



# Silica-poly(styrenesulphonic acid) nanocomposites for the catalytic dehydration of xylose to furfural

I. Sádaba<sup>1</sup>, M. Ojeda<sup>2</sup>, R. Mariscal, M. López Granados\*

Instituto de Catálisis y Petroquímica (CSIC), C/ Marie Curie 2, Campus de Cantoblanco, 28049 Madrid, Spain

## ARTICLE INFO

### Article history:

Received 27 October 2013

Received in revised form 5 December 2013

Accepted 13 December 2013

Available online 22 December 2013

### Keywords:

Xylose

Furfural

Sol-gel

Poly(styrene sulphonic acid)

Acid catalyst

## ABSTRACT

This investigation reports on the catalytic properties and hydrothermal stability of hybrid organic–inorganic nanocomposites based on aminopropyl-functionalised SiO<sub>2</sub> and poly(styrenesulphonic acid) (PSSA). The nanocomposites were characterised by chemical analysis, thermogravimetric analysis (TGA), N<sub>2</sub> adsorption–desorption isotherms, transmission electron microscopy (TEM), as well as Raman, Diffuse Reflectance Infrared Fourier Transform (DRIFT), X-ray Photoelectron (XPS) and <sup>1</sup>H and <sup>13</sup>C solid Magic Angle Spinning–Nuclear Magnetic Resonance (MAS–NMR) spectroscopies. The results have proved that the presence of amino-functionalised silica results in stabilisation of the polymer molecules within the particle network of SiO<sub>2</sub>. The polymer is anchored to the silica matrix via electrostatic interactions between the sulphonic groups of the polymer molecules and the amino-functions present in the silica. These nanocomposites exhibited promising catalytic activity in xylose dehydration to furfural (at 443 K and after 5 h, ca. 90% xylose conversion, 65% furfural selectivity). When reused for several cycles, deactivation during the first run was observed due to polymer leaching. In successive runs catalytic properties remain stable.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Furfural is considered a platform molecule that can be transformed into a variety of valuable bio-based chemicals and biofuels [1,2]. Furfural is one of the compounds of the “top 10 + 4” revised list of bio-based product opportunities from carbohydrates [3]. Furfural is obtained from xylose by stepwise dehydration catalysed by acids. These consecutive steps involve a complex mechanism, and several side reactions occur simultaneously (Scheme 1) [1,4]. Industrially, xylose dehydration is conducted using an aqueous solution of a mineral acid (e.g., H<sub>2</sub>SO<sub>4</sub>) as catalyst [5]. A desirable and greener alternative is to develop reusable catalysts that can minimise waste effluents. One possible approach consists in the use of solid catalysts that can be easily recovered after the reaction and reused subsequently. Many examples of solid catalysts can be found in the recent literature, including zeolites, metal oxides, functionalised silica and commercial sulphonic resins [6–28]. Nevertheless, the main disadvantages of using solid catalyst are: (i) poor stability in the reaction medium because of the presence of highly polar solvents (typically H<sub>2</sub>O), and

(ii), the deposition of heavy compounds over the active sites, resulting in the catalyst deactivation by fouling and/or poisoning [15,29].

We have previously reported the use of a water-soluble catalyst consisting of poly(styrenesulphonic acid) (PSSA) in xylose dehydration to furfural. It did not experience poisoning or fouling of the active sites by coke deposition, which eliminated the calcination step typically required to regenerate the spent solid [30]. In addition, this polymer was stable and did not present leaching or any other deactivation process driven by the severe hydrothermal reaction conditions. The polymer could be recycled without loss of catalytic activity and separated from the reaction medium using an ultrafiltration process. The utilisation of ultrafiltration for reusing other soluble sulphonic polymer applied to other reactions of interest in biomass valorisation has been reported elsewhere [31].

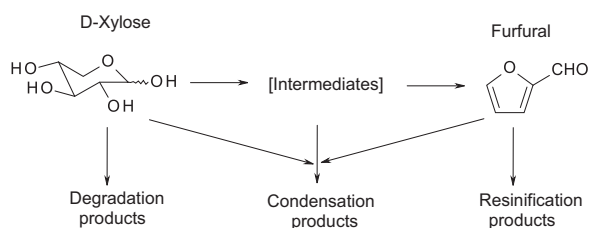
The polymer ultrafiltration procedure is laborious, it requires special equipment and it takes longer operational time than more conventional procedures, such as filtration or centrifugation; this make the latter separation techniques more preferred options. We report here the results obtained with an inorganic–organic hybrid prepared by the incorporation of the PSSA in a silica matrix. In this way the resulting solid SiO<sub>2</sub>–PSSA nanocomposite can be separated from the reaction mixture by conventional procedures. Silica was chosen as a support because of its relative inertness under the reaction conditions of the xylose dehydration. Besides its preparation and characterisation is well documented.

\* Corresponding author. Tel.: +34 915854937; fax: +34 915854760.

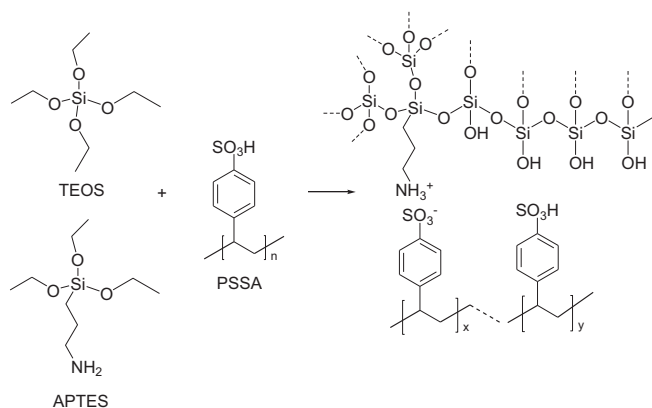
E-mail address: [mlgranados@icp.csic.es](mailto:mlgranados@icp.csic.es) (M.L. Granados).

<sup>1</sup> Present address: Haldor Topsøe A/S, Nymøllevej 55, 2800 Kgs. Lyngby, Denmark.

<sup>2</sup> Present address: Conversion Technology Centre, BP Chemicals Ltd, Saltend, Hull HU12 8DS, United Kingdom.



**Scheme 1.** Simplified overview of the mechanism of D-xylose dehydration to furfural.



**Scheme 2.** Preparation of the SiO<sub>2</sub>-PSSA catalyst in the presence of APTES.

Several methods have been described for the synthesis of polymer-silica nanocomposites in which strong polymer-silica interactions are formed either via the formation of covalent bonds or via electrostatic interactions [32–34]. These methods result in the fixation of the polymer on the silica surface. A very frequent approach is using in situ polymerisation routes: the monomer is subjected to polymerisation in the presence of the inorganic solid, which is previously formed [35–41]. However a different approach has been selected by us, the anchoring of previously formed PSSA macromolecules. This is more interesting from an environmental point of view because PSSA can be potentially prepared from polystyrene waste [42,43] and therefore this approach paves the way to the reclamation of waste polystyrene as acid catalyst.

Our strategy involves the use of ionic interactions for anchoring the polyelectrolyte macromolecule on the silica surface. Chujo et al. have reported on a synthetic route in which a PSSA polymer with a low sulphonation degree is retained on an amino-functionalised SiO<sub>2</sub> by electrostatic interactions between the sulphonic group of PSSA and the amino groups of the silica [44]. They used sol-gel routes and silica precursors like tetramethoxysilane (TMOS) and 3-aminopropyl trimethoxysilane (APTMO). The hydrolysis and condensation of these precursors were achieved by the presence of HCl (acid catalyst) and PSSA.

We have used a modification of this synthetic route, no HCl was incorporated and the sulphonic groups of PSSA act as the acid sites for catalysing the hydrolysis and condensation of the silica precursors. Tetraethylorthosilicate (TEOS) and 3-aminopropyltriethoxysilane (APTES) were chosen as SiO<sub>2</sub> precursors which generate environmentally friendly ethanol after hydrolysis, avoiding the presence of methanol in the medium. Moreover we have used a PSSA polymer with a high sulphonation degree to get larger loading of sulphonic sites. The formation of silica nanoparticles through sol-gel route provides high surface area to the final solid. A summary of this protocol is shown in Scheme 2.

Particularly we have explored the effect of incorporation of APTES on the following properties of nanocomposite: formation

of electrostatic interactions between sulphonic and amine groups, the hydrothermal stability of the nanocomposite, the leaching of the polymer and the catalytic stability. To achieve such information we have basically studied the incorporation during the synthesis of different amount of APTES with respect to PSSA (no APTES), a minute amount of APTES (mol APTES/TEOS = 0.001) and a larger concentration of APTES (mol APTES/TEOS = 0.5). The rest of variable of synthesis; for example temperature of synthesis, mol H<sub>2</sub>O/Si used during the synthesis, type of solvent, etc.; were kept constant.

## 2. Experimental

### 2.1. Synthesis of the nanocomposites

First, the required amounts of an aqueous solution of PSSA (Sigma-Aldrich, 18 wt.% in water), tetraethylorthosilicate (TEOS, Sigma-Aldrich, 99%) and 3-aminopropyltriethoxysilane (APTES, Fluka, 96%) were introduced in a round-bottom flask. A reflux condenser was connected, and the flask was immersed in an oil bath at 373 K with magnetic stirring. After 2 h, the formation of a nearly solid gel was observed, and the agitation was terminated. The reactor was maintained under reflux for 17 h, and the solid was filtered thereafter. To remove the residual polymer not retained by the SiO<sub>2</sub> particles, the collected solid was washed with H<sub>2</sub>O (ca. 200 mL) under stirring, filtered again and washed until neutral pH. Next, the collected solid was dried at 383 K overnight. Similarly, a blank silica catalyst, which is referred to as Si-5, was synthesised following the same method described above, but using H<sub>2</sub>SO<sub>4</sub> instead of PSSA. For the synthesis of Si-5, the amount of H<sub>2</sub>SO<sub>4</sub> used equals the amount of sulphonic groups (molar basis) incorporated by the addition of PSSA in the synthesis of the Si-PSSA-5 nanocomposites family.

The catalysts are hereafter named as Si-PSSA-X-Y, where X represents the nominal Si/S atomic ratio (different polymer loading), and Y indicates the nominal APTES/TEOS ratio (different proportions of amino groups). When Y is 0, the number is omitted in the nomenclature. We have explored two different polymer loadings (Si/S = 5 and 12) and two TEOS/APTEOS ratios (0.001 and 0.1) in order to achieve a high polymer loading. It is important to note that when the amount of APTES is notably high, an ammonium sulphonate polysalt can be formed due to the interaction between the different functional groups [43] so we restricted to APTES/APES ratios < 1.

### 2.2. Characterisation of the nanocomposites

The Si/S atomic ratio of the samples was determined by total-reflection X-ray fluorescence (TXRF) using an Atomika 8030C TXRF spectrometer (Cameca, Germany) equipped with a 3 kW Mo/W dual target X-ray tube and a W/C double monochromator multilayer. A Si(Li) detector with an active area of 80 mm<sup>2</sup> and a resolution of 150 eV at 5.9 keV (Mn K $\alpha$ ) was used for detection and measurement of the produced X-rays. The Si/S atomic ratio was determined using Si K $\alpha$  and S K $\alpha$  emission lines in the XRF spectra after proper calibration with standard samples.

The elemental analysis of the solids to determine the S content was performed on a LECO CHNS-932 analyser. Typically, 1 mg of the nanocomposite was placed in an Ag crucible and combusted at 1333 K under a pure O<sub>2</sub> atmosphere. The CO<sub>2</sub>, H<sub>2</sub>O and SO<sub>2</sub> gases were quantified by Fourier transform infrared (FT-IR) spectroscopy, while N<sub>2</sub> was determined by differential thermal conductivity.

Thermogravimetric analyses (TGA) of the nanocomposites were performed with a Mettler Toledo TGA/SDTA 851e instrument by heating the samples in synthetic air from room temperature to 773 K at a heating rate of 5 K min<sup>-1</sup>.

N<sub>2</sub> adsorption-desorption isotherms were recorded at 77 K using a Micromeritics TRISTAR 3000 apparatus. The samples were

Download English Version:

<https://daneshyari.com/en/article/45948>

Download Persian Version:

<https://daneshyari.com/article/45948>

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