next procedure: 250 mg of MWCNTs (or graphene) were dispersed by ultrasonication in 100 mL of HNO_3 (1.0 mol/L) and vigorously stirred at 80 °C for 6 h. After that, the separated solids were washed with distilled water until a neutral pH, and dried at 80 °C for 24 h. Then the oxidized supports were treated with i) concentrated triflic acid (10 mL acid/g support) under the same vigorous stirring at 80 °C for 10 h, and ii) sulfuric acid (50 mL H_2SO_4 98%) following the same protocol resulting in a sulfonated MWCNT/GO (μ-CNT-SO_3H and GO-SO_3H). However, the treatment of MWCNT with triflic acid failed. The graphene oxide functionalized with triflic acid was abbreviated as GO@SO_3CF_3.

Further, magnetic nanoparticles were inserted in both the oxidized and sulfonated MWCNTs by using a method reported elsewhere [29]. Briefly, 1.8 g of Mohr's salt $(NH_4)_2Fe(SO_4)_2·6H_2O$, were dissolved in a mixture of 60 mL of degassed deionized water and hydrazine hydrate solution 50% wt in a ratio of 3:1, v/v. Then 0.5 g of MWCNTO or μ-CNT-SO_3H was added in obtained grass-green solution, sonicated and stirred overnight under inert atmosphere and precipitated with ammonia solution (25 wt%) until the a pH = 13. The resulted precipitate was kept under stirring for another 3 h, at 80 °C and then washed with water several times and separated by applying an external magnet. The resulted solids were denoted as μ-CNT-OH (magnetic carbon nanotubes) and μ-CNT-SO_3H (sulphonated magnetic carbon nanotubes).

μ-CNT has also been modified by deposition of niobia in two loadings, *e.g.* 30 and 60 wt.%, on its surface. Two different precursors were used for this purpose: niobium ammonium oxalate $C_{10}H_5NbO_{20}·6H_2O$ (NAmOx) and niobium ethoxide $Nb(OCH_2CH_3)_5$ (NbOEt). Thus, appropriate amounts of NAmOx or NbOEt were dissolved in ethanol that was followed by the subsequent addition of μ-CNT. The resulted suspensions were maintained at 200 °C for 48 h [30,31]. Then, the solids were separated with the aid of an external magnetic field, washed with distilled water, dried at 80 °C and calcinated in air at 200 or 500 °C, for 4 h (with a heating rate of 10 °C/min). The μ-CNT catalysts were denoted as μ-CNT@A_B_C, where A is niobia precursor (NAmOx or NbOEt), B – niobia loading (30 or 60 wt%), and C – calcination temperature (200 or 500 °C).

Table 1 summarizes the composition of the final catalysts and the preparation parameters.

2.2. Catalyst characterization

The obtained catalysts were exhaustively characterized using different techniques as powder X-ray diffraction (XRD), Raman and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, adsorption-desorption isotherms of nitrogen at −196 °C, ICP-OES, and elemental analysis.

Powder X-ray diffraction (XRD) patterns were recorded using a Schimadzu XRD-7000 diffractometer with Cu Kα radiation (λ = 1.5418 Å, 40 kV, 40 mA) at a step of 0.2θ and a scanning speed of 2° min^{-1} in the 5–90° 2θ range.

Raman spectra were collected with a Horiba Jobin Yvon – Labram HR UV–visible–NIR (200–1600 nm) Raman Microscope Spectrometer, using a laser with the wavelength of 633 nm. The spectra were collected from 10 scans at a resolution of 2 cm^{-1}.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) spectra were collected with a Thermo 4700 spectrometer (200 scans with a resolution of 4 cm^{-1}) on a domain of 600–4000 cm^{-1}.

Surface areas were determined from the adsorption-desorption isotherms of nitrogen at −196 °C using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer.

To investigate the chemical stability of the catalysts the content of the leached metal into the reaction liquid was determined by ICP-OES (Agilent Technologies, 700 Series).

Elemental analysis was performed using an EuroEA 3000 automated analyzer. The sample (less than 1 mg) was weighted in tin containers and was burned in a vertical reactor (oxidation tube) in the dynamic mode at 980 °C in an He flow with the addition of O_2 (10 mL) at the instant of sample introduction. Portions of the sample in tin capsules were placed in the automated sampler,

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