Silica functionalised sulphonic acid groups: synthesis, characterization and catalytic activity in acetalization and acetylation reactions

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Abstract

A simple synthesis procedure for the immobilization of propyl thiol groups on silica is investigated using various concentrations of 3-mercapto propyl trimethoxy silane (3-MPTS) in the range of 5–40%. The thiol group functionalised silicas (SiO_2–SH) were then oxidized to Bronsted sulphonic acid silica materials (SiO_2–SO_3H) using aqueous H_2O_2 as oxidizing agent. The surface structures of the functionalized catalysts were analyzed by a series of characterization techniques like elemental analysis, FTIR, TG-DTA, Surface area measurements, XPS, ^{13}C CP MAS NMR and ^{29}Si MAS NMR. The ^{13}C CP MAS NMR analyses confirm that disulphide species are not formed under the present preparation condition of catalysts. The acidity of the synthesized catalysts were further confirmed by the temperature programmed desorption of ammonia. The catalytic activity of the sulphonic acid functionalized silicas was evaluated in the liquid phase acetalization of ethyl acetoacetate with ethylene glycol and in the acetylation of anisole with acetic anhydride. The catalysts were found to be active in the acetalization reaction, which needs mild acidic sites, while the acetylation reactions gave lower activity, probably it needs stronger acid sites. A 30 wt.% –SO_3H loaded silica (SiO_2–SO_3H30) was recycled two times in the acetalization of ethyl acetoacetate and no major change in the conversion of EAA and selectivity to fructone is seen, which further argue against the possibility of leaching of the anchored sulphur containing species during reactions.
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1. Introduction

The increasing demand for safe industrial processes requires the development and implementation of eco friendly solid benign catalysts for value added acid catalyzed reactions. The catalysts used earlier for these reactions are the homogeneous, hazardous and corrosive acids like HF, H_2SO_4 which are well known for corrosion, trouble some workup procedure and for the excessive waste stream production. Heterogeneous strong acid catalysts such as the perfluorinated ion exchange polymers and Nafion had shown high acidity to promote many acid catalyzed reactions due to the presence of electron withdrawing perfluro alkyl groups which activates the acidity of the sulfonic groups and enhances its activity in acid catalyzed reactions [1]. But the low surface area of these beads (Nafion NR 50-S.A.; $0.02 m^2/g$) compels the requirement of large amount of catalyst and longer reaction times.

Many heterogeneous catalysts are less active than the homogeneous catalysts because the reaction rates are limited by the transport of the reactant to the active sites on the particle surfaces. The utility of heterogeneous catalysts can be improved by using high surface area materials since the transport of the reactants to the active site on particle surface can be enhanced by this method. Mesoporous silicas functionalised with sulfonic acid groups have been obtained by the condensation of alkoxy silanes and 3-mercapto propyl trimethoxy silanes, which are further oxidized to obtain their corresponding propyl sulfonic acid groups [2,3]. Diaz et al. [4] had recently reported [SO_3H]-MCM-41 mesoporous catalyst, which was prepared by the oxidation of the thiol ending groups and the performance of the catalyst was tested in the esterification of glycerol. Even though the mesoporous materials offered high surface area and large pore sizes, the aforementioned transport phenomena problems, instability, the partial oxidation of thiol groups and formation of unwanted disulphide species focused our attention to the use of an amorphous silica support for the functionalization of sulphonic acid using a modified preparation procedure.

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Synthetic inorganic substrates containing simple or complex molecular groups bonded on their surface are finding increasing application especially in the field of catalysis and separation science. Among a large number of inorganic oxides present, silica gel is found to be thermally stable, have high surface area, good accessibility of reactive centers and also fulfills the anchoring of organic chain containing different functional groups with ease [5,6]. Furthermore, the reactivity of the trialkoxy silyl groups of the silylating agents towards the free silanol groups of silica surface leads to the successful incorporation of different functional groups. The use of environmentally demanding oxidation processes like H_2O_2 further helps in the oxidation of thiol groups on the support to the corresponding sulfonic acid groups [7]. This method had found numerous applications in acid catalyzed reactions since pure Brönsted acid sites can be selectively created through this procedure.

In this work, we had synthesized a series of alkyl sulfonic acid functionalised silicas, by the immobilization of propyl thiol groups and their selective oxidation using aqueous H_2O_2 as the oxidizing agent. The theoretical sulphur loadings are maintained in the range of 5–40 wt.% in order to see the extent of partial oxidation, formation of disulphides, acidity and on the conversion of the substrates. The nature of sulphur species formed using this procedure was investigated by a series of complementary characterisation techniques and it is found that the formation of unwanted sulphur species is lower. The influence of catalysts properties and the acidity of the surface anchored sulphonic acid groups are seen in the acetalization of ethyl acetoacetate and acetylation reaction of anisole.

2. Experimental

2.1. Synthesis procedure

Silica gel having a high surface area of $444 \, m^2 \, g^{-1}$ was used for the incorporation of 3-mercaptopropyl trimethoxy silane (3-MPTS, Sigma). Functionalisation of 3-MPTS is done with slight modification as reported with other silylating agents like the chloro and amino propyl silanes on silica support [8]. Prior to functionalisation, the silica gel was activated by heating for 10 h at 150 °C under nitrogen atmosphere and was used immediately.

In a typical synthesis procedure, 3 g of silica gel suspended in 25 g of dry toluene was refluxed and magnetically stirred for 1 h, under nitrogen atmosphere. To this suspension, required amount of 3-MPTS in the range of 5–40 wt.% was added drop wise using a syringe. To ensure a complete covalent anchoring of the precursor over silica, the mixture was kept at reflux conditions for 48 h. The solid material obtained was then allowed to stand for few hours. Finally, the material was filtered, washed with toluene and ethanol and dried at 80 °C for 2 h. Relatively long oxidation times (12–24 h) and a six fold excess of H_2O_2 are recommended to avoid the disulphide contamination and to achieve the selective oxidation of mercapto groups into sulphonic acids [3]. Hence the oxidation of the mercapto propyl groups anchored on the silica surface to the corresponding sulphonic acids was carried out by treating 2 g of the sample with 20 ml of H_2O_2 (30 wt.%) for 12 h under nitrogen atmosphere (Scheme 1). In order to confirm that all the sulphonic groups are protonated, the solid material was further acidified with $0.05 \, M \, H_2SO_4$ for 2 h. The solid material obtained was then filtered, washed with water for several times and dried in air at 80 °C for 24 h.

2.2. Characterization

Analysis of the organic material incorporated on the solid silica material was carried out by using EA1108 Elemental Analyzer (Carlo Erba Instruments). FTIR spectra of the solid samples were taken in the range of $4000–400 \, cm^{-1}$ on a Shimadzu FTIR 8201 instrument by diffuse reflectance scanning disc technique. The specific surface area, total pore volume and average pore diameter were measured by N_2 adsorption–desorption method using NOVA 1200 instrument
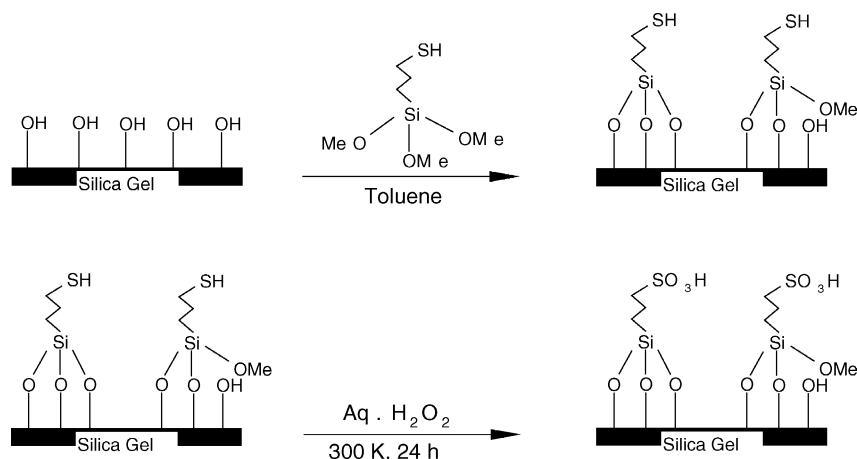
Scheme 1.

(Quanta chrome). The samples were activated at 180 °C for 3 h under vacuum and then the adsorption–desorption was conducted by passing nitrogen into the sample, which was kept under liquid nitrogen. Pore size distribution (PSD) was obtained by applying the BJH pore analysis applied to the desorption of the nitrogen adsorption–desorption isotherm. TG-DTA and DTG analysis of the catalysts were carried out on a Mettler Toledo 851 using an alumina pan under air (80 ml/min) atmosphere from ambient to 1000 °C with a heating rate of 10 °C/min. XPS measurements were performed on a VG Microtech ESCA 3000 instrument. The general scan and the core level spectra of S 2p were recorded with non-monochromatized Mg K radiation at a pass energy of 50 eV and an electro take off angle of 60°. The solid state NMR spectra were recorded on a Bruker MSL 300 NMR spectrometer with resonance frequencies of 75.5 and 59.6 MHz for ^{13}C and ^{29}Si, respectively. Temperature programmed desorption of ammonia was carried out on a Micromeritics Autochem 2910 catalyst characterization system, equipped with a TCD detector. Fresh, dried samples were pretreated by passing high purity He for 2 h. After cooling to ambient temperature, the He atmosphere is replaced by 5% NH_3/He mixture and the catalyst samples were heated in this atmosphere to 300 °C. The flow rate of NH_3/He mixture was kept at 20 ml/min and 0.04 g of the catalyst was used throughout the experiments.

2.3. Catalytic experiments

2.3.1. Acetalization reaction

Ethyl acetoacetate (EAA, 12 mmol) was added to a solution of ethylene glycol (EG, 12 mmol) in toluene (20 ml) containing 0.2 g of catalyst (pre-activated at 100 °C for 2 h). The reaction mixture was magnetically stirred at 100 °C in a silicone oil bath (Scheme 2). Samples of the reaction mixture were taken periodically and analyzed by a gas-chromatograph (HP 6890) equipped with a flame ionization detector (FID) and a capillary column (5 μm thick cross-linked methyl silicone gum, 0.2 m × 50 m). Further, the products were identified by GC–MS (Shimadzu 2000 A) and confirmed by ^{1}H and ^{13}C NMR spectra (Bruker AC-200). The catalysts were filtered from the reaction mixture and recycled two times to confirm its heterogeneity and the organic phase was separated for the NMR analysis.

2.3.2. Acetylation of anisole

The acetylation reaction was carried out in liquid phase using 0.5 g of catalyst (previously activated in air at 100 °C)
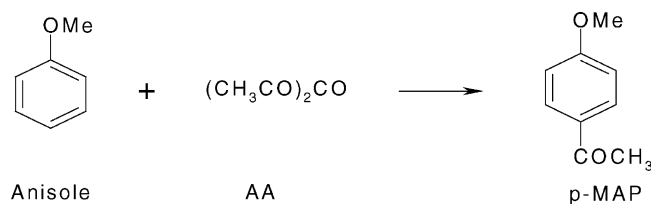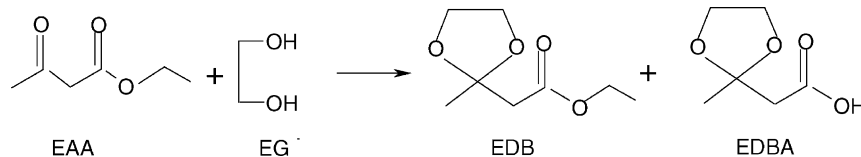
Scheme 3. .

and an equimolar mixture of anisole and acetic anhydride (AA). (Scheme 3). Product samples were taken at regular time intervals and analyzed by a gas chromatograph using the above procedure and further confirmed through GC–MS.

3. Results and discussion

3.1. Elemental analysis

A range of propyl thiol groups (5–40 wt.%) was incorporated into the silica surface in order to get the maximum loading of sulphonic acid groups and to monitor the formation of any disulphide or partially oxidized species. The extent of the incorporation of the thiol groups on silica surface were determined by the elemental analysis and it is found that the sulphur loading gets increased linearly with the 3-MPTS loading. The amount of sulphur loading was found to be lower than that of the theoretical amount used for the functionalisation. The extent of 3-MPTS incorporation determined after the recovery of the solid materials indeed had shown that the efficiency of sulphur loading is >80% for higher thiol loaded samples and >90% for the lower propyl thiol incorporated catalysts (Table 1). The C:S ratio of the functionalised materials is found to be greater than three instead of the theoretical value of three for the propyl thiol fragments which shows that some unhydrolysed methoxy species are present on the anchored catalysts. The transformation of thiol groups to the sulphonic acid groups was carried out by using aqueous H_2O_2 as the oxidizing agent. An interesting observation as reported with other porous silica catalysts is that the oxidation processes with H_2O_2 is usually accompanied by sulphur losses and the amount of sulphur present is always less than the theoretical values. The loss of sulphur becomes more pronounced for the higher amount of thiol functionalised catalysts, which may be due to the solubilisation of the surface anchored thiol groups during the oxidizing conditions [9]. These results further points to the fact that during preparation procedure some hydrophobic

Scheme 2.

Table 1
Physico-chemical properties of silica anchored sulphur catalysts

Catalysts	Loading of 3-MPTS (wt.%)[a]		Sulphur (%) after 3-MPTS oxidation	BET surface area ($m^2 g^{-1}$)[b]	NH_3-TPD	
	Input	Output			T_{max} (K)	NH_3 chemisorbed at 100 °C (mmol/g)[c]
SiO_2–SO_3H5[d]	5	4.8	95.6	384	452.5	0.348
SiO_2–SO_3H10	10	9.1	92.8	379	453.5	0.430
SiO_2–SO_3H20	20	17.8	88.3	374	480	0.812
SiO_2–SO_3H30	30	25.5	85.6	368	481.3	0.844
SiO_2–SO_3H40	40	32.1	81.2	362	482.5	0.902

[a] 3-MPTS: 3-mercapto propyl trimethoxy silane.
[b] Measured by the nitrogen adsorption–desorption at 77 K.
[c] Total acid sites determined by TPD analysis using NH_3 as adsorption–desorption agent.
[d] Numbers denote the wt.% of 3-MPTS loaded on SiO_2.

sites are needed, which can prevent loss of sulphur due to the excess role of water on the anchored surface species.

3.2. Infrared spectroscopy

The infrared spectra of silica gel, SiO_2–SH5, SiO_2–SH40, SiO_2–SO_3H5 and SiO_2–SO_3H40 are shown in Fig. 1. The spectra of pure silica show peaks in the range of 3600–3200 cm^{-1} attributed to the hydroxyl stretching of the hydrogen bonded internal silanol groups. The bands at 1200, 1100 and 800 cm^{-1} are the characteristic bands of SiO_2 assigned to the Si–O stretching vibrations while the bands at 950 and 470 cm^{-1} are assigned to the bending vibrations of the surface silanols and Si–O, respectively [10]. The propyl groups attached to the silicon framework are identified by the methylene stretching bands in the 2950–2850 cm^{-1} region that corroborates the attachment of
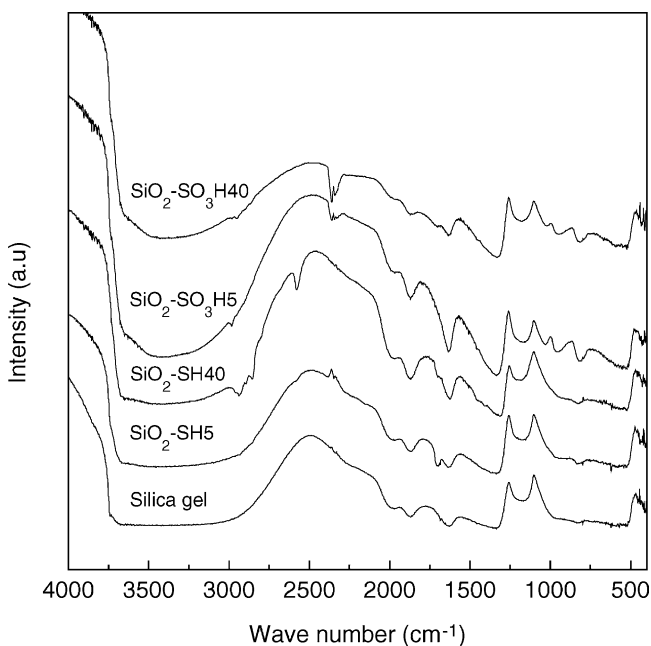

Fig. 1. Infra red spectrum of Silica gel, SiO_2–SH5, SiO_2–SH40, SiO_2–SO_3H5 and SiO_2–SO_3H40.

organic moiety into the silica surface. Their deformations bands are not characterized due to the strong absorption of silica in the 1460–1410 cm^{-1} regions but as the loading of 3-MPTS is increased these bands become visible to some extent. The weak band at 1430 cm^{-1} would be related to the methylene group adjacent to the thiol group, while the band at 1450 cm^{-1} can be assigned to the methylene symmetric bending mode vibration as seen in alkanes [11]. The spectra do not clearly say any unhydrolysed methoxy groups since the methyl symmetric and asymmetric bending modes of methoxy species are also in the overlapping region of silica. The band for the thiol stretching vibrations are clearly seen at 2575 cm^{-1} and its intensity is found to gets increased with the increase in percentage of 3-MPTS loading. Disappearance of this band after treatment with H_2O_2 could be taken as for the complete oxidation of the thiol groups and new IR bands are found to develop at 1350 cm^{-1}, which is assigned for the asymmetric stretching band of the SO_2 moieties and thus confirms the formation of sulphonic acid species [12].

3.3. Thermal analysis

The thermal analysis curves of silica gel, SiO_2–SH30 and SiO_2–SO_3H30 are depicted in Fig. 2. The DTG spectrum of pure silica gel shows a sharp weight loss below 100 °C when heated under airflow, which corresponds to the loss of physisorbed water. On the contrary, the TG/DTG spectrum of SiO_2–SH30 shows two steps of weight loss, one below 100 °C and the other in the region of 340–380 °C. As mentioned, the former weight loss may be due to the desorption of water, but the percentage of water loss is very less compared to pure silica gel and the second weight loss is attributed to the loss of organo sulphur fragments. The DTA results further confirms the above fact that a strong exothermic peak is observed around 360 °C due to the decomposition of the 3-mercapto propyl groups on the silica surface. The DTG curve of the oxidized sample, SiO_2–SO_3H30 also shows the presence of low temperature peak already observed in the pure silica gel and an intensive doublet at 480 and at 540 °C corresponds to the decomposition of the
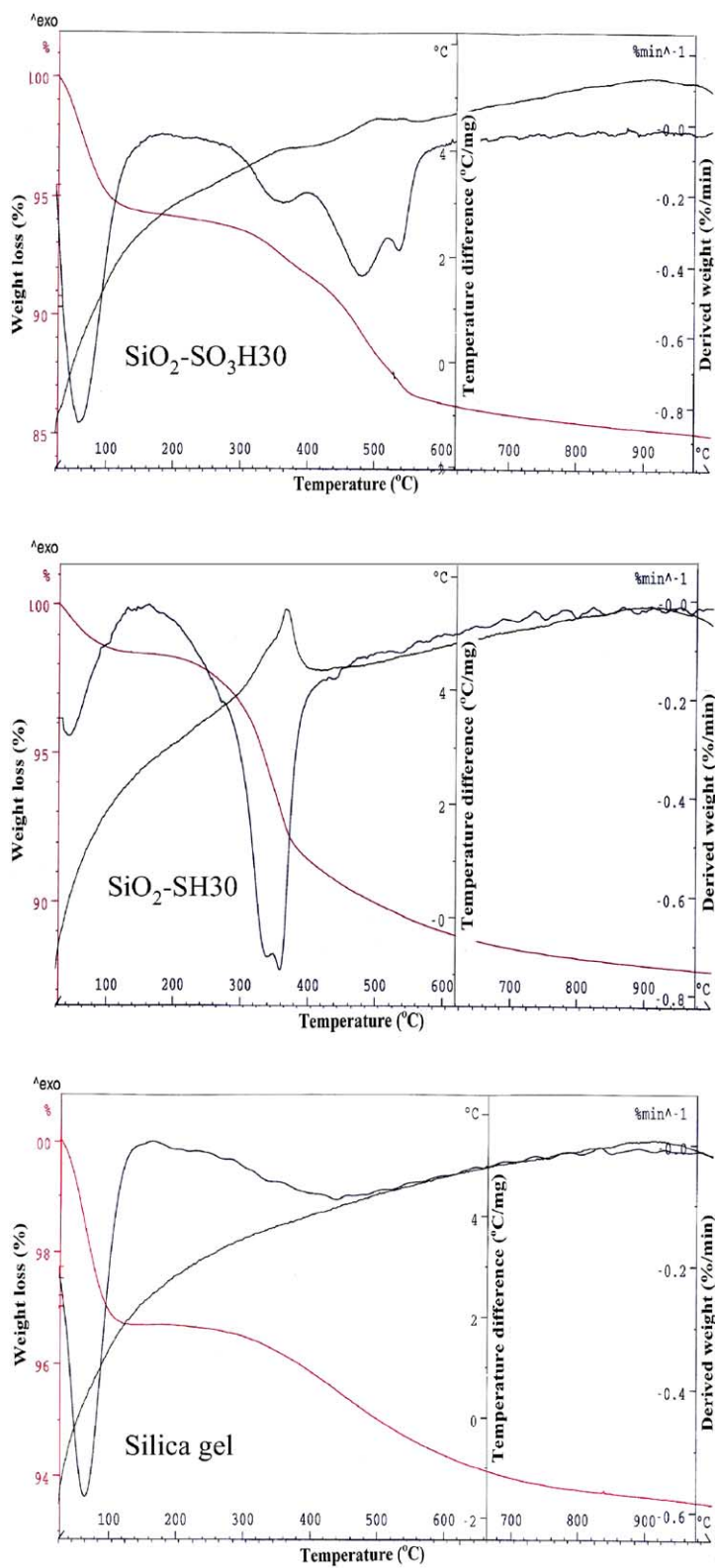
Fig. 2. Thermo gravimetric analysis (TG, DTG, DTA) of Silica gel, SiO_2–SH30 and SiO_2–SO_3H30.

organic bearing fragments and the sulphonic acid groups [13]. Furthermore, from the spectrum of SiO$_2$–SO$_3$H30, it is clear that a small amount of the thiol fragment can be seen at 360 °C, which reveals a partial oxidation of the thiol groups to the sulphonic groups at higher loadings, which necessitates a prolonged time for the oxidation and/or an excess of the oxidizing agent. The higher percent of weight loss observed after 100 °C for the thiol and sulphonic acid groups reveals the extent and nature of the organic species anchored on the silica support and hence the catalytic reactions are done in low temperature regions in order to avoid the sulphur loss at reaction conditions and thus to prevent the possibility of leaching.

3.4. Nitrogen adsorption–desorption studies

It is well known that incorporation of homogeneous catalysts or metals on porous supports shows a decreasing trend in the surface area with the percent of loading [14,15]. The silica support shows a high surface area of 444 m^2 g^{-1} and with the percent of sulphonic acid loading the surface area gets decreased gradually (Table 1). 40 wt.% sulphonic acid loaded catalyst (SiO$_2$–SO$_3$H40) had shown a surface area decrease of 82 m^2 g^{-1} compared to the silica support. The decrease in surface area with the percent of loading further confirms a higher ordering of the sulphonic acid groups inside the pores of the support and consequently an increase in number of the sulphonic species. The surface area, pore volume and pore diameter of 5 and 30 wt.% sulphur loaded catalysts are found to be 384 m^2 g^{-1}, 0.26 cm^3 g^{-1}, 44 Å and 368 m^2 g^{-1}, 0.189 cm^3 g^{-1}, 40 Å, respectively. The adsorption desorption isotherms of silica gel, SiO$_2$–SO$_3$H5 and SiO$_2$–SO$_3$H30 catalysts were of the type IV according to the IUPAC classification (Fig. 3).

3.5. XPS analysis

The surface incorporated sulphur species of the present catalysts are further verified by XPS measurements. The possibility of formation of different sulphur species over 30 wt.% catalyst before and after oxidation (SiO$_2$–SH30, SiO$_2$–SO$_3$H30) was checked. For the catalyst having a 30 wt.% loading of 3-MPTS, the S 2p core level shows a peak around 162.6 eV which is the binding energy region of the thiol species (Fig. 4). The presence of disulphide species is not distinguishable by this technique, since the binding energy of the disulphide species lies around the binding region of the thiol group (>1 eV) and hence can be overlapped. After oxidation of the thiol groups into sulphonic acids, the S 2p core level spectra shifted from 162.8 to 168.5 eV, which shows a high oxidation state of the sulphur species in the form of sulphonic acid moiety [16]. Thus, the presence of thiol and sulphonic acid groups is apparent but necessitates the need of different characterization techniques to identify the disulphide species.
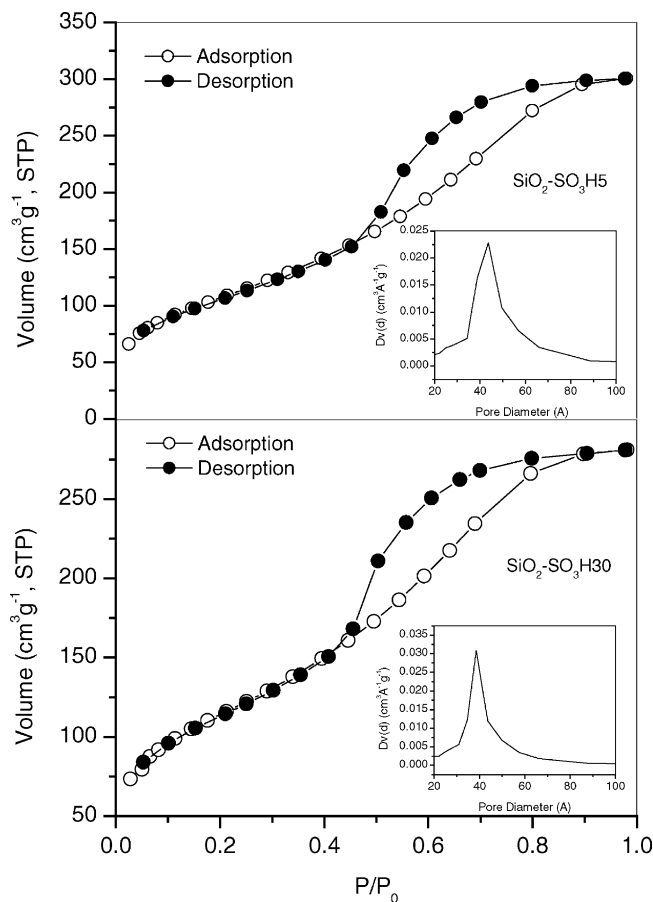
Fig. 3. Nitrogen adsorption–desorption analysis of SiO$_2$–SO$_3$H5 and SiO$_2$–SO$_3$H30.

3.6. Solid state ^{13}C CP MAS NMR analysis

The chemical nature of the organic moieties anchored on the silica surface is further exploited by NMR techniques. The ^{13}C CP MAS NMR spectrum shows several resonances
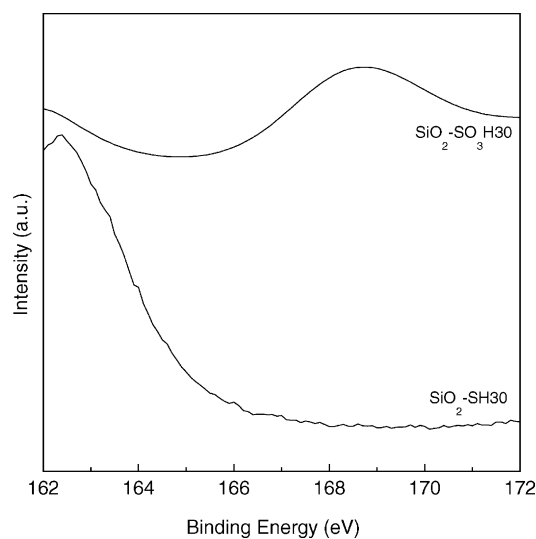
Fig. 4. XPS spectrum of SiO$_2$–SH30 and SiO$_2$–SO$_3$H30.
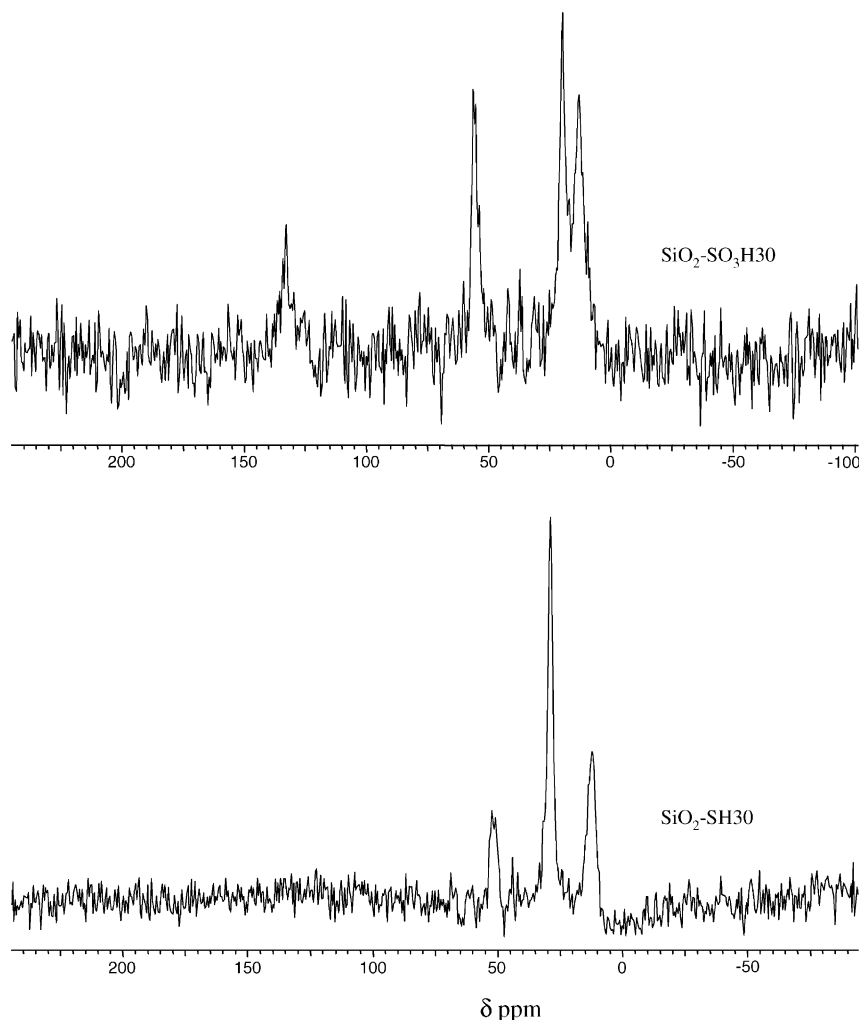
Fig. 5. ^{13}C CPMAS NMR spectrum of SiO_2–SH30 and SiO_2–SO_3H30.

that can be assigned to the different types of organic moieties present in the sample before and after oxidation. Before oxidation, the peak obtained at 29 ppm can be accounted for the carbon atom (C^1) adjacent to the thiol moiety and to the central (C^2) carbon atom while the carbon atom (C^3) bonded to the silicon had shown a somewhat broad band at 12.33 ppm (Fig. 5). Since no peaks are formed at 13 ppm, formation of dipropyl disulphide species by the interaction between two adjacent thiol moieties or to a more oxidized sulphur species is neglected [17]. The overlap between C^1 and C^2 carbon atoms can be seen even in a 30 wt.% of 3-MPTS loaded catalyst, which is in contrary to a conformational effect reported for the separation of these two peaks at higher loadings [18]. Upon oxidation, the resonances obtained earlier for the C^1, C^2 and C^3 carbon gets changed. The signal obtained at 29 ppm assigned to the C^1 carbon atom gets disappeared and a new peak appeared at 20.04 ppm for the central carbon atom and the C^3 carbon atom gets shifted to a higher value of 13.26 ppm. After oxidation no peaks are detected at 41 ppm and at 23 ppm, which shows that disul-

phide species are not formed under the present preparation conditions [19]. The peaks obtained at 52 ppm can be accounted for the presence of unhydrolysed methoxy species present in the 3-MPTS moieties as interpreted from the elemental analysis.

3.7. Solid state ^{29}Si MAS NMR studies

^{29}Si MAS NMR spectrum had also taken for finding the nature of anchoring of the precursor, 3-MPTS, with the silica support. The spectrum of the silica gel had shown a signal at -110.08 ppm assigned to the Q^4 (SiO_4) silicon atoms and another signal at -101.11 ppm assigned to the Q^3 (O_3Si–OH) species (Fig. 6). The spectrum of sulphur bearing species shows additional signals at -56.02 ppm and at -47.11 ppm, assigned to the presence of isolated and terminal organic groups bonded to the silica surface, respectively [8,19]. These results further confirm the successful incorporation of the organo functional groups in the framework of the silica gel.
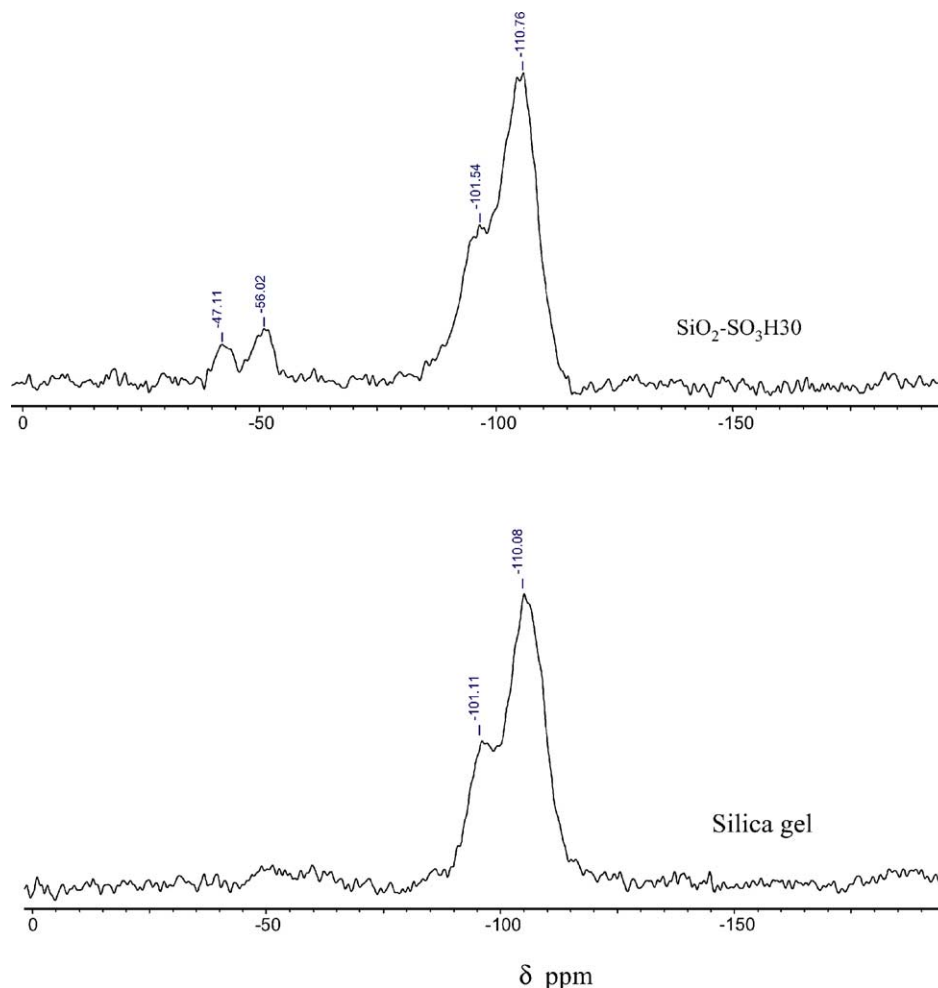
Fig. 6. ^{29}Si MAS NMR spectrum of Silica gel and SiO$_2$–SO$_3$H30.

3.8. Temperature programmed desorption of ammonia

The acidity of the sulphonic bound catalysts was checked by the temperature programmed desorption analysis using ammonia as the adsorbate (NH$_3$-TPD). Fig. 7 shows the NH$_3$-TPD curve obtained for the various amounts of –SO$_3$H loaded samples and silica gel. The NH$_3$ concentration and the T_{max} are found to get increased with the increase in the percentage of –SO$_3$H loading, which points to an increase in the number and strength of the acid sites.

4. Catalytic studies

4.1. Acetalization of ethyl acetoacetate

The results of the acetalization of ethylacetoacetate (EAA) with ethylene glycol (EG) to fructone (EDB) show that the sulphonic acid functionalised catalysts are very active and selective in the formation of fructone. The conversion of EAA over the sulphonic acid catalysts is found

to increase with the increase in reaction time and reaches 73.5, 81.3, 82.4, 84.3, and 81.9 wt.% over SiO$_2$–SO$_3$H5, SiO$_2$–SO$_3$H10, SiO$_2$–SO$_3$H20, SiO$_2$–SO$_3$H30 and SiO$_2$–SO$_3$H40, respectively, after 2 h of the run. The selectivity for fructone is found to be >90% in all cases (Fig. 8). The formation of the hydrolysis product, 3, 3, ethylene dioxy butanoic acid (EDBA) was very low under the present experimental conditions, which further confirms that the hydrolysis of ethyl aceto acetate and the trans acetalization reactions are not predominant. The observed activity can be explained in two-folds: the catalysts were porous to promote the activity and sufficiently acidic for the protonation of the hemiacetal intermediate product and also for the stabilization of the cationic intermediate formed during the reaction. Since pure Brönsted acidic sites are increased with the percentage of loading of sulphonic groups, the conversion of EAA is also increased but selectivity to fructone decreases at longer reaction times, which may be due to the hydrolysis of fructone to its corresponding acid. The silica gel is completely inactive under the present reaction conditions but with a 5 wt.% loading of the –SO$_3$H groups, the conversion
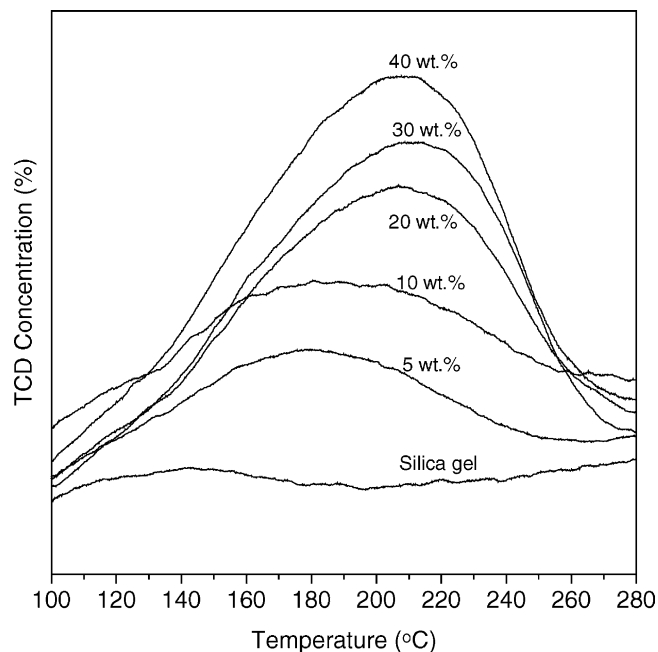
Fig. 7. TCD curves of Silica gel and different amounts of acid loading over silica gel.

is found to get increased which confirms that mild acid sites can promote the reaction to a suitable extent. The reusability of the sulphonic acid anchored catalysts is investigated two times in order to see its stability and heterogeneity and found that the decrease in conversion is lower after
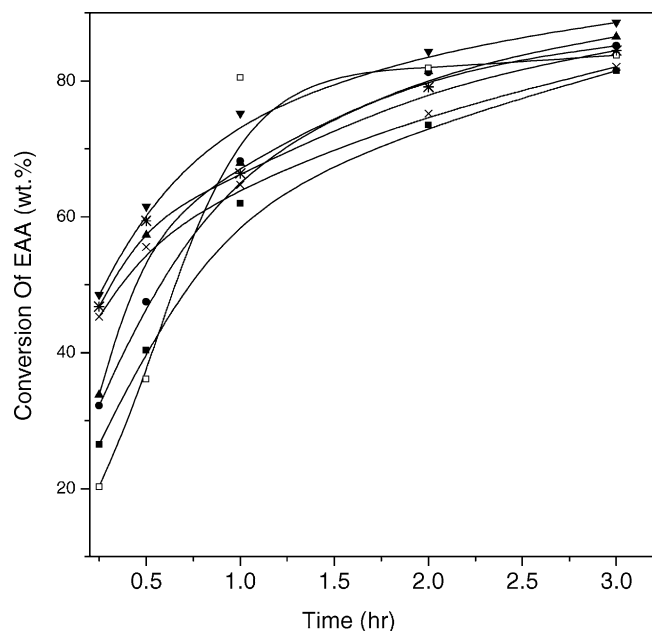
each cycle which strongly argue against the contribution of leached sulphonic acid groups to the catalytic activity.

4.2. Acetylation of anisole

The acetylation of anisole with acetic anhydride (AA) was carried out in liquid phase at 100 °C using an equimolar mixture of anisole and acetic anhydride. In order to deny the formation of corrosive HCl, acetic anhydride was opted as the acylating agent instead of acetyl chloride. In all the sulphonic acid functionalised catalysts, the selectivity for p-methoxy acetophenone was 100%, and the conversion of acetic anhydride was found to increase with an increase in the sulphonic acid groups and reaction time (Fig. 9). The conversion of AA obtained after 12 h was found to be 2.1, 4.3, 4.6 and 4.9 wt.% for SiO_2–SO_3H10, SiO_2–SO_3H20, SiO_2–SO_3H30 and SiO_2–SO_3H40 catalysts, respectively. Catalytic data show that a maximum conversion of 15 wt.% was obtained over 40 wt.% sulphonic acid containing catalyst (SiO_2–SO_3H40) after 48 h. Literature shows that anisole rich reactant mixture helps in better performance for the zeolite catalysts [20] and the deactivation of zeolite catalyst is claimed due to the strong adsorption of the p-methoxy acetophenone, one of the main products obtained in this reaction, on the acid sites of the zeolites. Elemental analysis of the present catalyst after reaction shows an increase in carbon percentage and hence it is assumed that the reaction products are anchoring on the acidic sites in the pore channel of the porous silica and thereby hindering its further catalytic activity.
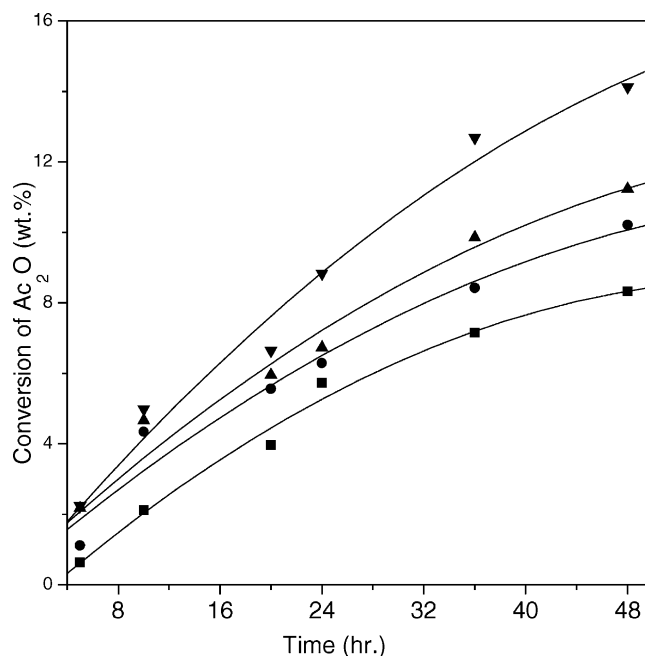

Fig. 8. Influence of reaction time on the acetalization of ethyl acetoacetate with ethylene glycol (■) SiO_2–SO_3H5 (●) SiO_2–SO_3H10 (▲) SiO_2–SO_3H20 (▼) SiO_2–SO_3H30 (△) SiO_2–SO_3H40 (✳) SiO_2–SO_3H30 (first recycle) (×) SiO_2–SO_3H30 (second recycle). Reaction conditions—EAA: 1.3 g (10 mmol); EG: 0.69 g (10 mmol); reaction temperature: 100 °C; solvent: toluene (20 ml); catalyst amount: 0.2 g.

Fig. 9. Influence of reaction time on the acetylation reaction of anisole with acetic anhydride. (■) SiO_2–SO_3H10; (●) SiO_2–SO_3H20; (▲) SiO_2–SO_3H30; (▼) SiO_2–SO_3H40. Reaction conditions—anisole: 5 g, Ac_2O: 4.72 g; reaction temperature: 100 °C; molar ratio of Anisole/Ac_2O: 1; catalyst amount: 0.5 g.

5. Conclusions

In conclusion, silica gel is successfully functionalised using various amounts of 3-mercapto propyl trimethoxy silane (3-MPTS) and then the mercapto groups were oxidized into sulphonic acid groups using aqueous H_2O_2 as oxidizing agent. The functionalised materials characterized by various physico-chemical techniques shows that disulphide species are not formed under the present preparation conditions. The acidity of the catalysts evaluated by the temperature programmed desorption of ammonia is found to increase with the increase in the loading of 3-MPTS. The catalysts were found to be active in the acetalization reaction, probably it needs mild acid sites, whereas acetylation of anisole gave lower conversion of acetic anhydride.

Acknowledgements

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