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Study by TG–MS of the oxidation of SH-MCM-41 to SO₃H-MCM-41

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Abstract

Functionalised SH-MCM-41 materials have been prepared *via* grafting and co-condensation. A detailed thermogravimetric–mass spectrometry (TG–MS) study of SH-MCM-41 and the correspondent acid form SO₃H-MCM-41 materials has been carried out. The influence of the oxidation procedure in the final sulphur species is described. It has been demonstrated that the use of concentrated H_2O_2 optimises the oxidation process and minimises the formation of intermediate species not active in acid catalysed reactions.
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1. Introduction

Since the recent discovery of the named ordered mesoporous materials (OMM) [1,2], they have been subject to numerous investigations. Their applications as catalysts or catalysts supports have been one of the fields most widely studied [3,4]. One of the limitations for their application as acid catalysts is the low acidity that the aluminium-containing materials usually present. For this reason, different methods to enhance their acidity have been developed, specially their functionalisation with different reactive groups precursors of acid centres such as sulfonic acid (–SO₃H) [5–8]. Functionalised SO₃H-MCM-41 materials have been described lately as interesting catalysts in different acid catalysed reactions, such as the esterification of glycerol with fatty acids [9–13]. The improved catalytic performance of these materials as compared with zeolites has been attributed to their larger pore size and increased hydrophobicity, inherent to the presence of the alkyl chain belonging to the organo-sulfonic group anchored on the surface. The success of this mesoporous-type of catalysts in obtaining high yield of glycerol monoesters is based upon both their chemical properties and porosity.

There are two main synthesis routes described in the literature to obtain functionalised mesoporous materials (Fig. 1). First, grafting or post-synthesis functionalisation with alkoxysilanes (3-mercaptopropyltrimethoxysilane, MPTS, is this case) onto a previously calcined or extracted pure silica MCM-41 [14]. Second, through a direct co-condensation reaction of different organosilanes, in the presence of a surfactant solution [12]. The latter method has the advantages of getting the functionalised material in just one step, incorporates higher amount of functional groups and those are distributed homogeneously in the surface of the final solid. The sulfonic form of these functionalised mesoporous materials is usually obtained through the oxidation of the precursor SH-MCM-41. This latter method of synthesis has been used very recently to prepare sulfonic acid functionalised materials with different sulphur contents active in esterification and condensation reactions [8].

The oxidation of thiol to sulfonic groups in these materials has been described by using different oxidising agents such us nitric acid or hydrogen peroxide [5,6,10]. The nature and number of the final acid groups depend on the agent used and it is closely related to the catalytic performance of the material. An incomplete oxidation of the thiol groups can produce sulphur species partially oxidised [9] which are not active in the acid catalysed reactions. So, a better knowledge of the oxidation process should be useful in order to optimise this process. In this sense, different thermal analysis techniques can help to understand this process.

In spite of the numerous studies focused on ordered mesoporous materials (OMM) published during the last decade, very few of them present detailed works on their thermal behaviour by using Thermal Techniques, and most of them are related to as-synthesised materials and not to

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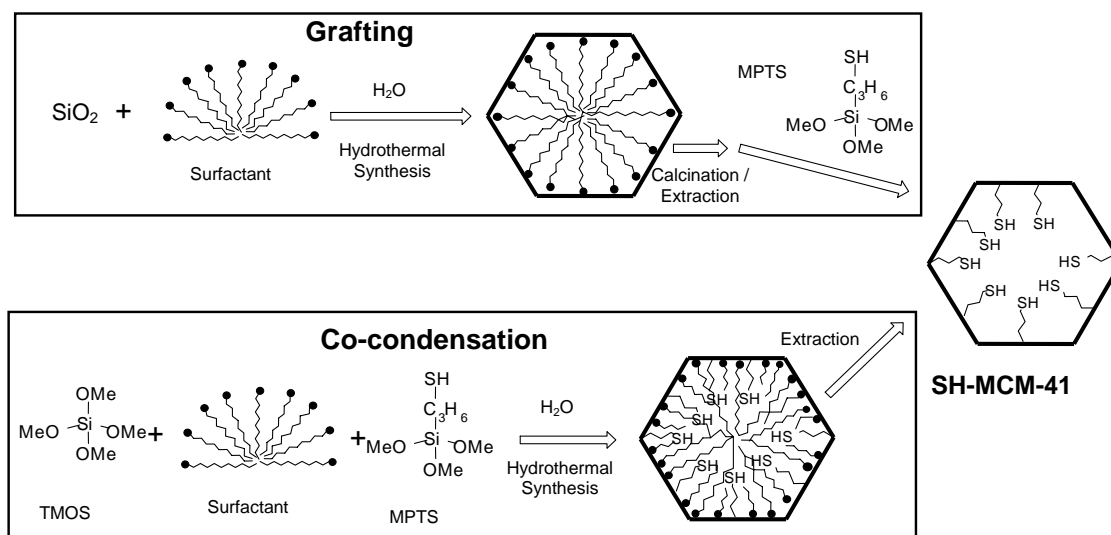*URL:* http://www.icp.csic.es/gtm.

Fig. 1. Scheme of the two synthesis methods used in this work.

the functionalised ones. TG–DTA has been used to compare the influence of the surfactant calcination versus extraction processes on the properties of the Al-MCM-41 materials obtained [15]. NH$_3$-TPD and pyridine adsorption-desorption at different temperatures followed by IR-spectroscopy, have been used to characterise the acidity of Al-MCM-41 materials [16].

Up to date, the thermogravimetric–mass spectrometry (TG–MS) technique, combined with in situ XRD, has been only used to study the surfactant decomposition and oxidation processes that take place during the calcination of as-synthesised aluminium, titanium and zirconium MCM-41 samples [17]. By analysing in the mass spectrometer the fragments obtained, the authors conclude that the decomposition of the surfactant involves three steps in the case of Al-MCM-41 and only one for the transition metal based materials.

By using this latter technique, TG–MS, we have analysed in this paper the oxidation of SH-MCM-41 materials (obtained either by grafting or co-condensation) to obtain the corresponding acid form SO$_3$H-MCM-41. The aim of this paper is to perform a detailed TG–MS study of different samples in order to determine which of the different oxidation processes proposed in the literature is more adequate to obtain the best catalyst. This work will demonstrate that the use of concentrated H$_2$O$_2$ optimises the oxidation process and minimises the formation of intermediate species not active in acid catalysed reactions.

2. Experimental

2.1. Synthesis of the materials

Siliceous MCM-41 was synthesised following the procedure described in the literature [18]. 1.5 g of the as-made

solid is treated with 225 ml of a mixture 10:1 of EtOH:HCl (35 wt.%) at 70 °C for 3 h three times to extract the surfactant, then filtered, washed and dried 40 °C for 24 h. The grafting procedure was carried out by reaction of extracted MCM-41 (1 g) and MPTS (5 meq.) in 10 ml of toluene under reflux and N$_2$ atmosphere [14] (sample SH-MCM-41-G). The co-condensation synthesis was carried out as follows [12]. A mixture of MPTS and tetramethoxysilane (TMOS) is added to an homogeneous solution of hexadecyltrimethylammonium bromide (CTAB) in H$_2$O:MeOH under continuous stirring. Finally, tetramethylammonium hydroxide (TMAOH, 25 wt.% in water) is added drop by drop. The resulting gel is maintained under continuous stirring until complete methanol evaporation (ca. 16 h) and introduced in Teflon-lined stainless steel autoclaves which were heated at 95 °C for 24 h. Following this procedure, gels with the initial composition: 0.71TMOS:0.29MPTS: 0.12CTAB:0.27TMAOH:18.8MeOH:77.7H$_2$O were prepared. The recovered white solid was filtered off, washed and dried at 40 °C overnight. The surfactant is then removed as it was described above (sample SH-MCM-41-C).

All the reactants were supplied by Aldrich and used without previous purification.

2.2. Oxidation of the materials

The SH-MCM-41 samples were oxidised according to different methods described in the literature [5,6,10] (Fig. 2). *Method A*—the sample is contacted with nitric acid (60 wt.%; solid/liquid ratio of 1/5, w/v) at room temperature and stirred during 8 h. The solid is then filtered, washed with water, ethanol and ether and dried at room temperature for 8 h (samples G–A and C–A). *Method B*—this method consists in a modification of the previous one. In this case, the solid is first wetted with a diluted solution of HNO$_3$ (20 wt.%) and then treated as in the previous method (sam-
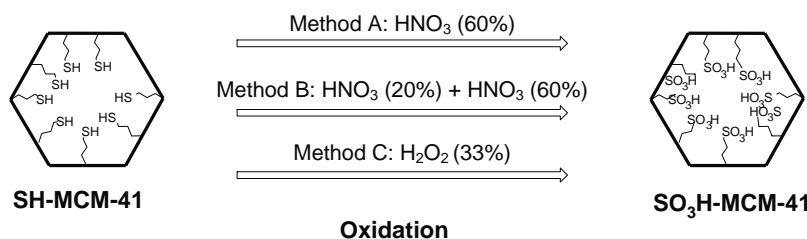
Fig. 2. Scheme of the oxidation methods utilised.

ples G–B and C–B). *Method C*—the sample is contacted with a solution of hydrogen peroxide (33 wt.%; solid/liquid ratio of 1/10, w/v) at room temperature and stirred for 24 h. The solid is then filtered, washed with water and ethanol, and treated with a 1.0N solution of H_2SO_4 (1/40, w/v) during 30 min and then filtered again, washed abundantly with water and dried at 60 °C during 12 h (sample C–C).

In all the cases, the concentration of sulfonic acid in the solid product was determined by base titration.

2.3. Characterisation and TG–MS studies

The SH-MCM-41 precursors were characterised by XRD, TEM, N_2 adsorption and chemical analyses and the results have been reported elsewhere [12]. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA7 from 30 to 900 °C with a heating rate of 10 °C min^{-1} under airflow. On-line TG–MS analyses of the gases evolved from the sample were carried out on the Perkin-Elmer TGA 7 thermobalance coupled to a Fisons MD-800 quadrupolar mass spectrometer through a transfer line heated at 150 °C. The TGA was operated from 30 to 900 °C at 20 °C min^{-1} under a continuous flow of He (100 cm^3 min^{-1}). A Perkin-Elmer transfer line, specially designed to avoid mass discrimination and connected to a vacuum pump in order to optimise the amount of gas sample transferred from the TG to the MS, carries on the evolved gas to the mass spectrometer. The ionisation of the sample was done by electronic impact −70 eV and a mass analysis is performed each 2 s recording mass fragments between 2 and 300 atomic mass units (amu).

3. Results and discussion

3.1. Differences between the methods of synthesis

Acidity measurements (by base titration) and the data obtained from thermogravimetric analyses of the different samples are listed in Table 1.

A noticeable difference in the acidity values (meq.$_{H+}$ g$_{SiO_2}^{-1}$) can be observed between the oxidised samples prepared by grafting (samples G–) or by co-condensation (samples C–). The samples obtained by using co-condensation method present more than twice number of acid centres than the ones prepared *via* grafting, which predicts a better performance as acid catalysts.

Anyhow, the different amount of the sulfonic groups in the oxidised samples C– and G– can be correlated with the organic content in the precursor thiol form. SH-MCM-41-G sample, prepared by grafting, presents a total weight loss of ∼14.5% ($T < 900$ °C), while in the sample prepared by co-condensation (SH-MCM-41-C) this total weight loss is twice higher (∼26.5%). From these data, it can be deduced that the number of propylthiol groups anchored to the mesoporous walls, and suitable to be oxidised to –SO$_3$H, are much higher in the latter case. Recently, it has been described a correlation between the amount of sulphur in the synthesis gel and in the final materials synthesised by the co-condensation method which confirms these results [8].

After oxidation of the samples, it can be observed that the total weight loss in the samples prepared by co-condensation increase from 26.5 up to 33.5–35.8%, depending on the oxidation method. This can be attributed initially to the in-

Table 1
Thermogravimetric analyses of the different materials (thiol and sulfonic samples)

Sample	Acidity[a] (meq.$_{H+}$ g$_{SiO_2}^{-1}$)	Weight losses (%)			Total
		I ($T < 250$ °C)	II (250–425 °C)	III ($T > 425$ °C)	
SH-MCM-41-G					14.5
G–A	0.52	2.1	3.7	7.9	14.7
G–B	0.40	0.2	2.6	5.2	8.0
SH-MCM-41-C					25.6
C–A	2.02	6.3	12.7	16.8	35.8
C–B	2.05	6.8	8.9	18.1	33.8
C–C	2.22	2.9	9.9	21.8	34.6

Oxidation methods: (A) HNO$_3$ (60%); (B) HNO$_3$ (20%) + HNO$_3$ (60%); (C) H$_2$O$_2$.
[a] Acidity measured by base titration.
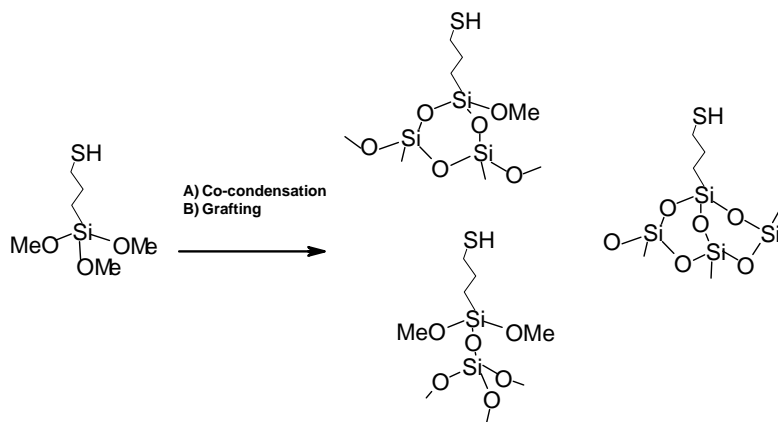
Fig. 3. Scheme of the distinct possibilities of condensation of the MPTS precursors.

crease of the molecular weight of the –SO$_3$H groups compared with the parent –SH groups. In spite of this, it has been previously demonstrated that during the oxidation process part of the organic groups are lost [12], this effect being more pronounced in the grafted samples. As it will be discussed below, some methoxy groups of the thiol source, MPTS, remains unaltered after grafting, leading to a weaker binding of the propylthiol groups to the pore walls (Fig. 3). This can be avoided by using the co-condensation procedure, so the thermal stability of the functional groups will increase.

However, minor differences in acidity and in the thermogravimetric analyses are observed among the samples synthesised by using the same method after oxidation. All the samples present the most intense weight loss above 400 °C, while the weight loss below 250 °C, which can be attributed mainly to water physically adsorbed, is more intense in the co-condensated samples, probably because the higher amount of –SO$_3$H groups increases their hydrophobic character.

3.2. TG and TG–MS analyses

3.2.1. SH containing samples

Fig. 4 presents the TG–MS analysis of sample SH-MCM-41-C, synthesised by co-condensation. The thermogravimetric plot presents three marked weight losses. The first one, very small, centred at ∼100 °C can be assigned to adsorbed water. The second one, more intense, at ∼400 °C can be attributed mainly to the lost of the –SH molecules of the propylthiol groups, as can be confirmed by the MS analyses (below). In Table 2 are detailed the characteristic m/z values of the different species analysed. The m/z values of 47 and 34 are characteristic of R-SH (methanethiol) and SH$_2$ molecules, respectively, while mass 76 is characteristic of propanethiol. From the data of these masses, it looks like the propanethiol molecules decompose at this temperature (∼400 °C) losing the sulphur atoms. Masses 41 and 39 are present in the peak at higher temperature (∼520 °C), and can be assigned to propene, which is the decomposition product

of the organic chains attached to the siliceous walls after the thiol elimination. These organic moieties are decomposed at higher temperature.

It has been previously described in the literature the formation of condensed species with S–S bonds during the synthesis or oxidation of SH-MCM-41 materials [9]. These species can decompose during the thermal analysis as
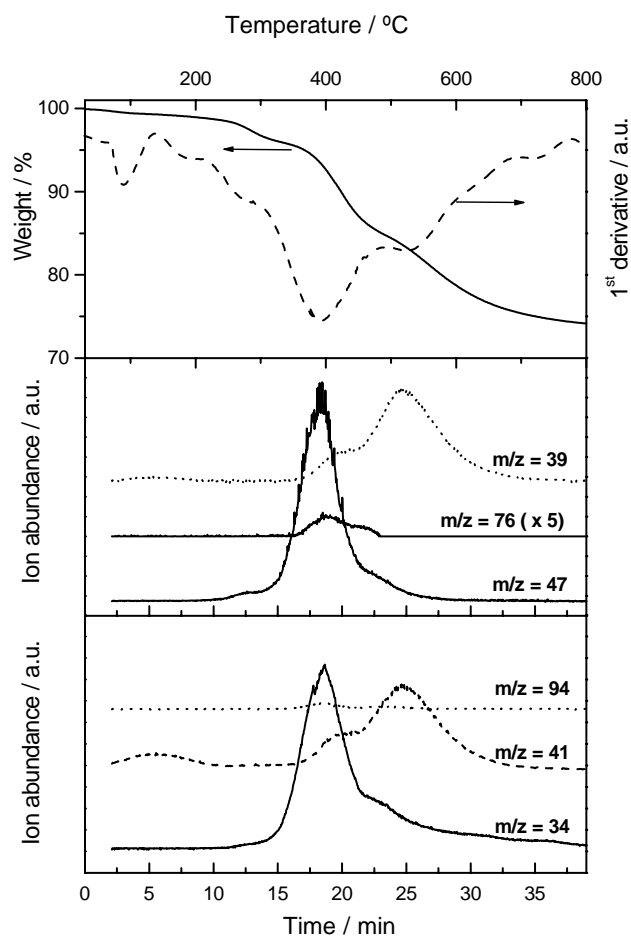

Fig. 4. TG–DTG plot and mass analyses of sample SH-MCM-41-C.

Table 2
Selected mass-ions

m/z	Assignment (fragments)
47, 48	Thiol species (methane thiol) [CH_3S; CH_4S]
76	Thiol species (propane thiol) [C_3H_8S]
34	Thiol/sulphide species (hydrogen sulphide) [SH_2]
47, 62	Sulphide species (dimethyl sulphide) [CH_3S; C_2H_6S]
94	Sulphide species (dimethyl disulphide) [$C_2H_6S_2$]
39, 41	Propene [C_3H_3; C_3H_5]
64, 48	Sulfonic groups [SO_2; SO]

dimethyl sulphide or dimethyl disulphide fragments, which characteristic mass-ions are 47 and 62 or 94, respectively (Table 2). Due to the fact that 47 m/z is also characteristic of the presence of thiol, the 94 m/z plot is used to determine the presence of these S–S condensed species. In the case of sample SH-MCM-41-C (Fig. 4) no evidence of this kind of species is observed.

3.2.2. Oxidised samples (SO_3H containing samples)

When sample SH-MCM-41-C is oxidised under mild conditions (method B) it can be observed in the TG plot (Fig. 5) the presence of three peaks in addition to the water desorption below ∼100 °C. From the combined TG–MS analysis,

it is possible to assign these peaks as following. The peak at ∼200–250 °C presents intense m/z 94, 47 and 62 (not shown) characteristic of sulphide species which allows to assign it to partially oxidised thiol groups. The second peak centred at ∼400 °C presents also a high amount of fragments with $m/z = 47$, but not 94 neither 62, which indicates the presence of –SH groups which have not been oxidised. The presence of disulphide species produced during the oxidation treatment has been already described from ^{13}C-CP-NMR measurements [9]. These authors observe a NMR signal attributed to organic moieties containing S–S bonds in samples oxidised under mild conditions, but if a more severe oxidation treatment is used, no disulphide species are observed.

The last weight loss takes place at 500–550 °C, and the most intense mass signals detected are 64 and 41, corresponding to the decomposition of the propylsulfonic groups formed during the oxidation of the thiol species (64 corresponds to SO_2 and 41 to propene). This analysis demonstrates that this mild oxidation process (method B) does not oxidise completely all the thiol groups of the parent material.

Fig. 6 presents the TG–MS analysis of sample C–C, synthesised by co-condensation and oxidised with H_2O_2
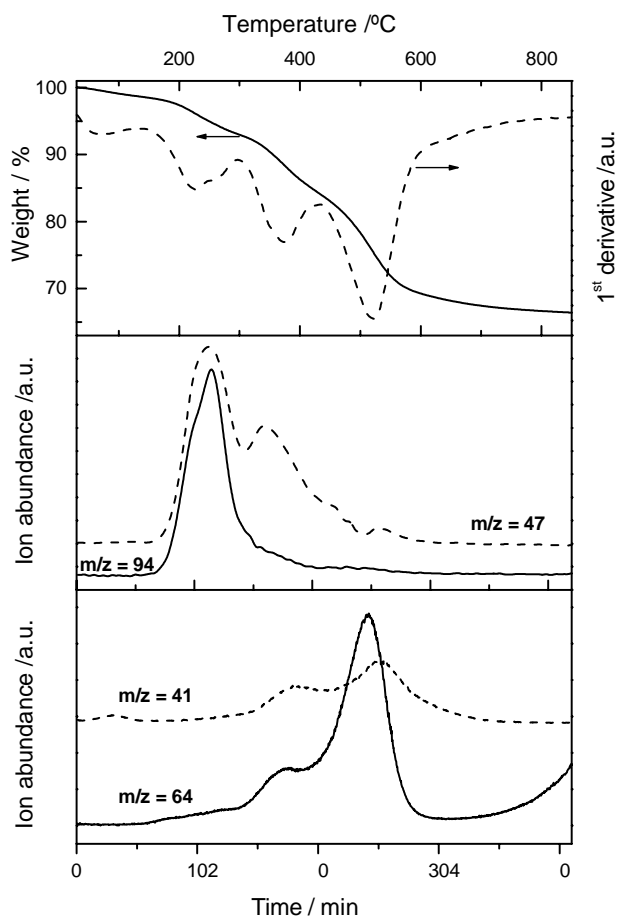

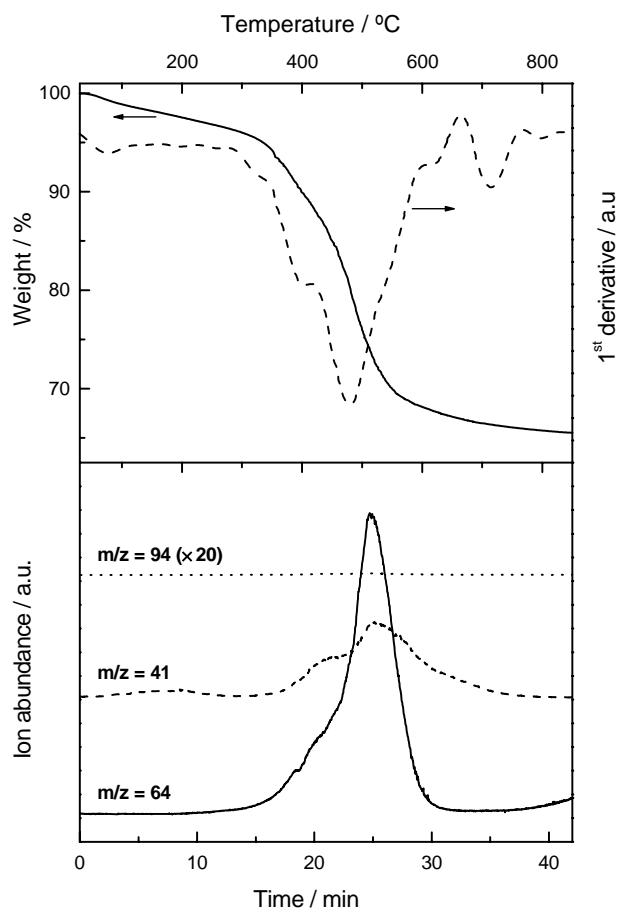Fig. 5. TG–DTG plot and mass analyses of sample C–B.

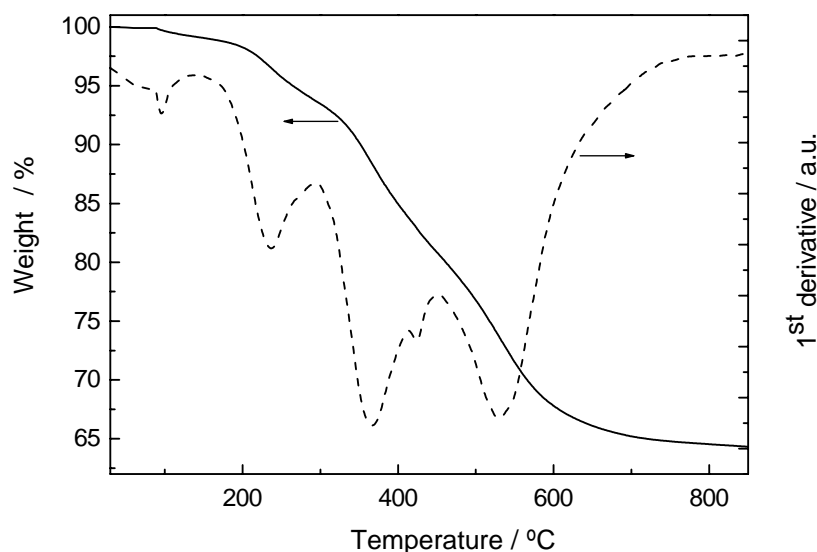Fig. 6. TG–DTG plot and mass analyses of sample C–C.

Fig. 7. TG–DTG plot of sample C–A.

(method C). It can be observed in this case the presence of an intense weight loss at 500–550 °C that can be certainly attributed to the decomposition of the propylsulfonic groups because the intensity of the m/z signals 64 (SO_2) and 41 (propene). No traces of sulphide neither thiol species can be observed, which demonstrate that this oxidation method is more adequate than the one previously described using HNO_3 under mild conditions. This observation agrees with the results published recently [8] that confirm from XPS and Raman analyses the complete oxidation of high loading thiol functionalised silica by using H_2O_2 as oxidation agent.

Fig. 7 presents the TG–DTG plots of sample C–A, synthesised by co-condensation and oxidised according to method A. In addition to the weight loss centred at ∼500–550 °C, which corresponds to the decomposition of the sulfonic groups, it can be observed the presence of two intense peaks at ∼200 and ∼380 °C assigned previously (sample C–B) to sulphide species and thiol groups not oxidised under these conditions. This demonstrate that this method, as the oxidation process B, is not convenient to transform completely all the thiol groups to the corresponding sulfonic ones in samples synthesised by the co-condensation method.

Otherwise, when the amount of thiol groups of the parent material is much lower, such as in the case of the samples prepared by grafting, a treatment with nitric acid under the more severe conditions (method A) can be sufficiently effective to oxidise completely all the thiol groups. In Fig. 8, the TG–MS analysis of sample G–A it has been plotted and it is possible to observe that neither sulphide (m/z 94) nor –SH (m/z 34, not shown) species are present, and the weight loss at ∼400 °C corresponds mainly to masses 64 and 41 attributed to SO_2 and propene from the decomposition of the propylsulfonic groups.

Fig. 9 plots the TG–DTG of sample G–B, prepared by grafting and oxidised with the softest method (method B). The intense weight loss at ∼310 °C demonstrates that not all the thiol groups have been successfully oxidised (like in sample G–A). This observation confirm that this soft oxidation method is not adequate to oxidise these materials, not even samples with such reduced number of thiol species as the prepared by grafting.
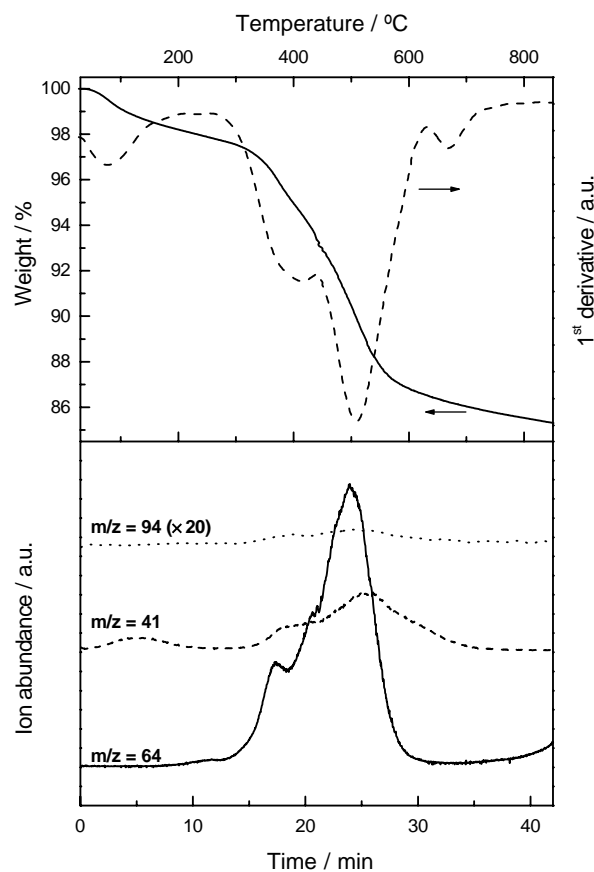

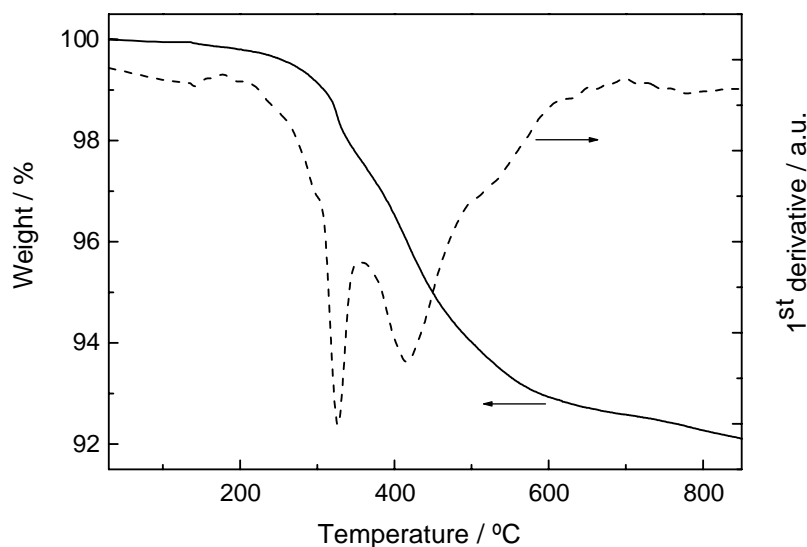Fig. 8. TG–DTG plot and mass analyses of sample G–A.

Fig. 9. TG–DTG plot of sample G–B.

It can be concluded that samples obtained by co-condensation, which posses a high number of thiol groups are only completely oxidised with the most severe treatment (method C, with H_2O_2), while samples prepared by grafting, with a significant lower amount of thiol groups can be effectively oxidised by using a milder method (method A).

4. Conclusions

According to the results reported in this paper, it can be concluded that the synthesis of SH-MCM-41 *via* co-condensation leads to higher amount of functional groups anchored to the pore walls than the grafting procedure. In addition the functional groups incorporated by co-condensation are thermally more stables than those anchored by grafting, probably due to a more efficient condensation of methoxy groups coming from the precursor, MPTS.

However, the oxidation method used to transform the –SH groups to –SO_3H, is determinant of the number of acid sites in the final catalysts. The TG–MS studies reported in this work demonstrate that in this case, the use of concentrated H_2O_2 optimises the oxidation process and minimises the formation of intermediate species not active in the acid catalysed reactions. On the other hand, sulphide species and not oxidised thiol groups are present in the samples when milder methods of oxidation are employed.

Acknowledgements

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