Contents lists available at ScienceDirect

Catalysis Today



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

Esterification of acetic acid with butanol over sulfonic acid-functionalized hybrid silicas

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A R T I C L E I N F O

Article history: Available online 19 June 2010

Keywords: Mercaptopropyl Esterification Acid catalyst Silica

ABSTRACT

Sulfonic acid-functionalized hybrid silicas with different loading of organic moieties were synthesized by grafting and co-condensation followed by oxidation of the precursor thiol groups with hydrogen peroxide or by *in situ* oxidation methods involving the oxidation by hydrogen peroxide during the condensation reaction. As determined by photoelectron spectroscopy (XPS) complete oxidation of the thiol groups in the differently prepared materials was achieved at room temperature. In the esterification reaction of acetic acid with butanol the samples prepared by the *in situ* oxidation method exhibited the best catalytic activity. During recycling test with a selected sample, in spite of some sulfur leaching, stable activity was observed.

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1. Introduction

Esterification is an industrially important reaction used in several fields from pharmaceutical and organic chemistry, in fragrance and flavor industry, cosmetics, to biofuel production. Concerning the last application, in recent years, due to the increasing price of fossil fuel and to the environmental concern there has been a considerable interest in developing biodiesel as alternative fuel. Biodiesel is a mixture of fatty acid methyl ester (FAME) produced by the transesterifications of triglycerides with methanol. Biodiesel presents several advantages, being a renewable source, therefore decreasing the greenhouse-gas emission, with no sulfur and aromatics release and it can be used with the actual compression-ignition engines without major modification [1]. However, a main drawback of the biodiesel production is represented by the large surplus of glycerol formed during the transesterifications of triglycerides [2]. Then, the esterification of glycerol with acetic acid is used as a successful way to transform it in acetvlated derivatives which are utilized as additives to biofuel [3]. Another important application of esterification in the field of biofuel is in the production of bio-oil. The bio-oil is obtained by the thermal processing under fast pyrolysis of the biomass. The so obtained bio-oil contains, as by-products, water and a large number of organic acids which by self-interaction destabilize and age the bio-oil, leading to an increase in its viscosity. Then, in order to avoid this degradation, the undesired organic acids, through esterification processes in the presence of catalysts, react with alcohols already present in the bio-oil or added purposely [4]. Traditionally, esterification reactions are industrially performed under batch conditions in homogeneous liquid phase. Strong Brønsted acids, such as sulfuric acid, hydrochloric acid or ortophosphoric acid are generally used as catalysts. These substances are very corrosive and toxic for the environment, they need to be used in quite significant quantities and they are difficult to separate and recover [5]. For these reasons, efforts to replace the homogeneous catalysts by the heterogeneous ones are being made. Due to their potential benefits, numerous attempts have been made to develop solid acid catalysts to replace liquid acids in chemical industry. Zeolites [6], resins [7], heteropolyacids [8], and mesoporous silicas functionalized with organic acid groups [9-12] have been used as heterogeneous catalysts in esterification reactions. Sulfonic-functionalized silicas are among the most used acid catalysts for esterification reaction. Cano-Serrano et al. prepared sulfonic acid-functionalized silica by a simple procedure consisting of grafting followed by hydrogen peroxide oxidation. In spite of some leaching of sulfur during the oxidation of the thiols, the samples exhibited good catalytic activity and stability in the esterification of acetic acid with methanol [13,14]. In the present study, aiming to obtain materials with high resistance to sulfur leaching and superior catalytic activity, different synthesis methods are used to anchor sulfonic groups in the amorphous silica. The acid-functionalized silica materials, characterized by N₂ adsorption/desorption measurements and by X-ray photoelectron spectroscopy, are tested in the esterification reaction of acetic acid with butanol. The effect of the functionalization procedure and of the -SO₃H loading on the catalytic behavior is discussed.



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^{0920-5861/\$ -} see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.cattod.2010.05.027

2. Experimental

2.1. Sample preparation

The propyl sulfonic functionalized SiO₂ catalysts were synthesized adopting three different procedures: grafting, cocondensation and *in situ* oxidation. Materials were purchased from commercial suppliers and used without further purification.

2.1.1. Grafting method

The silica was previously synthesized by sol-gel technique according to a published procedure [15]. A mixture of 2.00 g of calcined silica in 35 ml of dry toluene and 3-mercaptopropyltrimethoxysilane (MPTMS) (1.66 or 3.33 or 6.66 mmol, corresponding to 5, 10, 20 mol% loading, respectively) was refluxed for 24 h. The materials were then recovered by filtration, washed several times with toluene and dried at 120 °C overnight. Thereafter, the mercaptopropyl groups were oxidized to sulfonic groups with hydrogen peroxide (33% w/v solid:liquid ratio of 1:18) at room temperature during 24 h. After filtration the solid was dried at 120 °C overnight.

2.1.2. Co-condensation method

A mixture of 7.5 ml of tetraethyl orthosilicate (TEOS) with 5 ml of ethanol was stirred for 15 min at 45 °C. Then, 5 ml of acetic acid aqueous solution at pH 5 was added to the mixture followed by MPTMS addition to obtain 5%, 10%, 20% loading. The temperature was increased to 80 °C until the water was evaporated out, and finally, the solid was dried at 120 °C overnight. The solid was then oxidized by the same procedure described before.

2.1.3. In situ oxidation method

The samples were synthesized according to Margolese et al. [16], as described for co-condensation method except that MPTMS, in amounts corresponding to 5%, 10% and 20% loading, and hydrogen peroxide (33% w/v solid:liquid ratio of 1:18) were added at the same time. The temperature was increased to 80 °C until the water was evaporated out, and finally, the solid was dried at 120 °C overnight. Concerning the 20% loaded sample, since no reproducible materials were obtained, the characterization and catalytic results are not here included. This confirmed that, as reported in literature, the molar concentration of propyISH moieties should be limited to less than 20% [17].

2.2. Characterization

Acid capacity and concentration of sulfonic groups of samples were determined by titration with 0.01 M NaOH (aq) according to Yang et al. [18]. In a typical experiment, 0.1 g of solid was added to 10 ml of 0.2 M NaCl solution as exchange agent. The resulting suspension was allowed to equilibrate and thereafter titrated potentiometrically by dropwise addition of 0.01 M NaOH solution.

The textural characterization was performed with a Carlo Erba Sorptomat 1900 instrument. The fully computerized analysis of the nitrogen adsorption isotherm at 77 K allowed to obtain, through the BET method in the standard pressure range $0.05-0.3 p/p_0$, the specific surface areas of the samples. By analysis of the desorption curve, using the BJH calculation method, the pore size distribution was also obtained. The total pore volume, V_p was evaluated on the basis of the amount of nitrogen adsorbed at a relative pressure of about 0.98 [19].

X-ray photoelectron spectroscopy analyses were performed with a VGMicrotech ESCA 3000Multilab, equipped with a dual Mg/Al anode. The spectra were excited by the unmonochromatized Al K α source (1486.6 eV) run at 14 kV and 15 mA. The analyser

operated in the constant analyser energy (CAE) mode. For the individual peak energy regions, a pass energy of 20 eV set across the hemispheres was used. Survey spectra were measured at 50 eV pass energy. The sample powders were analysed as pellets, mounted on a double-sided adhesive tape. The pressure in the analysis chamber was in the range of 10⁻⁸ Torr during data collection. The constant charging of the samples was removed by referencing all the energies to the C1s set at 285.1 eV, arising from the adventitious carbon. The invariance of the peak shapes and widths at the beginning and at the end of the analyses ensured absence of differential charging. Analyses of the peaks were performed with the software provided by VG, based on non-linear least squares fitting program using a weighted sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley and Sherwood [20,21]. Atomic concentrations were calculated from peak intensity using the sensitivity factors provided with the software. The binding energy values are quoted with a precision of ± 0.15 eV and the atomic percentage with a precision of $\pm 10\%$.

Sulfur contents were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Horiba Jobin Yvan Ultima 2).

2.3. Esterification reaction

In a typical experiment, acetic acid (50 mmol) was added to a mixture of butanol (50 mmol) and catalysts (25 mg) (mass ratio of catalyst/alcohol = 0.006). Reagents were purchased from commercial suppliers and used without further purification.

The reaction was carried out in a 25 ml round bottom flask equipped with a water-cooled condenser. The contents were then refluxed at 110°C. The temperature was maintained using an oil-bath connected with a thermostat. The reaction mixture was continuously stirred during the reaction using a magnetic stirrer.

The products were analysed by GC–mass spectroscopy on a GC–MS-QP5050A Shimadzu mass spectrometer with ionisation energy of 70 eV and their chromatograms were in accord with those obtained from reference samples. As a proof of a *chemical* regime, varying the stirring speed either magnetic or mechanic between 200 and 700 rpm no changes in the conversion after 1 h were observed.

Recycling experiments were performed over the most active catalyst. After the reaction, the catalyst was filtered, washed with ethanol in order to clean the catalyst surface, dried and activated at 120 °C overnight and reused.

For comparison purposes, blank reaction and homogeneous reaction were performed by stirring acetic acid (50 mmol) and butanol (50 mmol) in absence of solvent at a temperature of 110 °C, without catalyst and with 3.35 mg *p*-toluensulfonic acid (pTSA), respectively. The amount of pTSA was chosen to have the same amount of mmol H⁺ with respect to 5% *in situ* oxidation catalyst. The products were analysed by GC–MS.

3. Results and discussion

3.1. Characterization results

As calculated by BET analyses of the N₂ adsorption curves, the specific surface areas of the silica samples functionalized with different loading of sulfonic groups and using the three different methods are listed in Table 1. In the case of grafting, the presence of the oxidized functional groups causes a decrease of the surface area of the original silica support. The decrease is independent on the group loading. BET analyses performed on selected samples before the H₂O₂ treatment, according to the obtained values showed in parentheses in the table, suggest that a further reduction in surface

Table 1	
Surface areas (S _{BET} m ² g ⁻¹) and pore volume (cm ³ g ⁻¹) values of SiO ₂ -propyISO ₃ H calculated by BET method. In parenthesis the values of the SiO ₂ -pr	opylSH.

Sample	Grafting		Co-condensation		Ox. in situ	
	$S_{\rm BET} (m^2 g^{-1})$	Pore volume (cm ³ g ⁻¹)	S_{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	$S_{\text{BET}} (m^2 g^{-1})$	Pore volume (cm ³ g ⁻¹)
0	520	1.7				
5%	249 (283)	0.46 (0.51)	284	0.38	480	0.44
10%	265 (296)	0.28 (0.36)	234 (213)	0.19 (0.46)	500	0.41
20%	265	0.27	121	0.13		

area is caused by the post-oxidation process. Such effect, already reported in literature [13,14,16], for grafting and co-condensed samples, may be attributed to a collapse of the silica framework due to H₂O₂ hydrolysis. Similarly to the samples prepared by grafting, the surface areas of the co-condensed functionalized silicas are smaller as compared to the bare silica. However, in this case, at variance with the grafted samples, the extent of the decrease of the surface area grows with the sulfonic group loading. Quite differently from the two previous cases, the in situ oxidation procedure allows to obtain materials with similar high surface area of a bare silica regardless the loading of the propylsulfonic groups. The attainment of the high surface area, in this case, is attributed to gas evolution during the step of the structure formation. The pore size distribution for all the materials is rather broad, centered in the mesoporous range of 3–5 nm. Pore volumes, listed in Table 1, in both cases, grafting and co-condensed samples, decreased with the increase of MPTMS loading, indicative of some structure modification. The in situ oxidation samples, in spite of the still high surface area and independently on the group loading, have quite lower pore volumes as compared to bare silica.

The materials were characterized by XPS technique yielding quantitative and qualitative information on the surface element composition and chemical state. The large chemical shift between S^{2-} and S^{6+} species (ca. $5\,eV)$ makes indeed XPS a useful tool for evaluating the degree of oxidation of thiol groups to sulfonic groups. The S 2p peaks obtained for the samples before and after the oxidation are shown in Fig. 1. They are quite broad being formed by the two unresolved spin-orbit components S $2p_{3/2}$ and S $2p_{1/2}$. The corresponding S/Si atomic ratios are given in Table 2. It is interesting to notice that using the grafting method, before oxidation, while increasing the loading of the sulfur moieties, silicon/sulfur ratio remains essentially constant with a XPS derived S/Si ratio well above the nominal amount, suggesting saturation of the surface already with 5% of the sulfur containing groups. On the contrary, when co-condensation method is used, in accord with the proportional increase of the S/Si ratio, a more homogeneous distribution of alkyl moieties into the materials is afforded.

As reported in literature [11], the grafted samples undergo a loss of the sulfur groups upon oxidation, as evidenced by the decrease of the XPS derived S/Si ratio, on the contrary the cocondensed samples show a higher stability keeping S/Si ratios comparable with the reduced precursors (Fig. 1 and Table 2). The *in situ* oxidation samples show the highest S/Si ratios. Overall the S/Si ratio of the oxidized samples change as *in situ* oxidation > cocondensation > grafting.

As shown in Fig. 1, the oxidation procedure affords total oxidation of SH groups as indicated by the disappearance of the peak

Table 2XPS S2p/Si2p derived atomic ratios of the catalysts.

Grafting		Co-condens	ation	Ox. in situ	
	Reduced	Oxidized	Reduced	Oxidized	Oxidized
5%	0.15	0.02	0.02	0.04	0.06
10%	0.15	0.04	0.05	0.06	0.13
20%	0.15	0.05	0.11	0.16	



Fig. 1. S2p XPS region modified silica; co-condensed samples: a reduced, a' oxidized; grafting samples: b reduced, b' oxidized; *in situ* oxidized samples: c.

at 164 eV characteristic of thiol species [22] and the presence of the peak at 170 eV characteristic of oxidized sulfonic group. The difference with literature work [23,24] on similar samples which otherwise were not completely oxidized by H_2O_2 at room temperature and neither at 50 °C, is probably attributed to the longer oxidation period adopted in the present study.

Table 3 lists the acid capacity of sulfonic silica materials as mmol H^+g^{-1} . Grafting and co-condensation procedures produce a lower amount of sulfonic acid groups in the silica, while *in situ* oxidation gives values in accord or even above the expected values. The hydrogen exchange capacity is in accord with the sulfur amount as determined by ICP-OES for the 5% grafting and the 5% co-

Table 3

Acid capacities (mmol $H^+\,g^{-1}$) of the different SiO_2 -propylSO_3H catalysts. The experimental sulfur amount (mmol S g^{-1}) determined by ICP-OES are also given in parentheses.

Sample	Grafting	Co-condensation	Ox in situ	Expected value ^a
5% 10% 20%	0.36 (0.4) 0.27 0.56	0.44 (0.4) n.d. 1.5	0.81 (0.5) 2.09	0.77 1.44 2.88

^a Values calculated for 100% incorporation of propyISH groups and 100% oxidation.



Fig. 2. Alcohol conversion as a function of mercaptopropyl loadings and synthetic procedure.

condensed samples. On the contrary, the hydrogen capacity of the 5% *in situ* oxidation sample is quite higher than the sulfur amount. Such behavior for the *in situ* oxidation materials could be attributed to an increased acidity of the silica which, according to Mbaraka and Shanks, may be caused by a site cooperation effect through formation of hydrogen bonds between adjacent acid pair [25].

3.2. Catalytic results

Conventional esterifications do not proceed to completion, but reach equilibrium. The equilibrium can be shifted towards higher conversion by using one reactant in excess and/or by selective removal of one of the products. However the contamination of products with excess substrates requires substantial energy and time for the purification of esters. In contrasts, catalytic direct condensation between equimolar amounts of carboxylic acids and alcohols, in principle, lacks these drawbacks. As a model reaction, catalytic esterification of acetic acid with butanol over various sulfonic-functionalized silicas was carried out in the equimolar amounts, in absence of solvent and at a temperature of 110 °C.

The reaction was monitored during 1h and thereafter the products were analysed by GC-MS. The only product of the reaction was the corresponding acetate with a selectivity of 100%. The alcohol conversion as a function of the various catalysts is summarized in Fig. 2. As compared to the blank reaction, quite higher conversions were obtained with the solid acid catalysts. A strong effect of the catalyst preparation method was observed. In particular when the reaction was carried out in the presence of the catalysts synthesized by in situ oxidation, a considerable increase in the conversion was obtained yielding, in all formulation, higher activity with respect to the homogeneous pTSA reaction. According to literature [10], the activity of the grafted samples decreases with increasing sulfur loading. In the present study the maximum is observed in correspondence of a 5% loading. Quite peculiar was the behavior of the 10% loaded catalysts. Indeed, among the series of synthesized catalysts when the 10% loading catalysts were used, in all cases low conversion in the synthesis of acetate was observed. At variance with Ref. [12] in which the grafted derived catalyst was quite better performing as compared to the co-condensed one, the results of the present study show comparable activity between the two series of functionalized silicas. Under the same reaction conditions, these catalysts resulted more active than the zeolite reported in literature [6].

In addition to the above experiments other investigations were carried out to check the influence of catalyst concentration and the



Fig. 3. Alcohol conversion of number of recycling cycles for 5% in situ oxidation sample.

reusability of catalyst. Concerning the effect of catalyst amount, the reaction was carried out varying the amount of a selected catalyst, the 5% *in situ* oxidation catalyst, as 12.5, 25 and 50 mg for 50 mmol of alcohol. It was observed that with the increase in the catalyst amount from 12.5 to 25 mg, the conversion, in the reaction time of 1 h, increases from 75 to 86% and thereafter remains almost constant.

Recycling experiments were performed over the most active catalyst, i.e. the 5% *in situ* oxidation catalyst. As shown in Fig. 3, after 5 cycles of reaction a 5% decrease of the alcohol conversion was observed. This catalyst, analysed by XPS both after the first and the fifth reaction cycle, exhibited, as shown in Fig. 4, a drastic decrease in the S 2p signal with respect to the fresh catalyst, already after the first cycle. The amount of sulfur determined by ICP-OES analysis (0.25 mmol S g⁻¹) of the recycled catalyst (after the fifth cycles) was accordingly much less as compared to the fresh sample. Therefore the leaching of sulfur, as determined by XPS and sulfur analysis, does not seem to affect drastically the catalytic activity of the reused sample. In accord with the enhanced hydrogen capacity found for this sample, the quite stable catalytic activity after recycling may confirm the presence of active acid sites due not just to



Fig. 4. Si2s and S2p XPS region of fresh and used 5% in situ oxidation sample.

sulfonic groups but to silica acidity produced during the material formation process.

4. Conclusions

In this study, three different approaches of standard silica synthesis were used to prepare propylsulfonic acid catalysts for esterification reaction. The *in situ* oxidation yielded materials with higher surfaces area and higher acid capacities, several times greater than those achieved with post-oxidation methods. For these reasons, even though all materials were active in the esterification of acetic acid with butanol, the catalysts synthesized by *in situ* oxidation resulted the most active ones. After recycling tests the activity was quite stable in spite of the decreased amount of sulfonic groups.

In conclusion the obtained materials, in terms of structural properties and catalytic performance, may represent good candidates as solid catalysts for the esterification reactions and for this reason deserve further investigation.

Acknowledgements

Support by European Community, Network of Excellence (NoE) IDECAT (Integrated Design of Catalytic Nanomaterials for Sustainable Production) and COST D36 action is acknowledged.

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