Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

Silica-poly(styrenesulphonic acid) nanocomposites as promising acid catalysts

M.J. Campos-Molina, J.J. Corral-Pérez, R. Mariscal, M. López Granados*

Institute of Catalysis and Petrochemistry (CSIC), C/Marie Curie 2, Campus de Cantoblanco, Madrid 28049, Spain

ARTICLE INFO

Article history:
Received 17 November 2015
Received in revised form 17 June 2016
Accepted 20 June 2016
Available online xxx

Keywords:
Polymer-SiO_2 composites
Xylose
Furfural
Biodiesel

ABSTRACT

Silica-poly(styrene sulphonic acid) nanocomposites (SiO_2-PSSA) were prepared using sol-gel methodologies. An amino functionalized organosilane (APTES) provides the anchoring sites for the retention of this acid polymer by the silica particles network. Aiming at optimizing the polymer loading and stability, different SiO_2-PSSA nanocomposites were prepared by changing the type of solvent used in the synthesis, the aging protocol of the gel and the relative concentration of APTES. The effect of these modifications on the catalytic properties of the nanocomposites was explored in two different reactions driven by acid catalysts: xylose dehydration to furfural and esterification of oleic acid with methanol to yield biodiesel. Both reactions are of interest in the valorization of biomass and represent two illustrative cases to exploring the hydrothermal stability of the SiO_2-PSSA nanocomposites under different conditions: aqueous phase at moderately high reaction temperatures (453 K) and organic medium (methanol and oil) at low reaction temperature (333 K), respectively. Polymer leaching was very intense in the case of furfural reaction because of the severe reaction conditions. On the contrary, for the case of the esterification of oleic acid, a reaction conducted under milder conditions, the deactivation by leaching is significantly prevented.

1. Introduction

Soluble polymers have found applications as catalysts in a very wide number of reactions [1]. Of special interest are those directed at transforming biomass to valuable chemicals and biofuels [2–4] as this strategy will have a definitive impact in the substitution of an economy based on oil by another based on renewable resources. Thus polymers like sulfonated hyperbranched poly(aryleneoxindole)s [5] and poly(styrene sulphonic acid) (hereinafter referred as PSSA) [6] have been tested in reactions for valorization of biomass to valuable products, like cellulose conversion to levulinic acid, biodiesel synthesis, xylose to furfural transformation and oxidation with hydrogen peroxide of furfural to maleic and succinic acids. The former polymers presented acid sites required to catalyse those reactions and moreover were soluble in the reaction medium (water or methanol). Consequently they presented the advantages of homogenous catalysts because the access of reactants to the active sites (and the way out of products) is easier than in solid catalysts. In addition they can be reutilized by separation of the reaction mixture by ultrafiltration membranes.

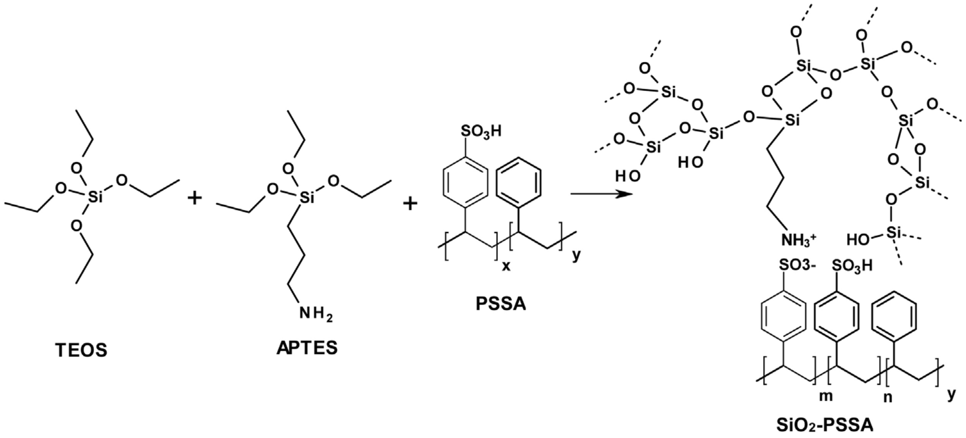
Other technologies can also be used to recover the polymer as dialysis or precipitation/recrystallization but all are perceived as cumbersome, not simple and cost effective for practical applications. Heterogenisation of the soluble polymers on inorganic solid supports can be an attractive solution. The so formed polymer composite (nanocomposites when the size of the particles of inorganic solid is in the range of nm) combines the advantages of soluble polymers (polymer will still be solvated by the liquid) and of the inorganic solids (ease of separation by more ordinary procedures like centrifugation or conventional filtration).

Within this context, the synthesis of SiO_2-PSSA nanocomposites has been achieved by polymerization of monomers like styrene or styrene sulphonic acid on the surface of the SiO_2 [7,8]. However we have followed a different approach and explored the preparation of these polymer-silica nanocomposites by anchoring the pre-formed sulphonated polymer on amino functionalized SiO_2 xerogel. Tetraethyl orthosilicate (TEOS) and 3-aminopropyl(triethoxysilane) (APTES) were used as source of SiO_2. A sol-gel method was used to obtain a silica xerogel through hydrolysis-condensation of the organosilanes (see Scheme 1). PSSA provides itself the acid pH required to form the SiO_2 gel and APTES provides the amino groups. The acid-base reaction between the sulphonic acid and the amino groups of the aminofunctionalised silica forms ionic interactions responsible of the retention of the polymer

---

* Corresponding author.
E-mail address: mlgranados@icp.csic.es (M.L. Granados).

http://dx.doi.org/10.1016/j.cattod.2016.06.042
0920-5861/



Scheme 1. Schematic representation of the preparation of the SiO_2-PSSA nanocomposites by the sol-gel methodology used in this study.

by the silica [9,10]. In our case an almost fully sulphonated PSSA was used (y, the fraction of non sulphonated rings, is smaller than 0.05; consequently x, the fraction of sulphonated rings, is >0.95). An at. S/N ratio (PSSA/APTES mol ratio) much larger than 1 was selected for the synthesis. Therefore m (the fraction of sulphonic groups supposedly anchored on amino groups) should be much smaller than n (the fraction non anchored on amino groups; $m + n = x$) and therefore free acid sites should be available.

As indicated above, the approach described in Scheme 1 makes use of already prepared PSSA. Interestingly PSSA can be obtained from polystyrene (PS) by sulphonation and, actually, we have also demonstrated that in practice PS waste can be sulphonated to form PSSA and be used as catalyst (Waste-To-Catalyst concept, WTC) [11]. Consequently there is no need of using fresh monomers to prepare this type of acid catalysts but to recycle PS waste.

In an attempt of finding the best preparation conditions in terms of polymer loading (acid sites loading) and hydrothermal stability, we have previously explored the effect of two variables of synthesis: temperature of synthesis and the S/N at. ratio initially used for the preparation (PSSA/APTES ratio). The rest of variables of synthesis were kept constant. We have found that an at. S/N ratio between 4.4–8.8 and a temperature of synthesis = 348 K resulted in nanocomposites with the largest acid sites loading and with the best hydrothermal properties in terms of stability of the catalyst [12]. However when the nanocomposites were used in the xylose to furfural reaction, the catalysts deactivated upon reutilization, mainly because of an intense polymer leaching.

Consequently improvement of the hydrothermal stability is still needed. In the investigation presented here, we report the effect of other variables of synthesis on the chemical and catalytic behavior of SiO_2-PSSA nanocomposite. These variables were the utilization of methanol as solvent to prepare the nanocomposite (instead of water), the time of aging of the gel, the slow evaporation of the water before the drying of the gel and the N/Si at. ratio used during the synthesis.

It is also interesting to explore other possible catalytic applications of these nanocomposites. Besides the xylose to furfural reaction, we have extended the study of the catalytic activity to the esterification of fatty acids with methanol to render fatty acid methyl esters (FAME). Both reactions are of interest in the valorization of biomass to renewable chemicals and to biofuels [6,10,11,13]. Furfural has been considered a valuable bio-derived chemical platform for a number of other commodities and biofuels [14]. The esterification of fatty acid to FAMEs is a key reaction for the valorization of low quality oils to biodiesel [15–17]. In addition to these practical reasons, these two reactions represent two extreme cases when exploring the hydrothermal stability of the SiO_2-PSSA nanocomposites: aqueous phase at moderately high reaction temperatures, on one side, and organic medium (methanol and oil) at low reaction temperature, on the other side. Therefore with these two reactions we are delimiting the type of reaction this catalyst can be applied for. We have paid specific attention to the reusability of the nanocomposites and, specifically, to the stability against leaching of the polymer.

2. Experimental

2.1. Preparation of catalysts

The nanocomposites were prepared by sol-gel methodology by co-condensation of tetraethyl orthosilicate (TEOS, Sigma-Aldrich, ≥99%) and (3-aminopropyl) triethoxysilane (APTES, Sigma-Aldrich, ≥98%) in the presence of PSSA (MW = 75000, 5.4 mmoles $H^+ g^{-1}$) according to a methodology described elsewhere [10]. PSSA was supplied by Sigma-Aldrich as a 18 wt.% aqueous solution. The required amounts of the aqueous PSSA solution, TEOS and APTES were introduced in a round glass flask vessel and the mixture stirred vigorously. The reactor was immersed into an oil bath at 348 K and kept at this temperature for 16 h (overnight). The solid so formed after aging was filtrated and to fully remove the weakly retained polymer, the solid was subjected to successive washes with water at room temperature until rinsing water displayed neutral pH. Finally, the solid was dried in air at 393 K for 16 h.

In a first series of samples the initial amount of APTES and TEOS were varied as to have an atomic N/Si ratio of 0.05, 0.09 and 0.20 respectively, maintaining constant the PSSA/APTES mol ratio (S/N = 4.4). In practice ca. 5 g of APTES, ca. 18.3 g of PSSA solution and ca. 89.4, 47.1 and 18.8 g of TEOS, respectively, were incorporated to the synthesis reactor. The nanocomposites of this series were named as *Si-(N/Si)-PSSA-4.4* where N/Si is refers to the ratio used in the synthesis whereas 4.4 is the initial at. S/N ratio. We kept the ratio S/N = 4.4 in the labeling to distinguish them from the other nanocomposites investigated in this article.

The effect of the utilization of methanol instead of water as the medium for the synthesis was also explored. APTES and TEOS are not soluble in water and therefore when using water two phases exist initially: the organic layer with APTES and TEOS and the aqueous solution of PSSA. On the contrary APTES, TEOS and PSSA are soluble in methanol and a single phase is available from the very beginning. 5 g of dried PSSA solid, ca. 9.18 g of water (the amount required to fully hydrolyze TEOS and APTES), ca. 25.7 g of TEOS and ca. 2.7 g of APTES were incorporated to the synthesis flask that was earlier filled with ca. 100 mL of methanol, enough to solubilize all