

Review

Sulfonic Acid-Functionalized Inorganic Materials as Efficient Catalysts in Various Applications: A Minireview

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Abstract: Acid catalysis is widely used in the chemical industry, and nowadays many efforts are being focused on replacing the more common homogeneous catalysts with heterogeneous ones in order to make greener the industrial processes. In this perspective, sulfonic solid acid materials represent a valid alternative to the homogenous mineral acid in several acid catalyzed reactions. In this minireview, an overview of the recent advances on the preparation, stability and application of these materials is reported. Special attention is addressed to the sustainability of the considered processes, starting from the catalyst's preparation, the use of green solvents and reducing the possible reaction steps. Ways to tackle the main drawback represented by easy leaching of acid groups are described. For an easy catalyst recovery, the use of a magnetic core in a catalyst particle, with the related synthetic approaches, is also illustrated. Finally, a section is dedicated to the principal characterization techniques to identify the structural properties of the catalysts.

Keywords: sulfonic acid catalysts; metal oxide support; sulfonic characterization techniques



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1. Introduction

Acid catalysis is widely used in the chemical industry due to a large variety of chemical transformations in which acids are involved. Unfortunately, the majority of plants are still based on homogenous catalysis, and although liquid mineral acids (such as H_2SO_4) perform excellent catalytic activity, they present several drawbacks. These substances are, in fact, very corrosive for the equipment and toxic for the environment, they need to be used in quite significant quantities and they are difficult to separate and recover. In order to make the industrial processes greener and more sustainable, many efforts are aimed at the use of heterogeneous catalysts as replacement of the more common homogeneous ones. In recent years, interest towards the design and production of solid acid catalysts has significantly increased. In this context, sulfonic solid acid materials represent a valid alternative to the homogenous mineral acid in several acid catalyzed reactions. They are efficient, sustainable and versatile catalysts in the achievement of different valuable chemicals. They can promote several acid catalyzed reactions such as esterification, transesterifications, acetylation, hydrolysis, alkylation, hydration and dehydration as also described in some older and recent reviews [1,2]. Moreover, they are applied in several organic reactions involved in heterocyclic chemistry catalyzing multi-component reactions (MCR) or condensation reactions [3]. Due to their versatile use, they are involved in pharmaceutical chemistry for the synthesis of new molecules as potential drugs [4], in environmental chemistry for the abatement of pollutants [5], in biomass conversion for the production of sustainable added value products or for the achievement of new eco-friendly biofuels [1,2].

Their use is indeed very favorable due to the simple separation, regeneration and recycling of the material, consequently accompanied by a decrease in processing cost. Moreover, depending on the structural characteristics of the inorganic material such as surface area and pore structure, sulfonic solid acid can provide a large number of catalytic

sites and they can drive the products' selectivity of the catalyzed organic reaction. Their main drawback, in the view of industrial application, is their weak stability during several reaction cycles that, most of the time, is strictly correlated to the leaching of the acid groups. In this minireview, an overview of the recent advances on the preparation, stability and application of these materials will be reported.

As for the supports used in the production of sulfonic solid acid catalysts, this contribution will be focused on the use of inorganic materials, including silica, titania, zirconia, alumina and their functionalization with sulfonic linkers by using different synthetic procedures.

The preparation procedures as well as the applications will be addressed with a special attention to those processes with higher sustainability. In particular, reducing the production steps, the use of green solvents, waste, energy and time saving will be considered. Moreover, a section will be dedicated to the principal characterization techniques to identify the structural properties of the catalysts.

2. Sulfonic Acid-Functionalized Materials: Synthesis and Applications

2.1. Sulfonic-Silica Based Materials

Silica (SiO_2) represents one of the most useful and versatile supports with several properties. In fact, it is a low-cost and ecofriendly material, and it is structurally stable in a large range of temperatures. Due to the presence of several OH groups on its surface area, it can be easily chemically modified by using different functionalization procedures with various linkers for the improvement of the stability and/or the chemical properties of the support [6]. Moreover, its variable porosity allows for size selectivity of the final products on the catalyzed reactions.

In the last decade of the 20th century, Van Rhijn et al. [7] proposed the covalent attachment of alkylsulfonic acid groups to the surface of MCM and HMS silica, via a stepwise approach as well as via direct co-condensation synthesis. The key precursor is 3-mercaptopropyltrimethoxysilane (MPTMS), which contains an SH group, a stable propyl spacer, and a hydrolysable $\text{Si}(\text{OMe})_3$ moiety. Hybrid mesoporous silicas were prepared either via silylation of preformed mesoporous silica (grafting method, Figure 1a), or via co-condensation (Figure 1b) of the primary building blocks. Then, the obtained functionalized silica undergoes oxidation of the thiol group to sulfonic one by using H_2O_2 .

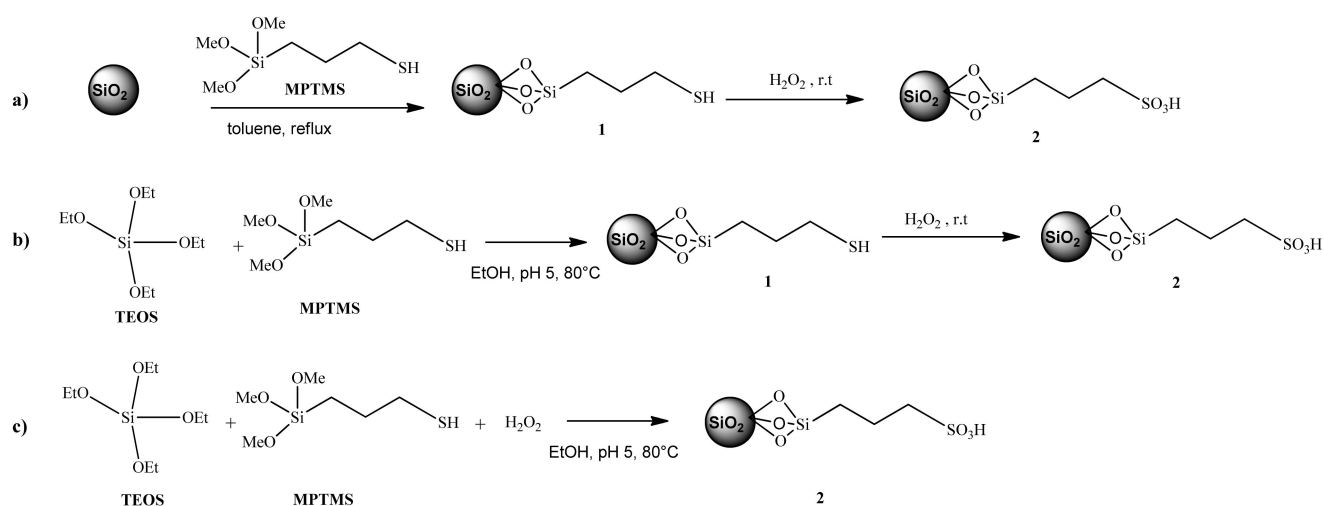


Figure 1. Synthesis of propyl sulfonic silica by three different methodologies: (a) grafting, (b) co-condensation and (c) in situ oxidation approaches.

According to the classical grafting method (Figure 1a), the sulfonic groups, representing the catalytic sites, are located essentially on the surface of inorganic material. By using this procedure, the textural properties of the oxide change, with a decrease in both surface area and pore volume. Moreover, the linkage procedure is usually carried out in

aprotic toluene, in order to avoid any water interference. As known, toluene is quite a toxic solvent so this procedure is not eco-sustainable. In order to avoid this drawback other sustainable solvents were used. Isopropanol was used for the grafting of the thiol group on the surface of mesoporous silica MCM-41 and SBA-15 [8], while absolute ethanol was employed for the synthesis of propyl sulfonic SBA-15 [9]. The resulting procedure is very efficient leading to high organic loadings when compared with the same procedure carried out in toluene. In general, the use of dry solvents is needed to prevent the hydrolysis of organics alkoxysilanes and its consequent condensation, which cause both pores blocking and an inhomogeneous functionalization of the support.

In the co-condensation method (Figure 1b), the functionalization of thiol groups occurs during the formation of the materials in the sol-gel procedure. This implies that the catalytic sites are also located in the internal surface and that the samples result in high surface area and pore volume. Moreover, the functionalization of the internal pore could have an important role in the selectivity of the catalyzed reaction. In fact, only some molecules with specific steric characteristics can enter the pores and react with the functional groups of the heterogeneous catalyst, that, in such way, instructs the performance of the reaction.

The above preparation procedure was then optimized by Melero and coworkers [1] who investigated the incorporation of thiol group in SBA-15 by co-condensation followed by *in situ* oxidation of -SH to -SO₃H in only one step. (Figure 1c) The one-pot reaction allowed production of material 2 to be greener because of a reduction in the number of steps and also because of the removal of toxic solvent such as toluene used in the grafting procedure.

A deep comparison among the three synthetic procedures for the production of propyl sulfonic acid-functionalized hybrid silicas 2 with different structures (amorphous, HMS, SBA-15) and different loading of organic moieties was studied by Testa et al. [10].

The characterization of these materials will be discussed in paragraph 3. Certainly, the *in situ* oxidation procedure yielded materials with higher surfaces area and higher acid capacities, with respect to those achieved with post-oxidation methods (grafting and co-condensation). In particular, the high surface area can be attributed to the gas evolution occurring in the *in situ* oxidation during the step of structure formation. Moreover, the oxidation procedure was more effective in inducing higher acid capacities with respect to the grafting one [10].

By using these types of approaches (grafting or co-condensation methods, oxidation or sulfonation) plenty of linkers can be introduced, allowing the design of new sulfonic heterogeneous catalysts with several features (hydrophilic, hydrophobic, zwitterionic...) chosen in relation to the reaction that these materials have to catalyze. Moreover, also the stability and the reactivity of the catalysts can be tuned by properly substituting the organic linkers [1]. The replacement of organic propyl linker with the phenyl groups allowed production of a more stable sulfonic acid catalyst towards its deactivation due to the leaching of -SO₃H group provoked by the water present in the reaction media. Lindlar et al. [11] reported the synthesis of arenesulfonic MCM-41 4 following a multistep approach. (see Figure 2) The grafting of phenyl groups to the silica surface was performed either by gas-phase or liquid-phase reaction. This latter procedure was more effective since the product contained a larger number of functional groups. Phenyl silica 3 was then acidified by a subsequent sulfonation with chlorosulfuric acid. In order to avoid the further sulfonation of free silanol groups, they were protected by capping agents such as trimethoxymethylsilane.

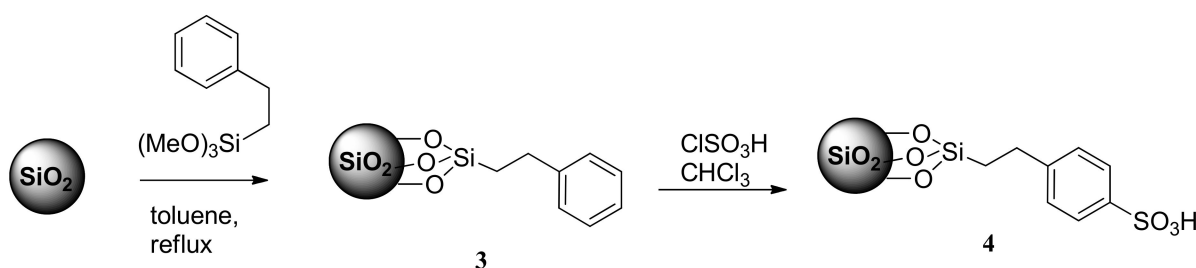


Figure 2. Synthesis of arenesulfonic MCM-41 based on Lindlar studies [11].

Following the optimized procedure for the production of the propyl sulfonic SBA-15, Melero et al. [1] investigated the one-step direct synthesis of arenesulfonic mesostructured materials through the co-condensation of the chlorosulfonyl phenyl groups, followed by the *in situ* oxidation to the corresponding sulfonic-acid groups. The catalytic benefit of arenesulfonic materials resulted in a higher stability and several recycles in different reactions in which it is used as a catalyst. Mbaraka et al. [12] applied the arenesulfonic-modified SBA-15 materials in the production of methylesters by the esterification of fatty acids with methanol. The materials showed a significantly higher activity with respect to propyl sulfonic-functionalized SBA-15 and similar activity to the homogeneous sulfuric acid.

For the synthesis of an efficient acid catalyst an important factor to take in consideration is the sulfonic loading of the silica and mesoporous materials. According to Timm et al. [13], the principal drawbacks for a correct sulfonation load that may occur are represented by the collapse or the synthesis of non-ordered structure when the co-condensation method in a template-assisted synthesis is carried out. In the case of grafting procedure, the low functionalization loading despite the use of alkoxysilane in huge excess means it is an inefficient, uneconomic and environmental unfriendly process. Taking into account these considerations, in order to optimize the sulfonation load of silica, the same authors proposed a chemical vapor deposition-type method. This grafting method proceeds under mild conditions (120 °C, 48 h), is solvent-free, and has a simple experimental setup, simply filling the silica and the silane in autoclave, giving a highly functionalized material.

Tenorio et al. [14] described the surface modification of mesoporous silica SBA-15 with thiol groups (MPTMS) by a grafting method in supercritical CO₂ (scCO₂) at temperatures above 80 °C and a pressure above 25 bars. The functionalization, considering the grafting density and surface coverage, was higher than those obtained refluxing toluene. The authors ascribed the obtained results to better transport properties of scCO₂ which allow a higher penetration and diffusion of the silane into the support pores. Moreover, by the use of scCO₂ the process can be considered sustainable and ecofriendly. In fact, as opposed to the carcinogenic toluene, scCO₂ is considered a green solvent because it is nontoxic, nonflammable and does not produce byproducts. Nowadays, most of the used CO₂ is obtained as a sub-product of many industrial processes and its use can be considered also a waste recycle.

The introduction of sulfonic group on mesoporous silica was carried out according to a microwave-assisted synthetic route that allowed for the control of the acid loading, therefore maintaining the structural order. By using this procedure, Gonzalez et al. [15] achieved the production of sulfonic SBA-15 with a faster incorporation of higher numbers of sulfonic acid groups than by conventional heating. The samples were tested in the etherification of glycerol showing higher selectivity toward di- and tri-ethers of glycerol (83–91%) than those sulfonated by conventional heating. Domingues et al. [16] studied in depth the optimization of the microwave-assisted procedure, confirming that the synthesis occurred in about 30% of the time needed with conventional heating and that it was possible to decrease the oxidation step from 24 h under a conventional heat source down to 30 min when using MW. The use of microwaves represents a green and sustainable process since it saves energy and time.

The propyl thiol groups were used as linker to extend the chain length for the synthesis of a variety of sulfonic acid catalysts.

Mercaptopropyl silica **1** was directly sulfonated by Nikman et al. [17] with a grafting procedure. (see Figure 3) The authors tested the catalytic performance of the sample **5** in several organic reactions including acetylation, amidation, silylation, mainly oriented towards the synthesis of heterocycles. The enclaved $-S-SO_3H$ was very stable allowing for the recycling of the catalyst several times without any leaching of sulfonic group and loss of activity. Following the same approach, they also produced a sulfonic catalyst **7** with an extended chain and a sulfonic group selectively linked to the final oxygen [18].

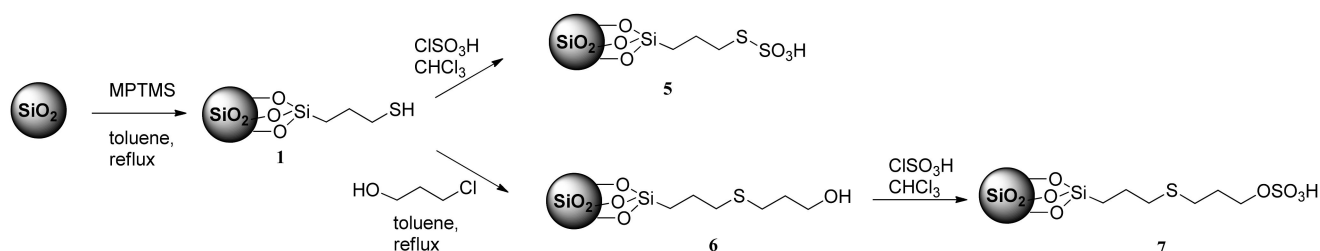


Figure 3. Synthetic approaches for catalysts in which the SO_3H group is directly linked to heteroatoms based on Nikman's group studies [17,18].

Propane- or butane-sultones were successfully used as sulfonic precursor, reacting with mercaptopropylsilane [19] (Figure 4a) and aminopropylsilica (Figure 4b) [20] respectively. Alkylsultones are in fact cyclic sulfate esters and can be used to generate sulfonic acid groups via a ring opening approach. The sulfonic catalyst produced by using sequence **a** was used in the multicomponent reactions for the synthesis of heterocycles, while the corresponding amino analogue was tested in the MW assisted Friedel–Crafts tertbutylation of hydroquinone. Both materials showed good stability during several reaction cycles without any leaching of the sulfonic groups.

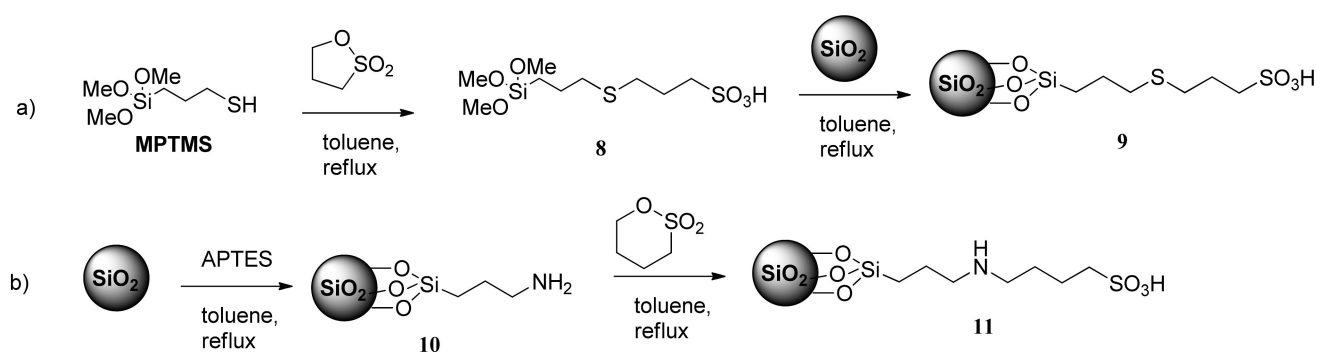


Figure 4. Use of sultones for the synthesis of long chain sulfonic materials containing S (route (a)) and NH (route (b)) based on the refs [19,20].

Butyl sultone was successfully used by Chermanhini et al. [21] in the grafting sulfonation of mesoporous KIT-5 silica and tested on the dehydration of fructose for the synthesis of 5-(hydroxymethyl)furfural (5-HMF) as a platform chemical. The fructose dehydration was carried out in DMSO as organic solvent at $135^\circ C$. Butyl sulfonic silica also showed good catalytic performance in the synthesis of 5-HMF after 5 cycles reaction. The characterization of the spent material showed how the cubic mesoporous structure was maintained, as well as the sulfonic functions.

Aminopropyl silica **10** was used for the synthesis of sulfamic acid derivatives. Jeti et al. [22] reported the preparation of silica-bonded N-propyl sulfamic acid (SBNPSA) **12** by sulfonation of the amino group from chlorosulfonic acid and tested them as catalysts in organic

heterocycles chemistry, for the synthesis of dihydropyrimidin-2-ones. Moreover, the authors studied the catalytic performance of the sulfonic materials in a green microwave-assisted one-pot condensation reaction of aldehydes, β -ketoesters, and urea in solvent-free condition. With respect to the classical reaction, the microwaves assisted procedure showed the advantages of good yields, short reaction times, and experimental simplicity [23]. Due to the simple approach to producing SBNPSA and the potential as versatile catalysts, the sulfamic material was tested in several organic reactions. In particular, Ghorbani et al. [24] studied its catalytic performance in the preparation of multisubstituted imidazoles, while Gharib et al. [25] used the catalyst in the microwave-assisted synthesis of spirooxindoles. The use of SBNPSA for the transesterification reaction of soybean oil with methanol was described by Xie et al. [26]. In addition, Niknam et al. [27] tested the catalyst on the acetylation of aromatic alcohols and amines, while Beejapur et al. [28] used SBNPSA in the glycerol acetylation. In particular, these latter authors investigated several organic frameworks containing both the sulfonic and the amino functions (materials 12–14) studying the effect of the amino group and the influence of aliphatic or aromatic chains on the sulfonic acidic active sites (see Figure 5). The amino group had a positive effect on the catalytic activity when it was directly linked to the sulfonic group due to its participation as acidic function. In fact, the sulfamic function is in equilibrium with its zwitterionic structure in which the amino group is protonated by the sulfonic acid and its acidity is enhanced by the closeness of the two groups.

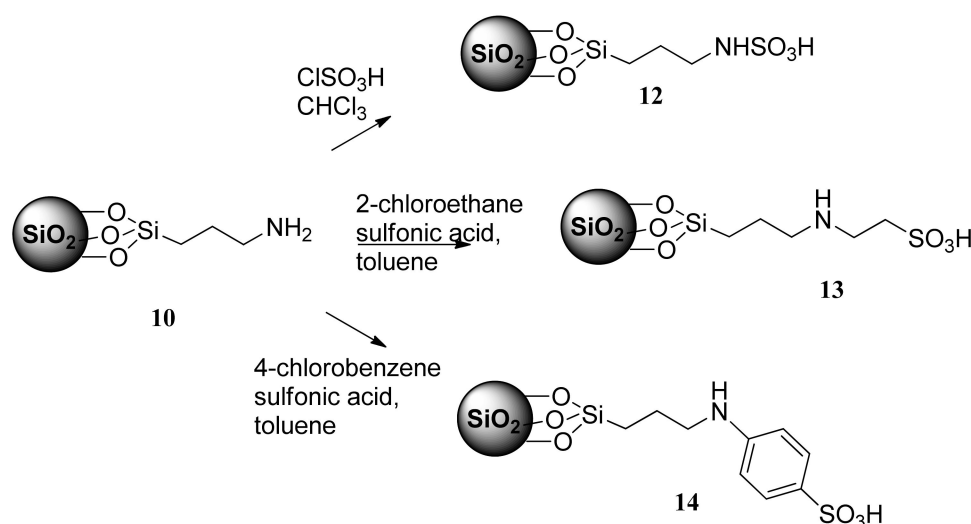


Figure 5. Different catalysts containing both the sulfonic and the amino functions synthesized by Beejapur et al. [28].

In these studies, the SBNPA catalyst confirmed its versatility towards different types of reactions and its high stability during its reuse.

Once silica is functionalized by linkers containing thiol, amine or chloro groups, several organic functions (aromatic, aliphatic, hydrophilic and/or hydrophobic) can be introduced through the reaction with these groups allowing the chain extension and, therefore, the synthesis of plenty of sulfonic catalysts with different characteristics.

In order to improve the acidity of the sulfonic catalysts, the introduction of fluorine atoms in the structure was investigated. It is well-known that the presence of electron-withdrawing fluorine atoms significantly increases the acid strength of the terminal sulfonic acid groups, which is quite comparable to that of pure sulfuric acid. Alvaro et al. [29] studied the functionalization of MCM-41 with a 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid beta-sultone to obtain sulfonic acid groups anchored to the silanol groups with perfluoroalkyl tethers 15 (Figure 6a).

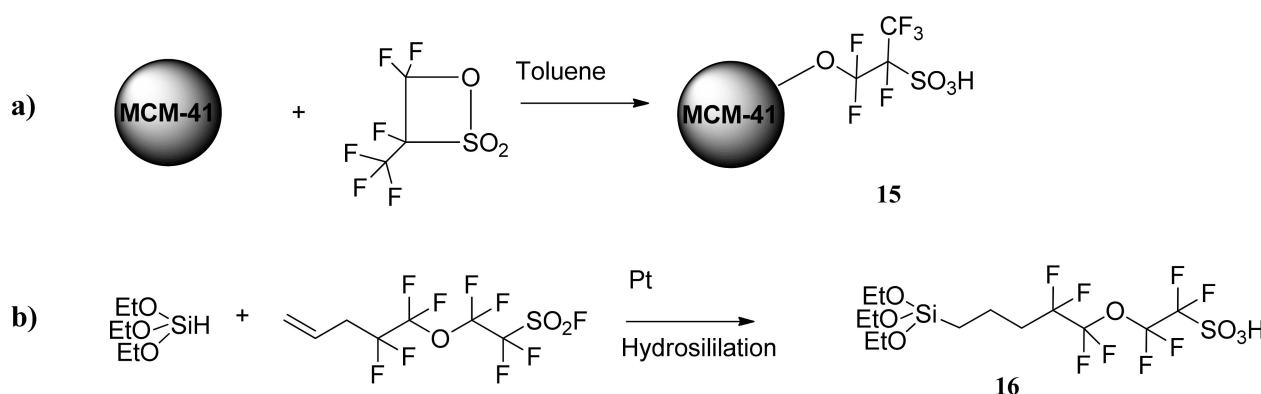


Figure 6. Fluoro derivatives sulfonic materials. (a) synthesis of sulfonic MCM-41 based on ref. [29]; (b) fluoro-based linker synthesized by Harmer et al. [30].

Moreover, a fluoro-based linker **16** was synthesized by Harmer et al. [30] and it was anchored to silica both by the co-condensation method and grafting procedure (Figure 6b). Despite the high acidity and hydrophobicity, these types of materials showed an important leaching of active groups with consequent deactivation of the catalyst.

For the improvement of the sustainability of the process, one of the most important steps is the reuse of the catalyst. Recently, magnetic nanoparticles (MNPs) have received great attention for their easy handling, for the possibility of recovery from the reaction mixture simply applying an external magnetic field and, consequently, its easy reuse [31]. In this context, Fe_3O_4 nanoparticles have attracted high interest due to their low toxicity, biocompatibility, high surface area, large-scale production with low cost, thermal and mechanical stability [31]. All these characteristics make them very suitable in catalysis and green chemistry. In spite of these advantages, bare MNPs tend to aggregate and to be easily oxidized in acidic media with the loss of their efficiency. In order to avoid these problems, the surface coating of the magnetic Fe_3O_4 nanoparticles allows not only for protection from agglomeration but also improves their dispersibility and stability. The preparation of Fe_3O_4 nanoparticles occurs by different approaches, and among them the co-precipitation procedure [32] is the most used due to its simplicity. Surface modification with silica is very common due to the versatility and the advantages (costs, eco-compatibility, easy functionalization) of this support. Different research groups have carried out the preparation of silica coated Fe_3O_4 nanoparticles [33–35] according the Stober process [36], in which silica polycondensation occurred around the MNPs under alkaline conditions in ethanol. Silica can be functionalized with several types of linkers that address the final material features during its formation by the co-condensation procedure, or in a second step by using the classical grafting method. Recently, Shaker et al. [37] reported the synthesis of propyl sulfonic silica containing a magnetic core shell (see Figure 7). The solid acid catalyst was synthesized by a synthetic approach via co-condensation of tetraethyl orthosilicate (TEOS) and 1,2-bis(triethoxysilyl)methane (BTEM) around magnetite nanoparticles, then the grafting of MPTMS on the silica, followed by the oxidation of the thiol group to the sulfonic one. The catalyst **18**, characterized in depth, was tested in the esterification of carboxylic acids with alcohols for its potential use in biodiesel production. The nanocatalyst showed good performance in term of efficiency, selectivity and above all in terms of recovery and reusability.

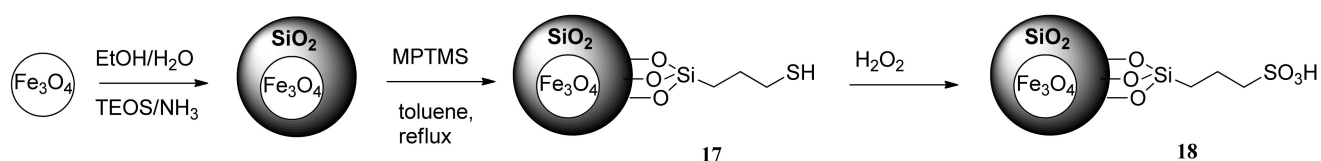


Figure 7. Production of propyl sulfonic magnetic silica based on ref [37].

Very similar approaches were used by Moradi et al. [38], Mobaraki et al. [39] and Kassaei et al. [40] as showed in the three sequences reported in Figure 8. The grafting procedure of different linkers (alkyl thiol, phenyl and amine) on the magnetic silica was followed by the sulfonation of the corresponding groups with chlorosulfonic acid allowing, respectively, the synthesis of a propyl S-sulfonic magnetic acid catalyst **19** (approach a), a sulfonic material with hydrophobic features **21** (approach b) and a sulfamidic derivative characterized by zwitterionic properties **23** (approach c). While propyl S-sulfonic magnetic acid material (approach a) was tested in the synthesis of heterocycles, the other two were investigated as catalysts in the one-pot synthesis of amino nitriles by the Strecker reaction of aldehydes and amines.

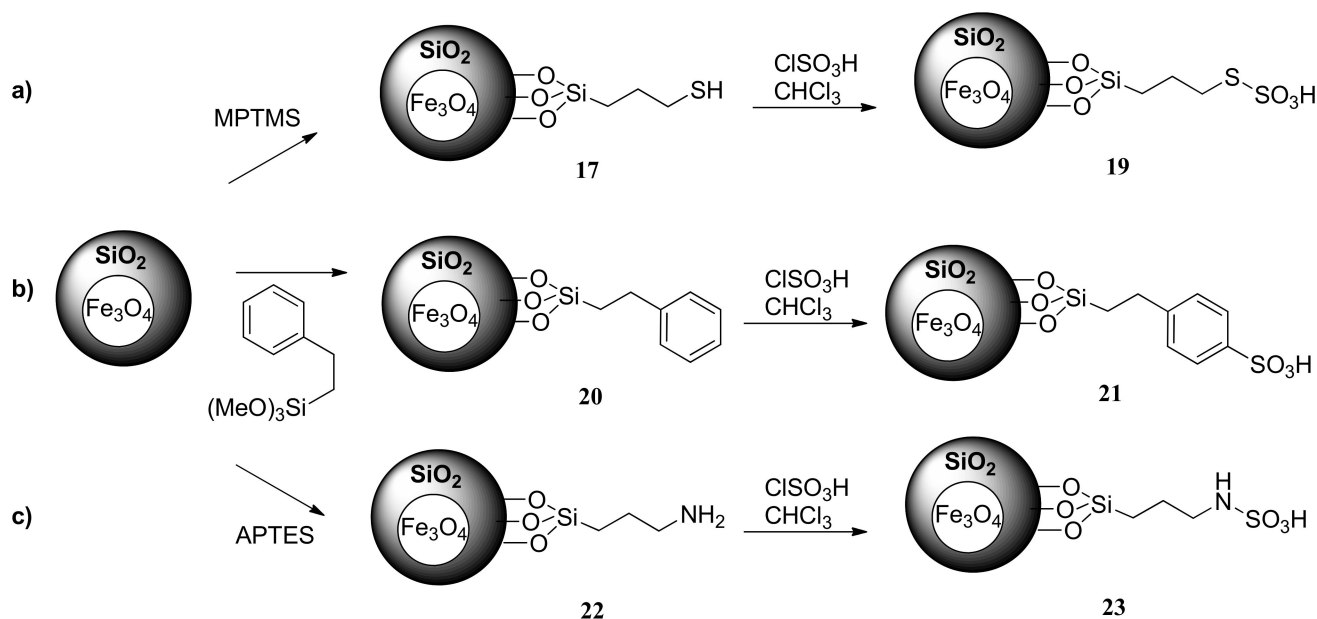


Figure 8. Sulfonic magnetic silica materials synthesized by (a) Moradi et al. [38], (b) Mobaraki et al. [39] and (c) Kassaei et al. [40], respectively.

Among the different MNPs as the core magnetic supports, cobalt ferrite nanoparticles were also chosen for use as magnetic supports due to their moderate saturation magnetization, the fact that they are inexpensive and their high chemical stability. Firstly, the use of silica-coated cobalt ferrite nanoparticles for the immobilization of different sulfonic acids was reported by Gill et al. [41]. In particular, by using the known procedures, aliphatic, aromatic and fluoride magnetic sulfonic acids were prepared, deeply characterized and tested in the acid-catalyzed deprotection reaction of benzaldehyde dimethyl acetal. These materials showed a comparable activity with respect to other commercial and homogeneous catalysts with easier recovery and reuse. The characterization of spent catalysts also confirmed the presence of the sulfonic groups, indicating a good stability of these types of catalysts. Afshari et al. [42] prepared long-chain sulfonic silica-coated cobalt ferrite nanoparticles. The immobilized sulfonic acid was tested, with good results, for the synthesis of α -aminophosphonates under solvent-free conditions at room tempera-

ture. Analogously, the material was easily recovered by simple magnetic decantation and recycled several times with no significant loss of catalytic activity.

Hereinbefore, the synthetic procedures of sulfonic organic–inorganic silica were described. However, silica can be directly and covalently sulfonated by the use of chlorosulfonic acid by a grafting procedure. The silanol groups present on the surface of silica provide a convenient anchoring point for the inorganic sulfonic acid functionality, allowing for the preparation of $\text{SiO}_2\text{-SO}_3\text{H}$. Vekariya et al. [43] applied this approach on MCM-41 following a previous study on the production of sulfonic titania (the synthesis of $\text{TiO}_2\text{SO}_3\text{H}$ is shown in the appropriate paragraph in Figure 10). The simple synthetic procedure implies the sulfonation by ClSO_3H in dichloromethane at room temperature during 30 min. In the review the authors gave an overview of the use of this catalyst in several organic reactions involved in industrial and pharmaceutical application. Optimizing the synthetic steps, Hasan et al. [44] carried out the sulfonation *in situ* procedure for the preparation of acidic mesoporous sulfonated silica from tetraethyl orthosilicate and chlorosulfuric acid without any template. The materials were studied in esterification and acetylation reactions conducted with both conventional and microwave heating. Under the microwave reaction conditions the catalysts showed high efficiency, in terms of kinetic and product yield and stability. Considering that the synthesis of materials was very simple and cost-effective, and the application involved a green heating source, that study could be considered a sustainable process.

In order to improve different silica characteristics such as stability, acidity or catalytic properties, silica support can be modified with other inorganic materials before the sulfonic functionalization. The synthetic strategies are multiple. The most common is the co-condensation of different components. For example, Hakki et al. [45] prepared an acid-modified mesoporous SiO_2 decorated with TiO_2 via co-condensation of 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane and tetraethyl orthosilicate in presence of commercial TiO_2 . The obtained bifunctional catalyst was very efficient in the one-pot photocatalytic conversion of nitroaromatic compounds into polyalkylated quinolines. The same synthetic strategy was used by Samutsri et al. [46] who produced a propyl sulfonic mesoporous silica-ZSM-5 composite catalyst for anisole alkylation. The author added different amounts of ZSM-5 powder to the P123 surfactant solution followed by the addition of TEOS and MPTMS. After hydrothermal treatment, the surfactant was removed by acid extraction in EtOH and dried in order to obtain acid-functionalized composites at different zeolite compositions, which improved both the stability and the net acidity of the material. A slightly different approach was used in the preparation of carbon-mesoporous silica composite functionalized with sulfonic acid groups [47,48]. In this case, the materials were prepared by controlled carbonization of sucrose impregnated in SBA-15 and the subsequent sulfonation by means of fuming H_2SO_4 in an autoclave. In particular, after the optimization of the sulfonation conditions, Fang [47] obtained materials with considerable amounts of Brønsted acid sites (up to $0.7 \text{ mmol H}^+ \text{g}^{-1}$) that were highly active and selective in the esterification of palmitic acid and transesterification of soybean oil with methanol. Recently, Aguado et al. [49] prepared acid-functionalized SiO_2TiO_2 composites comparing the one-pot synthesis and the grafting one. The one-pot procedure involved in the simultaneous hydrolysis of TEOS, Titanium isopropoxide and MPTMS followed by *in situ* oxidation with H_2O_2 . In the classical grafting method, the MPTMS was grafted on the presynthesized SiO_2TiO_2 , then the thiol was oxidized with H_2O_2 . The materials were tested for microwave assisted glycerol etherification. The grafting procedure resulted in a material with a better catalytic activity towards the glycerol conversion and h-GTBE selectivity with respect to the one-pot procedure. Nevertheless, the introduction of Ti into the catalyst structure did not improve the performance of the materials.

2.2. Sulfonic-Titania Based Materials

Analogously to the silica supports, titanium dioxide (TiO_2) is a versatile support due to its properties such as chemical stability, low cost, dual acid-base properties, good oxidation

rate and photocatalytic applications. Different functionalizations of the surface of TiO_2 allow for the production of materials with several applications as active catalysts or catalyst supports in diverse catalytic processes, in the field of photovoltaics [50], heterocycles chemistry [51], chemical platform or biofuels [52].

Concerning the preparation of sulfonic derived material, titanium dioxide is much less exploited with respect to the silicon dioxide, even if most of the synthetic approaches applied for the synthesis of sulfonic titania-based catalysts are very similar to those used for sulfonic silica-based materials. Silica and titania present on their surface several –OH groups that in both cases can be functionalized with different links. One of the most remarkable differences between the two oxides is represented by the surface area (SSA) of the support that can influence the catalytic performance and reaction mechanism. Generally, TiO_2 presents a very low SSA with respect to silica (about 10%). This is strictly correlated also with the functionalization loading and the acidity of sulfonic groups. The sol–gel reactions of titanium isopropoxide, by using urea as a template, can be used for the achievement of mesoporous titania materials with high surface area. Changing the reaction conditions as well as the calcination temperature, Pizzio [53] succeeded in the titania with a SSA range between 124–287 m^2/g .

Moreover, TiO_2 , when compared to SiO_2 is chemically more reactive and the titanium oxidation state of Ti(IV) may more easily reduced to Ti(III).

The classical multistep approach typical of the grafting procedure, was used by Atghia et al. [54] for the preparation of sulfonic propyl titania **25** (Figure 9a). Once the titania surface was grafted with the thiol group of MPTMS, the material **24** underwent –SH oxidation with H_2O_2 to the corresponding sulfonic derivative. The catalytic performance of $\text{TiO}_2\text{-Pr-SO}_3\text{H}$ (**25**) was investigated in the N-tert-butoxycarbonylation of amines under solvent-free conditions at room temperature. The material showed high performance in terms of efficiency (yields, reaction rate and no side reactions), stability and reuse (any loss of activity after 15 runs). Another important advantage found in the study was the high chemoselectivity towards the amine functions with respect to the alcoholic ones, which makes it a very interesting material for several organic applications.

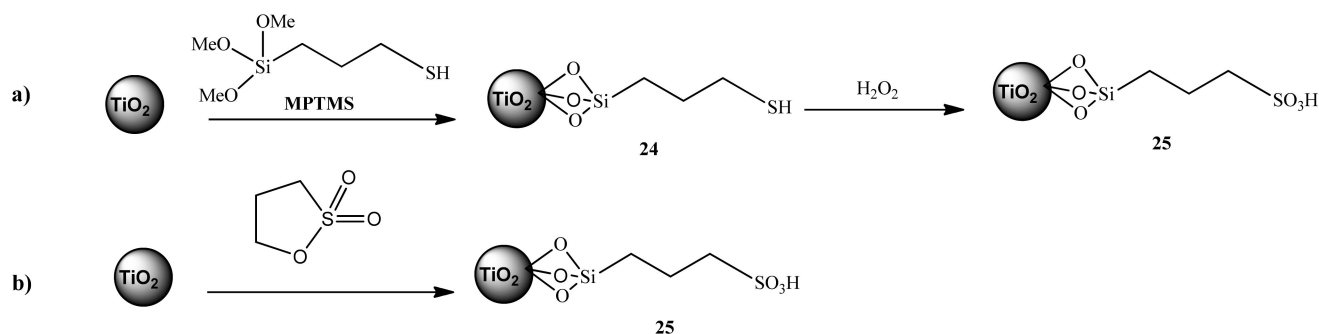


Figure 9. Grafting procedure of MPTMS (a) and 1,3-propanesultone (b) for the preparation of propyl sulfonic titania from refs [42,54] respectively.

The synthetic approach was optimized by the use of 1,3-propanesultone as a grafting linker for the achievement of $\text{TiO}_2\text{-Pr-SO}_3\text{H}$, (**25**) reducing the number of synthetic steps. The reaction was investigated by Gardy et al. [55] (Figure 9b) who tested the material on the production of the fatty acid methyl esters (FAME) via simultaneous esterification and transesterification reactions from used cooking oil during four consecutive cycles with no appreciable loss in catalytic activity.

By using the same synthetic approach, Husseini et al. [56] applied the material as an efficient catalyst in the multicomponent reaction for heterocycles synthesis. The $\text{TiO}_2\text{-Pr-SO}_3\text{H}$, (**25**) tested in very sustainable reaction conditions ($T = 100\text{ }^\circ\text{C}$, $t = 10\text{ min}$, solvent free), showed high stability and reusability for several runs with only a minor loss in its catalytic activity.

Sulfonic acid-functionalized TiO_2 was prepared by Shirini et al. [57] through the sulfonation reaction of TiO_2 using chlorosulfonic acid as the sulfating agent. (Figure 10) The material was used as an efficient and reusable solid acid catalyst for the promotion of the synthesis of biscoumarin derivatives in water showing excellent performances.

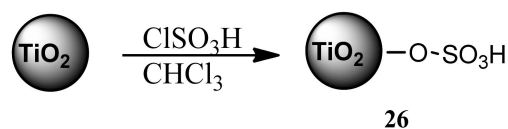


Figure 10. Sulfonic acid-functionalized TiO_2 based on Shirini et al. study [57].

Recently, $\text{TiO}_2\text{-SO}_3\text{H}$ (26) was tested in different acid catalyzed reactions from the pharmaceutical chemistry for the synthesis of thiazolidinones by the solvent-free multi-component reaction [58] to the organic reactions involved in the biomass conversion as the synthesis of levulinates [59], production of HMF [60] or glycerol etherification [49].

The synthesis of alkyl levulinates has attracted considerable attention as an alternative biosource due to their potential applications as fuel additives, green solvent and industrial chemicals. Zhou et al. [59] carried out the synthesis of sulfonic TiO_2 nanotubes, according to the approach described in Figure 10, and investigated the catalytic performance of the materials in mild conditions with good results both in terms of levulinate production and in terms of stability of the materials, without any leaching on sulfonic groups after several cycles.

Testa et al. [60] compared the catalytic performance of synthesized and commercial TiO_2 , functionalized both with a propyl sulfonic (25) (see synthetic approach Figure 9a) and a sulfonic group directly linked to the supports (26) (see synthetic approach Figure 10), on the hydrothermal dehydration of fructose to 5-HMF in water. The production of HMF, by using eco-compatible catalysts in sustainable procedure, is intensely investigated due to the use of the biomolecule as starting material of various intermediates as polymer feedstocks, chemicals and alternative fuels. During the screening of the materials, the synthesized TiO_2 directly functionalized with the sulfonic group ($\text{TiO}_2\text{-SO}_3\text{H}$) showed the best activity in terms of selectivity of furfural, and with respect to sulfonic materials used in similar conditions in the literature, such as sulfonic MCM-41 [61], $\text{HSO}_3\text{-fiber}$ [62] and metal supported catalysts [63].

The same authors investigated these materials in glycerol etherification [49], comparing the performance of titania derivatives ($\text{TiO}_2\text{-PrSO}_3\text{H}$, $\text{TiO}_2\text{-SO}_3\text{H}$) to those of the corresponding silica ones ($\text{SiO}_2\text{-PrSO}_3\text{H}$, $\text{SiO}_2\text{-SO}_3\text{H}$). In this paper it was found that the catalytic performance was influenced mainly by the surface area and the acidity, affecting both the interactions of the catalytic sites and reagents and the diffusion of reagents and products to and from the catalyst surface. For these reasons the sulfonic silica materials showed a better performance with respect to titania-based ones.

Very few examples are described in the literature on the synthesis of sulfamic titania. Tabrizian et al. [64] described the preparation of aniline-functionalized titania whose amino group was converted to a sulfamic derivative by the classical reaction with chlorosulfonic acid (Figure 11a). The material 28 used in the oxidation of sulfides and thiols with H_2O_2 exhibited high chemoselectivity and reusability.

Titania functionalized with polyamino chains containing different sulfamic groups was synthesized according to the synthetic sequence described in Figure 11b. Murugesan et al. [65] applied the sample 30 to the heterocycle chemistry for the one-pot synthesis of quinoline derivatives under solvent-free conditions with good results in terms of efficiency and stability of the catalyst.

Zolfigol et al. [66] developed the magnetic sulfamic titania 32 (Figure 11c). The synthesis of the catalyst was very simple, green and reusable due to a very easy magnetic separation. The material was tested once again in a multicomponent reaction for the prepa-

ration of heterocycles in relatively short times under solvent-free and mild conditions. All these advantages make it a very sustainable material in terms of synthesis and application.

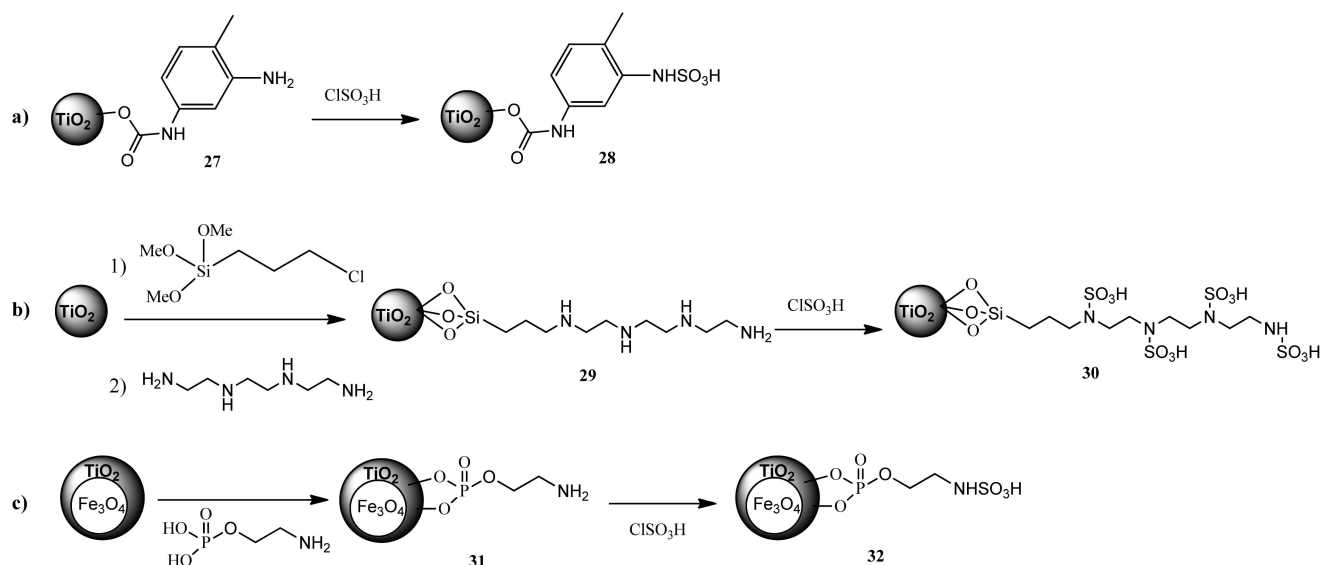


Figure 11. Sulfamic-functionalized titania-based materials: aromatic (approach (a)), aliphatic (approach (b)) and magnetic (approach (c)) derivatives from refs [63–65].

2.3. Other Sulfonic-Functionalized Metal Oxides: Zirconia (ZrO₂) and Alumina (Al₂O₃)

The synthetic approaches used for the preparation of sulfonic zirconia and alumina are very similar to those described for the most common silica and titania.

Acidic zirconia is widely used as sulfated zirconia, in which the sulfur is supported by impregnation. Sulfated zirconia is usually used as catalysts in several acid catalyzed processes for the synthesis and valorization of added value products, such as furfural [67], glycerol [68], cellulose [69] and levulinates [70]. However, these types of catalysts do not show high stability due to the weak enlace between the SO₄^{2−} anion group and the support that easily causes the leaching of functional groups. For this reason, after a few cycles these materials are often subjected to regeneration.

In order to focus the attention on more stable materials, this minireview approaches those procedures (such as grafting, co-condensation) involved in the formation of functionalized materials in which a covalent link between the functional groups and the support is formed. This should avoid sulfonic leaching with a higher performance of materials in terms of stability and activity.

Yadav et al. [71] carried out, for the first time, the functionalization of zirconia by a grafting procedure with chlorosulfonic acid as a source of a sulfonic group. (Figure 12) They compared the catalytic performance of the new catalyst **33** with that of sulfated zirconia (produced by impregnation) towards three different reactions: isomerization of n-hexane, benzylation of toluene with benzyl chloride and acetylation of tert-butylcyclohexanol. In all the acid-catalyzed reactions the performance of sulfonic zirconia was superior to sulfuric acid-treated ZrO₂ in terms of both acidity and stability. Afterwards, Yung et al. in 2013 [72], synthesized the same material with excellent catalytic activity towards the simultaneous esterification and transesterification in the production of biodiesel from rice bran oil. In this study, the authors also demonstrated the high tolerance towards both the presence of free fatty acid, and above all, water, maintaining high activity even in the presence of 40 wt% FFA and 3 wt% water. Taking into account the mild reaction conditions used (120 °C, 6 wt% catalyst), the sulfonic zirconia could be considered a potential catalyst for a one-step biodiesel production from low-grade feedstock which contains high portions of FFA and water. Amoozadeh et al. [73] applied the nanozirconia supported sulfonic acid in different multicomponent reactions under solvent-free conditions for the production of

several heterocycles. Moreover, it showed high efficiency and reusability during several cycles without any leaching of sulfonic moiety.

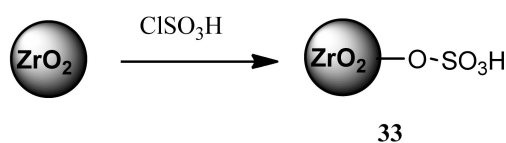


Figure 12. Sulfonic acid-functionalized ZrO₂ from ref [70].

Chidambaran et al. [74] carried out the preparation of benzylsulfonic acid-functionalized mesoporous zirconia **36** in four steps. The synthetic approach followed a series of grafting steps, and it is described in Figure 13. The sulfonic zirconia was tested in condensation reactions with the formation of diphenylmethane compounds but, unfortunately, exhibited poor stability due to the leaching of benzylsulfonic linker.

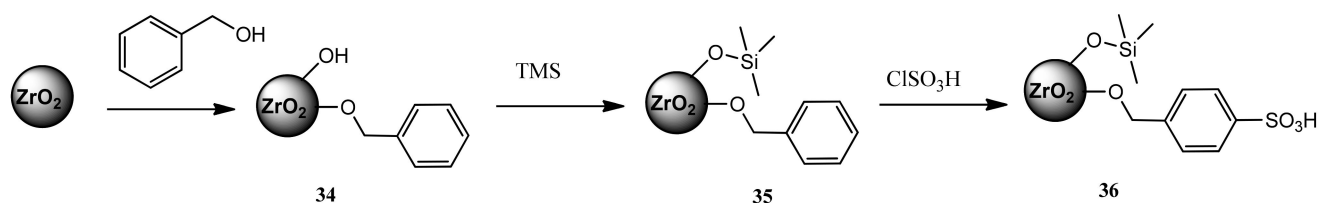


Figure 13. Benzylsulfonic acid-functionalized mesoporous ZrO₂ from ref. [74].

Sulfonic acid-functionalized nanomagnetic zirconia was synthesized, for the first time, by Tadjarodi et al. [75]. The material was prepared by the reaction of (3-mercaptopropyl) trimethoxysilane and nanomagnetic zirconia. The synthetic approach was the same used for silica showed in Figure 6, in which, after the preparation of Fe₃O₄-ZrO₂, the support was grafted with thiol groups that were oxidized to the corresponding sulfonic functions. Due to its important advantage of an easy separation, the material was tested as a new, efficient and recyclable solid acid catalyst for the protection of alcohols under solvent free conditions.

Similarly to silica and titania, alumina is also abundant, cheap with good thermal stability and has a highly specific surface area. However, with respect to the other supports, alumina contains a small amount of superficial hydroxyl groups, suitable for the functionalization by grafting or co-condensation procedures. For this reason, very few papers are present in literature on the functionalization of alumina with a sulfonic group by a covalent bond. The synthesis of nano n-propyl sulfonated Al₂O₃ was carried out by Wu [76] who used a grafting procedure with 1,3-propanesultone. The synthetic approach was analogous to that used for titania and described in Figure 9b. The material was applied in different heterocycle reactions: for the synthesis of heterocycles by a multicomponent reaction in sustainable reaction condition by using refluxing water [76]; for the synthesis of thioamides [77] or benzothiazines [78].

Recently, Solis [79] carried out the functionalization of different alumina (commercial and sol-gel lab-made) with both thiol and sulfonic groups by the grafting method. The synthetic approach for the bifunctional catalyst implied first the incorporation of the mercaptopropyl group, and second, functionalization by using sultone as sulfonic source. (Figure 14) The presence of both functions was designed for producing 5-hydroxymethylfurfural from fructose. In particular, due to its acidity, the sulfonic function catalyzed the reaction while the thiol group acted as promoter of fructose conversion.

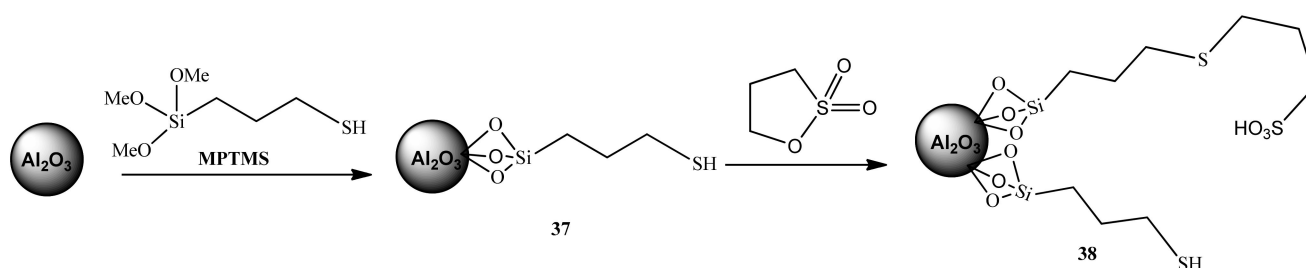


Figure 14. Bifunctional functionalized mesoporous Al_2O_3 from ref [78].

Following this study, in 2019 Lin et al. [80] achieved the functionalization of alumina beads with both propyl sulfonic acid and alkyl groups. Analogously to Solis study, these materials were tested as catalysts for the production of 5-hydroxymethylfurfural. In the optimization of the catalyst, an important step was the calcination temperature in the synthesis of alumina. Indeed, lower T induced the formation of Al_2O_3 with high surface area promoting an easier bi-functionalization and avoidance of competition between acid and hydrophobic groups on the surface support. Long chain organosilanes (C3, C8, C16) were required to enhance the hydrophobicity to the material in order to avoid the deactivation of the catalyst by water and to protect the aluminum pore structure from water damage.

3. Sulfonic Acid-Functionalized Materials: Characterization

The characterization of surface-functionalized oxides uses of a variety of techniques, such as solid-state NMR, XPS, FT-IR, TGA, XRD, Raman spectroscopy, acid evaluation by FT-IR of adsorbed pyridine/ NH_3 and titration, aiming to characterize both the support and the acidic function. Here, this section will be focused only on the principal techniques aimed to identify sulfonic functions linked to the aforesaid inorganic supports.

A powerful tool for the characterization of functionalized silica is ^{13}C and ^{29}Si NMR which permits analysis of the evolution of the chemical environment around silicon atoms introduced by addition of active components. The ^{29}Si NMR of bare silica presents features to be attributed to silicon without hydroxy groups $\text{Si}-(\text{O}-\text{Si})_4$, silicon atoms bearing one hydroxy group $(\text{Si}-\text{O})_3-\text{Si}-\text{OH}$ and silicon atoms bearing two hydroxy groups $(\text{Si}-\text{O})_2-\text{Si}-(\text{OH})_2$ called germinal silanols. The first species, whose peak is named Q^4 , is largely present in the bulk whereas the second and the third (respectively called Q^3 and Q^2) are present at the silica surface. In addition to the changes in proportion between these peaks, when functionalized, a new set of peaks in the range $\{-45; -80\}$ ppm appears giving evidence for the covalent incorporation of the functional groups. The peaks correspond to three different environments for the siloxanes groups: T^1 , T^2 , and T^3 assigned respectively to $[\text{T}^m = \text{RSi}(\text{OSi})_m(\text{OMe})_{3-m}]$ [11,13,81–85]. Khriksa et al. [86], for example, attribute the presence of more T^3 species in $\text{RSO}_3\text{H-MCM-41}$ compared to $\text{RSO}_3\text{H-SBA-15}$ to a higher number of Q^3 in the bare MCM-41 precursor indicating a more efficient condensation. $\text{RSO}_3\text{H-SBA-15}$ consists of T^2 and T^1 species, as the Q^3 species essential for bonding with organosiloxane groups of silylating agent are far apart, thus making complete condensation (T^3 species generation) less probable (see Figure 15).

Da Silva [87] also uses ^{29}Si NMR to evaluate the condensation degree during a one-pot synthesis. A higher $\text{Q}^4/(\text{Q}^2+\text{Q}^3)$ ratio would demonstrate a high condensation degree resulting in a material with superior chemical and mechanical stability. This technique was in some cases used to characterize functionalized alumina or titania. The use of a functionalized silane introduces silicon on the surface which give rise to the typical T^n signals. In the case of functionalized alumina by Maldonado et al. [79], which used three different synthesis procedures, it was found that even though the prevalent signal was, in each case, T^2 , each procedure produced a different proportion between T^1 , T^2 and T^3 signals (see Figure 16).

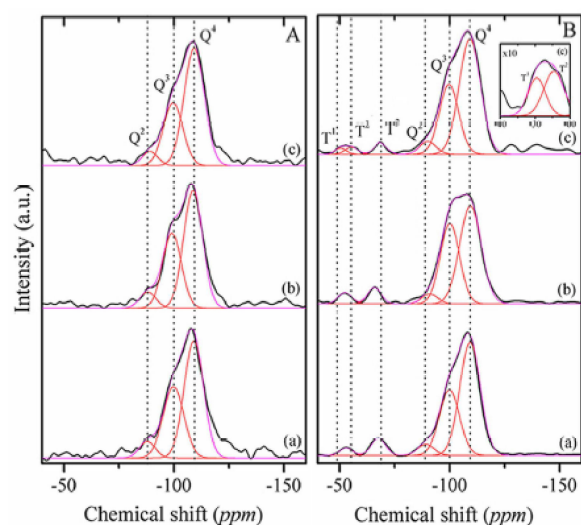


Figure 15. ^{29}Si MAS-NMR of: (A) silica and (B) sulfonic acid-functionalized analogues of (a) MCM-41; (b) IITM-56; (c) SBA-15 from ref [86]. Reprinted with permission from ref. [86]. Copyright 2018 John Wiley and Sons.

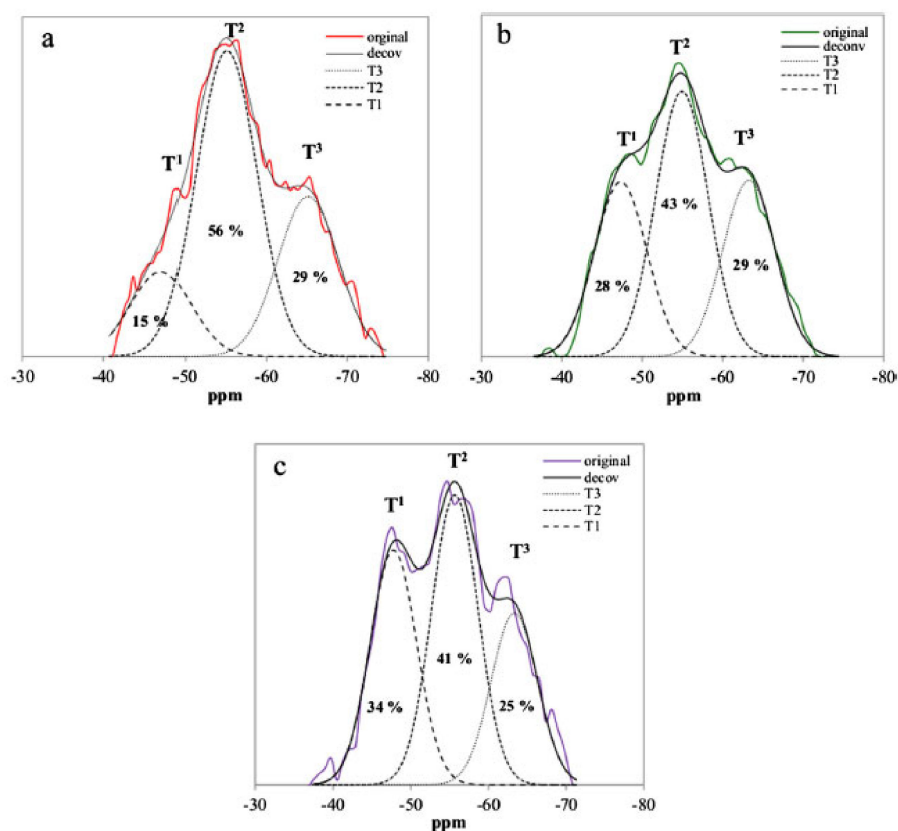


Figure 16. ^{29}Si CP/MAS NMR spectra of modified catalysts and resulting deconvolution bands for: (a) commercial alumina catalyst ACTS, (b) Synthesized alumina catalyst ASmTS and (c) sol-gel BSmTS, from ref [79]. Reprinted with permission from ref. [79]. Copyright 2017 Elsevier.

Alternatively, the ^{13}C NMR allows us to follow the functionalization by looking at the different types of carbon. According to the literature [79,85,88,89] the signal at 13–15 ppm is related to carbon directly linked to silicon and the sign at 50 ppm may be related to carbon linked to sulfonic groups (see Figure 17). In ref [85] the appearance of signals in the 50–20 ppm range has been assigned to disulfide bridges $(\text{Si}(\text{CH}_2)_3\text{S}-\text{S}(\text{CH}_2)_3\text{Si})$ arising

from the condensation of two mercaptopropyl chains. Schäfer indicates the appearance of three signals, upon the grafting of 3-MPTMS, at 9.8, 25.4 and 45.8 ppm to the 3-thiopropyl chain [90]. These resonances weakened upon oxidation of the thiol to sulfonated functions.

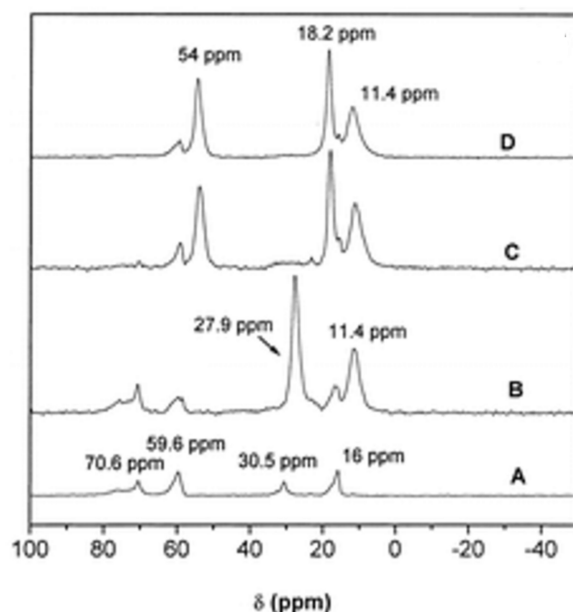


Figure 17. ^{13}C NMR spectra of different extracted SBA-15 mesoporous silicas: (A) conventional SBA; (B) thiol-functionalized SBA, (C) sulfonic-functionalized SBA-15 obtained through the direct-synthesis approach; (D) sulfonic-functionalized SBA-15 obtained through the direct-synthesis approach. Reprinted with permission from ref. [89]. Copyright 2000 American Chemical Society.

FT-Infrared spectroscopy is also able to evidence the incorporation of the organosulfonic groups in the silica structure. The bare support shows three characteristic Si-O-Si peaks centered at 1100 cm^{-1} , 770 cm^{-1} and 450 cm^{-1} which are assigned to asymmetric stretching, symmetric stretching and bending vibration respectively, moreover a broad envelop centered at ca. 3400 cm^{-1} is attributed to the surface OH stretching vibration and at 967 cm^{-1} to the bending vibration of noncondensed Si-OH groups [88]. Upon functionalization, due to the substitution of surface silanols by propyl silane groups, these last two features tend to decrease in intensity. Meanwhile peaks due to the presence of the organic groups arise with feature attributable to $-\text{CH}$ stretching ($2974\text{--}2893\text{ cm}^{-1}$) and to skeletal vibrations ($1600\text{--}1400\text{ cm}^{-1}$). Moreover the SO_3^- symmetrical and asymmetrical vibrational modes (at 1046 and 1125 cm^{-1}) arise above of the characteristic modes of the silica network ($1165\text{--}1150\text{ cm}^{-1}$) [14,85,91]. The absence of peaks due to $-\text{SH}$ functional groups (S-H stretching 2563 cm^{-1}) is an indication of the efficiency of the oxidation step [86,92].

The same technique is applicable to other functionalized supports such as TiO_2 [93], silica coated magnetite [37], Al_2O_3 [76–78]. Peaks at 1200 cm^{-1} (Ti-O-Ti vibration) 1623 , 3355 cm^{-1} (surface hydroxyl groups of TiO_2), 589 and 758 cm^{-1} (stretching vibrations of Al-O bonds in $\gamma\text{-Al}_2\text{O}_3$) and 576 cm^{-1} (stretching of Fe-O), are seen along with peaks related to the functionalization. In the case of sulfated zirconia the bands relative to bidentate sulfate ion coordinated to zirconium cation, found at 1034 , 1150 and 1231 cm^{-1} , are assigned to the typical bands chelating bidentate by Zhang et al. [72], while Yadav et al. [71] attributed them to the peaks found at 1218 , 1152 and 1066 and 997 cm^{-1} . Bands between 700 and 415 cm^{-1} are characteristic of crystalline zirconia.

The nature of the S surface species can be explored as well, by means of Raman spectroscopy which is more sensitive toward S-H vibrations than FT-IR. The disappearance of the strong peak at 2585 cm^{-1} attributed to the thiol groups is indicative of the efficiency of the oxidation step. Meanwhile the appearance of new bands at 1040 and 1100 cm^{-1} at-

tributed symmetric and asymmetric vibrational modes of SO_3^- permits direct identification of the creation of surface sulfonic acid groups (Figure 18). [85,94–96]. Furthermore, features at 1250 and 1300 cm^{-1} are usually found due to the $\text{CH}_2\text{-S}$ and $\text{CH}_2\text{-Si}$ wagging modes.

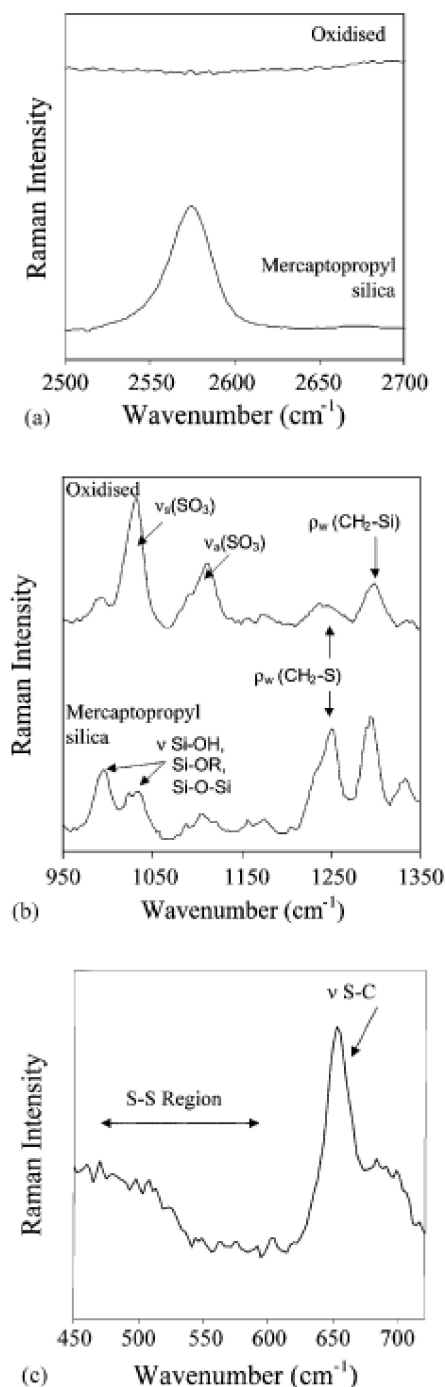


Figure 18. Raman spectra of mercaptopropyl silica before and after oxidation (a) S-H stretching region; (b) S-O stretching region; (c) S-S stretching region from ref. [94]. Reprinted with permission from ref. [94]. Copyright 2002 Elsevier.

Thermogravimetric analysis is used to evaluate the thermal stability of the hybrid materials and the functionalization degree. A first loss of up to 130 $^{\circ}\text{C}$ is usually observed related to desorption by the catalysts surface. The decomposition in air of the organic

sulfated moieties occurs usually around 350 °C and can be used to quantitatively determine the functional groups content [38,78,97].

X-Ray photoelectron spectroscopy is another tool used to corroborate the efficiency of the anchoring of functional molecules and of the oxidation procedure. The analysis of the characteristic core-level binding energy regions for silicon, oxygen, carbon and sulfur give information about the chemical state and the surface composition of the functionalized materials. The XPS peak at ca. 168–170 eV is typical of S2p for sulfonated materials and at 164 eV typical of thiolated compounds. The relative percentage of these two peaks is used for the evaluation of the oxidation step. The extended region comprising Si2s (ca. 154 eV) and S2p (164–168 eV) is useful for evaluating the differences in sulfur surface concentration with respect to silica (see Figure 19).

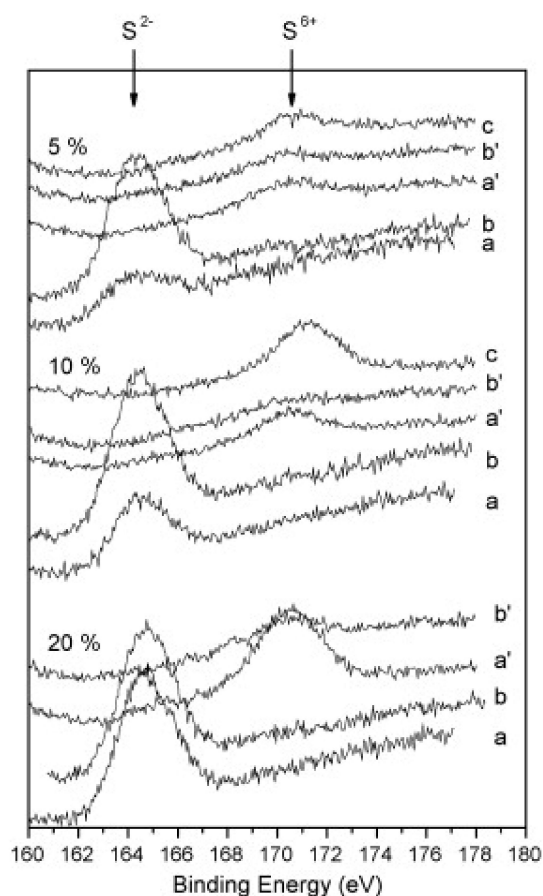


Figure 19. S2p XPS region modified silica; co-condensed samples: a reduced, a' oxidized; grafting samples: b reduced, b' oxidized; in situ oxidized samples: c from ref [97]. Reprinted with permission from ref. [97]. Copyright 2010 Elsevier.

XPS allows for comparison of the efficiency of different synthetic procedures by the measurements of the the S/Si ratio [10,98–100]. Moradi et al. confirmed by XPS the presence of two types of sulfur containing groups, sulfide (-S-S-) as a covalent bridge bond and sulfate (-SO₃) as active catalytic site (see Figure 20) [38].

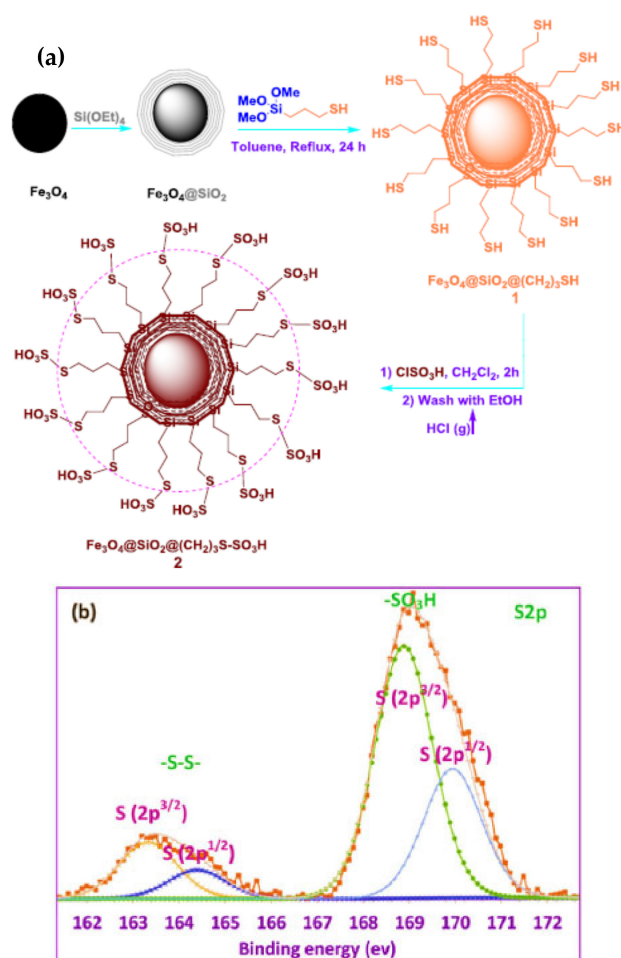
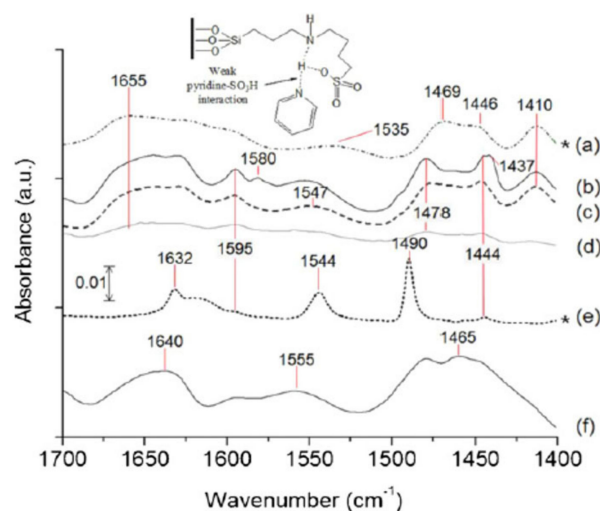


Figure 20. Scheme from ref [38]. Synthesis of magnetic nanocatalysts $\text{Fe}_3\text{O}_4\text{SiO}_2(\text{CH}_2)_3\text{S-SO}_3\text{H}$ (a) and $\text{S}2\text{p}$ XPS region (b). Reprinted with permission from ref. [38]. Copyright 2017 John Wiley and Sons.

In order to evaluate the acidity of the sulfonic functions, the analysis of pyridine and ammonia adsorption by FT-IR spectroscopy can be carried out. The interaction of pyridine via the nitrogen lone-pair electrons, with aprotic (Lewis) and protonic (Bronsted) acid sites, can be detected by monitoring the ring vibration modes. These modes, which appear at 1598 cm^{-1} , 1580 cm^{-1} , 1483 cm^{-1} , and 1437 cm^{-1} in the IR spectrum of liquid pyridine undergo upward frequency shifts upon coordination of the probe molecule to either type of acid sites. For sulfonic-functionalized silica it is expected to be Bronsted acidity which results in the formation of pyridinium (PyH^+) species, characterized by the bands at about 1640 and 1545 cm^{-1} (see Figure 21). The use of ammonia as a probe molecule would result in the appearance of broad multicomponent bands at 1465 and 1640 cm^{-1} which are assigned to the $\delta\alpha$ (N–H) and δs (N–H bending modes of NH_4^+ interacting with surface acid [1,20,37].



FTIR spectra of $\text{SO}_3\text{H-MCM-41}$. (a) After thermal activation under a vacuum at 200°C (used as the reference spectrum), (b) after pyridine adsorption at 25°C (1.33 mbar at equilibrium for 5 min), (c) followed by evacuation at 25°C , (d) evacuation at 100°C , (e) IR spectrum relative to pyridine adsorption over H-MOR for comparison purpose and (f) IR spectrum relative to ammonia adsorption over $\text{SO}_3\text{H-MCM-41}$ at 25°C (1.33 mbar for 5 min). Spectra labeled with (*) were multiplied by 0.025 and spectra (b), (c), (d) and (f) are corrected from the (a) reference spectrum. Inset: Possible way of interaction between pyridine and Brønsted acid site of $\text{SO}_3\text{H-MCM-41}$ catalyst perturbed by neighboring species.

Figure 21. FT-IR of adsorbed pyridine from ref. [20] The Figure shows the FT-IR spectra of $\text{SO}_3\text{H-MCM-41}$ after different treatments. See the legend of Figure 7 of ref. [20] for full information. Reprinted with permission from ref. [20]. Copyright 2013 Elsevier.

Another way to evaluate the acidity of the catalysts is titration by a solution of NaOH of a suspension of the catalysts. The acidity capacity in mmol g^{-1} is measured after letting the acid powder balance with a solution of NaCl used as cation exchanger. [88,91,101,102]. The direct titration with NaOH along with the reverse titration with HCl or H_2SO_4 [103] gives accurate indication of the functionalization degree. The comparison between the pyridine FT-IR and classical titration can provide information on the different types of Brønsted and Lewis acidities. For the evaluation of the functionalization degree a precise quantification of carbon, hydrogen and sulfur can be performed by elemental analysis by combustion of the organic moieties [14,15,91,101,104].

4. Considerations on the Stability of Sulfonic Solid Acid Catalysts

The synthetic approaches, illustrated in the previous sections, show how solid acid catalysts can be considered as sustainable materials. They are, in fact, heterogeneous materials that can be easily recovered from the reaction, can be used several times with a decrease in the processing cost and can be prepared by using economic and ecofriendly starting materials. Nevertheless, in view of a possible application into the industrial processes with a replacement of the traditional liquid acids, the stability of these materials must be improved.

Different strategies can be applied in both the preparation of the solid acid catalysts and in the application procedures in order to avoid their deactivation.

The main cause of deactivation is the leaching of the acidic function from the surface of the support. When an impregnation procedure is used for the preparation of the catalyst, due to the formation of weak bond between the functions and the support, leakage of the sulfonic groups may easily occur. In general, these materials show high hydrophilicity and are very sensitive to water even if it is produced as byproduct of the catalyzed reaction. Usually, these catalysts can be easily regenerated by further impregnation, but of course, the process is environmentally and economically unfriendly. The leaching of the acid groups can also occur when the organic sulfonic functions are covalently linked to the support, by

both co-condensation and grafting procedures. Sulfonic groups introduced by the grafting method, are mainly located on the surface of silica suffering from water deactivation more than materials synthesized by the co-condensation procedure in which the internal functionalized groups result more protected. For this reason, this latter procedure is recommended when conditions allow it.

Other important strategies to prevent the deactivation of the catalyst involve the introduction of additional functional groups. If the deactivation is caused by water as byproduct during the catalyzed reaction, one of the most used strategies is the increase in hydrophobicity of the material structure with the introduction of alkylorganosilane. Several research groups have followed this pathway: Diaz et al. [105] designed the synthesis of well-ordered MCM-41 functionalized with both alkyl and mercaptopropyl groups. The materials, tested in the glycerol esterification of fatty acids, showed an improvement of their catalytic activity due to the presence of the hydrophobic group ($-\text{CH}_3$), which leads to better adsorption of reactants on the catalyst, and consequently, to a high yield of bio-additives esters. Recently, Yang et al. [106] prepared a series of solid acid silica materials with different hydrophobic alkylorganosilanes, and evaluated the catalytic activity on the conversion of fructose to 5-HMF, an important platform molecule. The use of the most hydrophobic catalyst allows for the achievement of 5-HMF with the highest yield and selectivity. In this research, the synthesis of hydrophobic catalysts not only prevents the leaching of sulfonic groups, but also avoids contact between water and the just-formed HMF, preventing also the further hydrolysis of furfural and other byproducts. Kamegawa et al. [107] carried out the hydrophobic modification of sulfonic acid-functionalized mesoporous silica ($\text{SO}_3\text{H-MS}$) by the grafting of triethoxyfluorosilane (TEFS) as a silylation reagent. The material exhibited less water adsorption capacity allowing for an improvement in the catalytic performance as a solid acid catalyst in Friedel-Crafts alkylation. In order to impart hydrophobicity to the sulfonic solid acid catalysts, Kasinathan et al. [108] discussed both a simultaneous or sequential post functionalization of hydrophobic decyl ($-\text{C}_{10}$) chains. The materials, tested in the model esterification of octanol with acetic acid, showed an improvement in the catalytic activity as a result of strong synergistic effects of hydrophobic and acid groups when a simultaneous functionalization occurred.

High reaction temperatures can also influence the catalyst deactivation, thus favoring sulfonic leaching and changing the catalyst structures with the detachment of the catalyst with respect to amorphous silica. In their studies on the conversion of glycerol, Testa et al. [49,109] observed the influence of the heating source (reflux or microwaves) in the stability of propyl sulfonic amorphous silica. In particular, when the catalyst was applied in the synthesis of glycerol derivatives [109] in batch by refluxing at 105°C , the sulfonic amorphous catalyst became unstable with an important leaching of sulfonic groups already on second run, thus halving the conversion of the glycerol. Moreover, in the same study, mesoporous sulfonic silica presented a better performance in term of stability, with no leaching of sulfonic groups with respect to amorphous silica. In following research [49,100], propyl sulfonic amorphous silica was applied in the synthesis of glycerol derivatives by using a microwaves-assisted procedure. With the use of microwaves as source of energy, the material showed very high stability during several cycle reactions. These results are very important in terms of sustainability. Indeed, the synthesis of an amorphous silica decreases the production cost of the material with respect to the mesoporous ones. Recently, Wawrzynczak et al. [103] studied the catalytic performance of propyl sulfonic KIT-6 in several MW-assisted organic reactions as Friedel-Crafts alkylation, fatty acid esterification and Pechmann condensation. In the study, the efficiency (with an increase in the conversion values) and the stability of the material, when the reactions were conducted in the presence of microwave radiation with respect a conventional heating, were confirmed. Moreover, the use of microwaves represents an energy saving procedure due to faster reaction kinetics and therefore a reduction in process cost.

A common cause of deactivation is the poisoning of the catalyst often due to the adsorption on the surface material of the reaction byproducts. Organic deposition on the

active site of the catalyst results in the covering of pores, in a smaller pore size and a smaller surface area, thus influencing the catalytic performance of the material. In general, the poisoning of the catalyst is a reversible process, and the regenerating approach are related to the nature of the catalyst. When an inorganic sulfonic acid catalyst is used, the material can be easily regenerated by calcination at high temperature. It is important to control the temperature in order to avoid the sinterization of the active acid species. [109] In the case of an organic–inorganic acid catalyst, the material can be subjected to solvent extraction in order to carry away the organic contaminants [49].

5. Conclusions

In this minireview, several synthetic approaches for the synthesis of sulfonic acid-functionalized inorganic materials were reviewed, following the thread of efficiency and sustainability. Particular attention was devoted to the optimization of the synthetic procedures carried out in few steps, in sustainable solvents, and with easy recovery of the material. As inorganic supports, SiO_2 and TiO_2 , were deeper studied with respect to the others, due to their economic, ecofriendly and good chemical and thermal stability properties. Some examples of applications of sulfonic acid-functionalized materials were illustrated. In particular, their use in pharmaceutical chemistry for the synthesis of new molecules as potential drugs, in environmental chemistry for the abatement of pollutants and in biomass conversion for the production of added value products or of new eco-friendly biofuels were reported. The principal techniques for the characterization of the sulfonic groups, located both on the external and internal surface of the inorganic support, were also described. They included solid-state NMR, XPS, FT-IR, RAMAN spectroscopy, TGA, XRD, acid evaluation by FT-IR of adsorbed pyridine/ NH_3 and titration. A section was devoted to the stability of the materials by analyzing the major deactivation sources and suggesting ways that deactivation could be prevented for a better efficiency of the materials. As per the intended message of this minireview, the described materials emerge as efficient, sustainable and versatile catalysts in the attainment of different valuable chemicals. Their use is indeed very favorable due to simple separation, regeneration and recycling of the material, consequently accompanied by a decrease in the processing cost. Therefore, they may represent an effective alternative for the replacement of liquid acids, allowing for a green transition for the majority of industrial plants that are still based on catalytic homogenous systems.

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