Sulfonic acid-functionalized silica through quantitative oxidation of thiol groups

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A simple procedure for the preparation of amorphous silica containing thiol groups which quantitatively affords sulfonic acid groups has been developed, resulting in site densities and activity for the esterification of acetic acid with methanol greater than a commercial Nafion® silica composite.

Functionalized mesoporous materials, with a rigid structure, high surface areas and large pore sizes are of great importance because of their application in the fields of adsorption, sensing and catalysis. Recent developments have focused on mesoporous-ordered silica family incorporating organic groups either during the sol–gel process[1,2] or *via* post-grafting techniques.[3,4] This chemistry has been exploited to prepare pure Brønsted sulfonic acid-functionalized mesoporous silica.[5–7] However, mesoporous ordered silica family compounds, even though offering pore sizes in the 2–10 nm range, may also be susceptible to transport phenomena problems inside the channel structure and these solids do not have good mechanical strength. These problems can be avoided using an amorphous silica support, which has good mechanical strength and a high surface area.[8] On the other hand, techniques for the synthesis of sulfonic acid-functionalized silica use a thiol route involving grafting, or a sol–gel route, followed by thiol group oxidation, although no detailed attention has been paid to the oxidation step, leading to incomplete oxidation,[8,9] or disulfide species S–S.[7]

In the light of the foregoing, we have developed a simple methodology to quantitative sulfonic acid group formation on the pores of amorphous mesoporous silica by starting with the anchoring of thiol groups and then proceeding with selective oxidation in liquid media. This approach allows the *in situ* quantitative oxidation of –SH groups and a resulting acid exchange of the SO_3H groups formed.

Catalysts were prepared using the following procedure: silane precursors (3-mercaptopropyltrimethoxysilane (MPTMS) 3-mercaptopropylmethyldimethoxysilane (MPMDMS) and/or phenyltrimethoxysilane (PTMS)) were added dropwise to an amorphous silica support (2 g) (Grace Davison G952). All the liquid was adsorbed by the solid. To ensure complete reaction between the precursors and silica, they were kept at room temperature for 24 h. The thiol groups of the modified silica were oxidized with a 33% H_2O_2 solution (32 ml); the suspension of the solid was kept under stirring for 1 h at room temperature or 333 K, and the solid was filtered off and washed three times with water (32 ml). In order to ensure that all the sulfonic groups were protonated, the solid was suspended in a 10 wt% H_2SO_4 solution (32 ml) for 1 h. The solid was then filtered off and washed with water and dried at 333 K for 24 h. The catalysts synthesized are compiled in Table 1.

ICP-AES chemical analysis (Perkin-Elmer Optima 3300 DV) (Table 1) indicated that the amount of S incorporated depends on the type of S-precursor and also on the oxidation conditions employed. Moreover, S-loading was always below the theoretical amount used in preparation. This observation points to a partial solubilization of surface thiol groups along the oxidation process. Comparison of samples E1 and E2 with E3 and E4 indicated that amounts of S incorporated were higher with MPMDMS than with the MPTMS precursor. Surprisingly, the final S-content was also modified by the addition of PTMS in the sense that the presence of phenyl groups increased the S-content. This can be seen on comparing E1 *vs.* E2 and E3 *vs.* E4. This finding can be understood taking into account the hydrophobic nature of the catalyst surface as induced by the methyl groups of MPMDMS or the phenyl groups of PTMS precursor, which exclude water molecules from the neighbourhood of R–Si–O groups, thus limiting hydrolysis of R–Si–O–Si bonds and minimizing sulfur losses arising from hydrolysis. On the other hand, samples oxidized at 333 K had substantially lower S contents than on their counterparts oxidized at RT. This observation suggests that treatment at 333 K leads to a stronger desorption of S-containing groups. At this temperature, the protective effect of hydrophobic groups was clearer. Nitrogen adsorption–desorption isotherms (Micromeritics TriStar 3000, 77 K) of all the samples and the silica reference were type IV of the IUPAC classification. Incorporation of S led to a decrease in adsorption capacity, and this was even more marked in those samples containing phenyl groups (E1 and E3). The reduction in the adsorption capacity of functionalized silica samples is clearly illustrated by the decrease in specific area (Table 1). However, no changes with the nature of the thiol precursor (MPMDMS or MPTMS) were observed. Thermogravimetric (TG) analyses (Perkin-Elmer TG2, heating rate 10 K min^{-1}

Table 1 Catalysts prepared, precursor quantities added on 2 g of silica, synthesis conditions, S content, BET surface area and binding energy of the S 2p$_{3/2}$ level

Sample	Silane precursor/g MPMDMS	MPTMS	PTMS	Oxidation temperature/K	S content/ mmol g^{-1}	Ion exchange capacity/ mmol g^{-1}	BET surface area/ m^2 g^{-1}	S 2p$_{3/2}$ XPS BE^a/eV
E1$_{RT}$	0.68	—	1.32	RT	1.28	—	97	163.9 (78 %), 168.4 (22 %)
E1$_{333}$	0.68	—	1.32	333	1.04	0.46	98	168.5
E2$_{RT}$	0.68	—	—	RT	1.39	—	168	163.8 (83 %), 168.2 (17 %)
E2$_{333}$	0.68	—	—	333	0.89	0.27	199	163.7 (44 %), 168.2 (56 %)
E3$_{RT}$	—	0.68	1.32	RT	0.71	—	176	163.7
E3$_{333}$	—	0.68	1.32	333	0.69	0.53	164	168.4
E4$_{RT}$	—	0.68	—	RT	1.05	—	208	163.8 (43 %). 168.1 (57 %)
E4$_{333}$	—	0.68	—	333	0.50	0.40	211	168.2
Silica	—	—	—	—	—	—	224	—

^{a} Relative proportions of components in parentheses.

under 60 cm^3 min^{-1} air flow) of oxidized samples at ambient temperature and at 333 K afforded almost identical results. However, the use of different silane precursors revealed clear differences. At temperatures lower than 383 K, water desorption was observed, this desorption being less pronounced for the samples containing hydrophobic (phenyl and methyl) surface groups. Thus, weight loss followed the order: E4 > E2 > E3 > E1. A second weight loss, due to S-containing groups, occurred at 600–800 K, while the samples containing phenyl groups displayed an additional weight loss at 800–850 K. TG profiles for samples using MPMDMS and MPTMS precursors revealed that the decomposition of sulfur groups takes place in two steps although the latter requires a higher temperature for complete decomposition. Thus, the chemical nature of the precursor influences the thermal stability of the S-functionalized mono-layer. The nature of the anchored S-species was studied by FT-Raman (Bruker RFS100, NdYAG laser, 400 mW), which is more sensitive for S–H vibrations than FT-IR. The spectra of the original samples clearly exhibited a band at 2575 cm^{-1} characteristic of S–H vibrations;[10] this band, however, disappeared in samples treated with hydrogen peroxide, both at ambient temperature and at 333 K. This finding could be taken as indicative of the oxidation of –SH groups by hydrogen peroxide. In no case could vibration modes due to the formation of S–S species (475–575 cm^{-1}) be observed.[9,11] Photoelectron spectra (XPS) (VG Escalab 200R, Mg Kα ($h\nu$ = 1253.6 eV) were determined for all the samples. High resolution spectra of the S 2p core-level for the *in situ* outgassed samples pointed to the existence of two types of sulfur species: one at low BE (163.7 eV), corresponding to a –SH groups, and another at higher BE (168.5 eV), associated with –SO$_3$H groups. The samples oxidized with hydrogen peroxide at ambient temperature displayed a very small proportion of oxidized sulfur (Table 1), and only sample E4$_{RT}$ exhibited 57% of sulfur oxidized to –SO$_3$H. However, oxidation with hydrogen peroxide at 333 K proved to be much more effective for all samples. On comparing samples E4$_{RT}$ and E2$_{RT}$, or E2$_{333}$ and E4$_{333}$ it appears that the oxidation of thiol groups is easier with the MPTMS than with the MPMDMS precursor. In addition, and surprisingly, the presence of phenyl groups favoured the oxidation of thiol groups with hydrogen peroxide, as seen on comparing E1$_{RT}$ and E2$_{RT}$, E3$_{RT}$ and E4$_{RT}$, and E1$_{333}$ and E2$_{333}$.

To evaluate the amount of exchangeable protons, the acid capacity of the sulfonic-modified materials, previously oxidized at 333 K, was measured by acid–base titration, using Na$^+$ in propan-2-ol as ion-exchange agent. Exchange capacity values of MPTMS samples were high (>80% of sulfur content) and somewhat lower (*ca.* 50% of sulfur) for the MPMDMS counterparts. Even lower values were found for the E2$_{333}$ sample, which is in accord with the partial oxidation of thiol groups (see XPS section).

The catalytic performance of oxidized catalysts at 333 K was assessed with the esterification of acetic acid with methanol. 90 g of acetic acid and 48 g of methanol (molar ratio 1 : 1) were heated at 333 K, and then 1 g of catalyst was added. Acetic acid conversion was followed by acid titration with a 2.0 M NaOH solution. All the catalysts showed much higher conversion levels than in the absence of catalyst (Fig. 1), pointing to the involvement of the surface acid groups produced in silica functionalization. Interestingly, catalyst E2$_{333}$ exhibited a lower conversion than catalysts E1$_{333}$, E3$_{333}$ and E4$_{333}$. In agreement with the XPS data, sample E2$_{333}$ still retained 44% of sulfur atoms as thiol groups, which necessarily implies a lower density of –SO$_3$H groups in this sample. Samples with all sulfur atoms as sulfonic groups exhibited a higher conversion levels than the reference catalyst, a commercial Nafion® silica composite (SAC-13) purchased from Aldrich. After the reaction, E1$_{333}$ and E3$_{333}$ catalysts were filtered off, dried at 333 K and reused in test. In this second test only a slight decrease in conversion was detected (26 *vs.* 29% at 180 min).
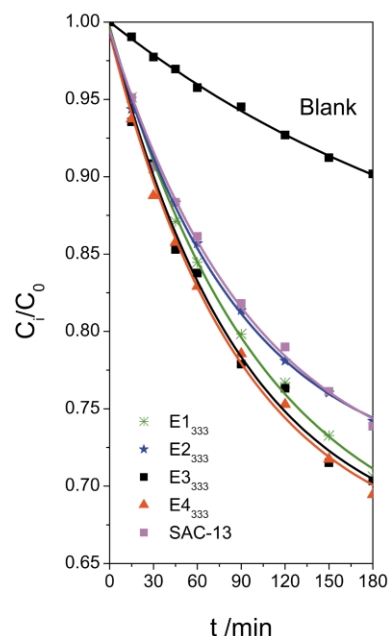

Fig. 1 Esterification of acetic acid with methanol in the absence of catalytst and with catalysts E1$_{333}$, E2$_{333}$, E3$_{333}$ and E4$_{333}$ at 333 K with an initial molar ratio of 1 : 1 of the reactants. A commercial Nafion® silica composite (SAC-13) was used as a reference.

Stability tests were also performed. For this purpose: 0.2 g of sulfonic-modified material was suspended in 25 ml of methanol and magnetically stirred at 333 K for 48 h: no sulfur loss was observed.

We have thus developed a simple and effective procedure to incorporate sulfonic groups on silica *via* monolayer thiol group functionalization which quantitatively renders –SO$_3$H groups. Along the oxidation of thiol groups, some leaching of sulfur occurs, and the amount of S released depends on the hydrophobicity of the surface and the treatment temperature. The extent of oxidation increases with temperature (more effective at 333 K) and depends on the nature of the functionalization agent. The XPS technique is a much more sensitive surface technique than FT-Raman for quantifying the degree of oxidation of thiol groups. The solids exhibited strong acid sites as revealed by catalytic activity in the esterification of acetic acid by methanol.

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