



Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research Paper

Direct growth of hydrotalcite nanolayers on carbon fibers by electrospinning[☆]

Luis B. Modesto-López^{a,1,2}, Ricardo J. Chimentão^{a,2}, Mayra G. Álvarez^{a,2}, Joan Rosell-Llompart^{a,b}, Francisco Medina^{a,*}, Jordi Llorca^c

^a Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, E-43007 Tarragona, Spain

^b ICREA – Catalan Institution for Research and Advanced Studies, Pg. Lluís Companys 23, E-08010 Barcelona, Spain

^c Institute of Energy Technologies and Centre for Research in Nanoengineering, Technical University of Catalonia, Diagonal 647, E-08028 Barcelona, Spain

ARTICLE INFO

Article history:

Received 13 September 2013

Received in revised form 25 June 2014

Accepted 2 July 2014

Available online xxx

Keywords:

Carbon fibers

Layered double hydroxide

Electrospinning

Glycerol

Glycerol carbonate

Basic centers

ABSTRACT

Hydrotalcite (HT) nanolayers have been grown directly on carbon fibers by carbonization and subsequent hydration of electrospun PVA/PEO/MgAl-nitrate fibers. The growth of the layered material was ascertained by X-ray diffraction and electron microscopy techniques. High resolution transmission electron microscopy indicated that HTs are adhered on the carbon fibers. The HTs presented very small crystallite sizes, which enhance the accessibility of their basic centers compared to bulk HTs, leading to significant differences in terms of catalytic activity.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Electrospinning is a versatile method for creating micro- and nanofiber-type templates from both polymeric and inorganic materials (Madhugiri et al., 2003, 2007; Li and Xia, 2004) as building blocks for membranes, sensors, catalysts and catalyst supports among others (Li and Xia, 2004). Typically, a suitable precursor is dissolved or suspended in a polymer–solvent mixture, and this mixture is pulled by an intense electric field into thin fibers (tens to thousands of nm in diameter). These polymeric template fibers can be thermally treated to transform any precursors into dispersed nanomaterials.

An interesting material, which could be grown to nanometric size by this approach are hydrotalcites (HTs). Nanometric sized hydrotalcites have been synthesized over different supports for a number of applications in gas permeable membranes (Lee et al., 2008), photodegradation (Wang et al., 2010), catalysis (Winter et al., 2005a, 2005b) and green chemistry (Álvarez et al., 2012, 2013). The broad applicability of these materials reflects the chemical versatility of the HT structure, which is

constituted by positively charged brucite-like layers, neutralized by interlayer anions (Cavani et al., 1991; Evans and Duan, 2006). Recent studies in catalysis indicate that the active sites in HTs are located at the platelets' edges (Roelofs et al., 2000), whose exposed surface is determined by the lateral size of the crystallites. These materials have HT crystallite sizes around 20–30 nm, and are reported to improve the catalytic activity in several organic reactions compared to bulk hydrotalcites (Winter et al., 2005a, 2005b; Álvarez et al., 2012, 2013).

Diverse techniques and supports have been used to synthesize supported nanosized HTs, for example, co-precipitation on carbon nanofibers (Winter et al., 2005a, 2005b) or on alumina particles (Álvarez et al., 2012). Another example is the synthesis of nanosized HTs inside the channels of well-ordered mesoporous materials (Dubey, 2007; Li and Shi, 2008).

In previous electrospinning works, pre-synthesized hydrotalcites have been mixed with polymer solutions and electrospun to produce polymer/HT composites for applications such as fiber reinforcement (Romeo et al., 2007; Zhao et al., 2008; Zhuo et al., 2011) or materials with improved thermal properties (Zhao et al., 2010). In those approaches the HTs are encapsulated within the polymer matrix (Romeo et al., 2007; Zhao et al., 2008, 2010; Zhuo et al., 2011). However, until now, there are no reports on a direct synthesis of HTs supported on carbonaceous materials using electrospun fibers.

Here, electrospinning is proposed as a vector to introduce a hydrotalcite precursor directly throughout a fiber matrix. The nanosized HT

[☆] Author Contributions: The manuscript was written through the contributions of all authors.

* Corresponding author.

E-mail address: francesc.medina@urv.cat (F. Medina).

¹ Current address: Department of Environmental Science, University of Eastern Finland, P.O. Box 1627, FI-70211 Kuopio, Finland.

² These authors contributed equally.

is prepared in situ by thermal treatment and subsequent hydration of the precursor fiber. The confined space of the microstructured fibrous template ought to help in limiting the size of the HT crystallites to within a few tens of nanometers.

Specifically, our approach consists of electrospinning a uniform aqueous solution containing a polymer matrix and nitrates of Mg and Al as HT precursors. The as-spun fibers are thermally treated in an inert atmosphere to carbonize the polymer simultaneously forming Mg–Al mixed oxides. Subsequently, the hydrotalcite nanolayers are grown upon hydration of the mixed oxides.

The morphology and composition of the resulting materials have been characterized after each synthesis step. In addition, the catalytic behavior of these HT supported on carbon fiber (HT-CF) materials has been tested in the transesterification of glycerol with diethyl carbonate, which is an innovative process to obtain valuable chemicals from non-petrochemical sources.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) [PVA, 99%, hydrolyzed, Mw 30,000–50,000], poly(ethylene oxide) [PEO; Mw 600,000], $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were purchased from Sigma-Aldrich. Except for PVA (see Subsection 2.2) all the chemicals were used as received. Deionized (DI) water was used as the solvent.

To perform the catalytic tests, glycerol (gly) (99%), diethyl carbonate (DEC) (99.5%, GC grade) and ethanol (98%), all purchased from Aldrich, were used without any further purification.

2.2. Preparation of electrospinning solutions

Initial experiments indicated the presence of Na species in the final carbon fiber-supported materials. These Na species were traced to the PVA as purchased. Therefore, a Na removal procedure reported in the literature (Shin et al., 2008) was implemented prior to the preparation of electrospinnable solutions (see Supporting Information).

For a typical experiment, aqueous solutions of Na-free PVA/PEO and of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Mg:Al ratio = 2:1) were prepared separately. First, the polymer solution was stirred vigorously in a water bath at 353 K, using a hot plate, until a uniform solution was obtained (overnight). Then, the Mg–Al precursor solution was added to the first solution under continuous stirring at 353 K; after approximately 1 h the temperature was turned off and the solution was ready for electrospinning experiments. The PVA/PEO/MgAl precursor solution was composed of 14.3 wt.% PVA, 2.14 wt.% PEO, 2.90 wt.% $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 2.12 wt.% $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The PVA/PEO solution comprised 19 wt.% PVA and 4 wt.% PEO. In both solutions the PVA/PEO weight ratio was kept constant at ~4.6. The solutions were prepared under ambient conditions. PEO was added to improve the spinnability of the solution by reducing its surface tension. When the Mg and Al precursors were added to the electrospinning solution we observed a progressive decrease in the solution viscosity. Thus, electrospinning experiments were conducted using fresh solutions.

2.3. Synthesis of HTs and their activity

The synthesis of HTs, from PVA/PEO/MgAl fibers is divided into three steps and is summarized in Chart 1: (1) fiber templating by electrospinning, (2) formation of mixed oxides on carbon fibers by carbonization, and (3) formation of HTs supported on carbon fibers by hydration. In the case of PVA/PEO fibers, the synthesis finished after the carbonization step. The activity of HT-CFs in the transesterification of glycerol with diethyl carbonate was compared with that of bulk HTs and of control fibers. After each of the three main steps, the fibrous

materials were characterized by microscopy, spectroscopy, and adsorption techniques (see Subsection 2.4).

2.3.1. Fiber template generation and collection

Both PVA/PEO fibers containing Mg and Al precursors (termed hereinafter PVA/PEO/MgAl fibers) and PVA/PEO fibers were produced using the following method. In a typical experiment, 1 mL of electrospinning solution was fed with a syringe pump through a square-ended stainless steel needle (300 μm outer diameter, G21) at a rate of 0.5 mL/h. The needle was connected to an 18 kV high voltage source. The fibers were collected on a Si-wafer, which was supported on a stainless steel plate placed perpendicular to the needle main axis. The distance from the tip of the needle to the collector electrode was typically 11 cm. The electrospinning was run continuously until ~2 g of fibrous material was collected, and only stopped to re-charge the syringe with electrospinning solution. The as-spun fiber mats were then dried in vacuum overnight to remove any trapped solvent.

2.3.2. Synthesis of hydrotalcites supported on carbon fibers (HT-CFs)

As-spun PVA/PEO and PVA/PEO/MgAl fiber mats were first pyrolyzed in a quartz fixed bed reactor under Ar flow (20 mL/min) (carbonization step of Chart 1). The sample temperature was increased from room temperature to 723 K at 5 K/min and kept at 723 K for 5 h. PVA/PEO fibers turned into carbon fibers (CFs) and PVA/PEO/MgAl fibers into Mg–Al mixed oxides supported on carbon fibers (MgAlOx-CFs). The system was then cooled down in an Ar flow to room temperature. Subsequently (hydration step of Chart 1), the MgAlOx-CFs were hydrated by exposing them to an Ar flow saturated (100 mL/min) with decarbonated water for 72 h at room temperature to obtain the Mg–Al hydrotalcite structure (i.e., HT-CFs).

2.3.3. Transesterification of glycerol

Transesterification reactions were performed in a 10 mL round-bottomed flask equipped with a condenser. Typically, the flasks were charged with an excess of DEC (DEC:glycerol molar ratio of 16) to shift the equilibrium toward the formation of glycerol carbonate. Freshly activated catalyst (40 mg) was added and the experiment started with mechanical stirring under argon at 403 K. Stirring was continued up to 10 h and 5 mL of ethanol was then added. The sample was filtered and quantified by gas chromatography equipped with a FID and the products were identified by GC coupled with a quadrupole mass analyzer. This was performed on a Shimadzu QP 2010 apparatus with a Zebtron ZW-WAX capillary column. The results were confirmed by ^1H NMR.

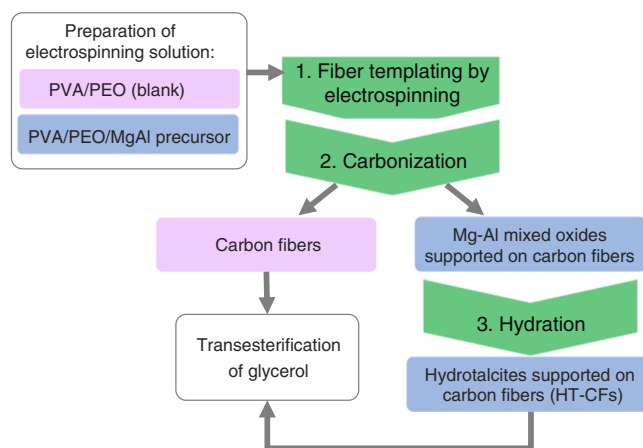


Chart 1. Procedure for the synthesis and activity test of hydrotalcites supported on carbon fibers (HT-CFs) and HT-free carbon fibers.

Download English Version:

<https://daneshyari.com/en/article/8046954>

Download Persian Version:

<https://daneshyari.com/article/8046954>

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