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Advances in the Synthesis and Catalytic Applications of Organosulfonic-Functionalized Mesostructured Materials

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1. Introduction

Since the discovery in the early 1990s of the FSM[1] and MCM[2] (mobil composition of matter) materials, the first mesoporous silica-based solids, this field of research has been tremendously expanded and reviewed several times.[3−7] These materials have relatively uniform pore sizes and high void volumes and surface areas as compared with nonordered amorphous silica. The pore sizes of these materials can be tailored depending on the synthesis method used, ranging from about 15 to about 100 Å. Moreover, larger pore sizes from 50 to 300 Å are also shown by the SBA family of solids, e.g., SBA-15.[8,9] The ordered mesostructured materials can serve as better-defined supports, in comparison to nonordered amorphous solids, onto which organic groups can be anchored. Hence, the attachment of organic functionalities to the surface of the silica mesoporous supports has been an interesting research area in heterogeneous catalysis and green chemistry during the last years. These hybrid mesoporous solids have been considered for a wide range of catalytic reactions.[10] Heterogenization of active species can result in an improvement of the overall efficiency of the process because of several features such as easier separation of the catalyst from the reaction medium, catalyst regeneration and reuse, and confinement of the active species within the mesopores which provides a way to introduce shape selectivity and thus greater specificity to a reaction product. A wide number of reviews deal with the functionalization of mesostructured silicates with organic surface groups.[10−15] Basically, two strategies have been described to anchor organic groups to a mesostructured silica surface via formation of covalent bonds: grafting methods (postsynthesis procedure) and co-condensation reactions (direct synthesis). Grafting procedures are based on modification of the silica surface with organic groups through silylation reactions occurring on isolated ($\equiv$Si−OH) and geminal ($=$Si(OH)$_2$) silanol groups using trichloro- or trialkoxyorganosilane and silylamines as organic precursors. In contrast, direct synthesis consists of the co-condensation of siloxane and organosiloxane precursors in the presence of the corresponding structure-directing agent, SDA. Each functionalization pathway has certain advantages. Direct method usually yields a uniform surface coverage with organic groups and also provides better control over the amount of organic groups incorporated to the structure. However, products obtained by postsynthesis grafting are often structurally better defined and hydrolytically more stable than samples obtained from direct synthesis method.

First attempts to incorporate the acid functionality in these mesostructured silica-based materials focused on incorporation of Al atoms tetrahedrally coordinated within the framework through hydrothermal methods analogous to those used in the preparation of zeolites. However, because of the amorphous ordering, their catalytic properties are closer to a mildly acidic amorphous silica−alumina than to a strongly acidic zeolite, which limits their potential catalytic applications.[3] Nevertheless, some interesting advances have been made recently in improving both the hydrothermal stability and acidity of Al-MCM-41 mesostructures through the use of protozeolitic aluminosilicate nanoclusters or “zeolite

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seeds” as framework precursors.[16−18] Recently, the covalent attachment of sulfonic groups on the pore walls of mesostructured materials by means of the above-mentioned functionalization techniques has emerged for the preparation of acid solid catalysts following the pioneering work from Badley and Ford published in 1989 using amorphous silica as support.[19] These sulfonated mesoporous silicas lead to materials with high surface area, narrow pore size distribution with high accessibility and loading of acid sites, as well as relatively high acid strength. Moreover, the bonding strength of sulfonic-acid groups covalently attached to the walls of mesostructured silica is supposed to be high enough to prevent sulfur leaching.

Gabriel Morales was born and raised in Madrid, Spain, receiving his Bachelor’s and Master’s degrees from Complutense University of Madrid in 2000. He earned his Ph. D. degree in Chemical Engineering from Rey Juan Carlos University in 2005. Gabriel’s Ph.D. project focused on the preparation and catalytic application of mesostructured materials functionalized with sulfonic-acid moieties. Currently, he is an assistant professor in the Department of Chemical and Environmental Technology of Rey Juan Carlos University in Madrid. His field of research is mainly directed toward characterization and application of organically modified mesostructured materials.

Increasing awareness of the environmental costs of traditional acid-catalyzed chemical processes has created an opportunity for new solid acid catalysts. In this review we describe how this opportunity is being addressed through the synthesis and application of these novel acid catalysts based on sulfonic-modified mesostructured materials. Special attention will be brought on the strategies to tune the acid strength and control the hydrophobic microenvironment of the sulfonic-acid sites and subsequent improvements of the catalytic performance.

2. Synthesis of Organosulfonic-Functionalized Mesostructured Materials

2.1. Postoxidation of Anchored Mercaptopropyl Groups

Pioneering works dealing with the preparation of sulfonic-acid-functionalized mesostructured silica date from 1998.[20−22] These materials are based on the covalent attachment of alkylsulfonic-acid groups to the surface of MCM and HMS-type materials. Preformed calcined MCM and HMS samples were first functionalized with propane−thiol groups by reaction of the surface silanols with 3-mercaptopropyltrimethoxysilane (MPTMS) as the key precursor.[20] Organosiloxane loadings tend to be significantly higher for mesostructured materials as compared with amorphous silicas because the former possess higher surface area and ordered pore structure.[10] Jacobs et al.[22] enhanced the incorporation of sulfur moieties using a modified grafting procedure. The surface of mesostructured MCM materials was coated with a cross-linked monolayer of mercaptopropyl−Si groups under well-controlled wet conditions. The authors demonstrated that the −SH site density can be adjusted by the degree of surface hydration, obtaining an incorporation of up to 4.5 mmol of S per gram of material in optimal conditions. The materials were characterized by IR spectroscopy, showing a signal at 2575 cm^{-1} corresponding to the S−H vibration, and by ^{13}C MAS NMR, with chemical shifts δ of 11 and 27 ppm corresponding to the mercaptopropyl group. Sastre and co-workers[23] recently optimized the preparation method of SO_3H-MCM-41 solid materials by grafting techniques. To avoid detrimental effects over the population of silanol groups, they performed a systematic study of the acid extraction of the surfactant from the as-made MCM-41 mesoporous materials and its effect on the grafting capacity of propylthiol functional groups. A 5-fold increase of the sulfur loading was obtained with the sample treated in optimized extraction conditions (washing with 1/100 (v/v) HCl/ethanol solution at 343 K for 16 h) with respect to its calcined counterpart. The authors attributed such a large difference to removal of the most accessible silanol groups during the calcination process. In grafting procedures the surface concentration of organic groups can be constrained by the number of reactive silanol groups as well as by diffusion restrictions. Hence, it is usually necessary to employ a large excess of organic silane and anhydrous conditions to avoid homocondensation reactions.

The limitations observed in grafting techniques can be overcome by direct incorporation of thiol groups during synthesis of the mesoporous support by means of the co-condensation of siloxane (tetraethyl orthosilicate, TEOS, or tetramethyl orthosilicate, TMOS) and organosiloxane (mercaptopropyltrimethoxysilane, MPTMS) precursors in a templating environment. In addition to grafted materials, Jacobs et al.[20,22] reported the direct synthesis of mercaptopropyl-modified HMS and MCM materials using neutral amine (*n*-dodecylamine) and ionic cetyltrimethoxyammonium bromide (CTAB) molecules, respectively, as SDA with TEOS as the silicon source. The template was removed by extraction with ethanol under reflux to yield the thiol-functionalized mesostructured material. Stein et al.[21] created thiol-functionalized porous MCM silicalites by means of this direct synthesis procedure using TMOS as the silicon source instead of TEOS in basic medium with CTAB as surfactant. The authors reported a final sulfur content for the synthesized material of 4.7 mmol of S per gram of silica, meaning almost 100% incorporation of sulfur species from the initial synthesis, which is appreciably higher than that obtained by Jacobs et al.[22] through their direct synthesis procedure. This value was comparable to that previously obtained for coating processes.[22] Likewise, higher structural order, as determined by XRD and TEM, was obtained using TMOS instead of TEOS due to its faster hydrolysis rate. The homogeneity of the silanes mixture as well as the hydrolysis rate was controlled using 30% methanol aqueous solutions. The template was extracted with an acidic methanol solution, and no structural damage or degradation of thiol groups was observed. In this micelle-templated synthesis the mercaptopropyl part of the MPTMS molecule is considered to be oriented along the apolar tails of the surfactant molecules, which leads to high accessibility of thiol sites for further modifications after removal of the SDA molecules.

Independent of the synthesis strategy, thiol groups must be postsynthetically treated to yield acid active sulfonic groups. This treatment implies oxidation with a large excess of an oxidant (mainly hydrogen peroxide[20,22] or nitric acid[21]), acidification, and finally washing. In this postoxidative procedure[20,22] the presence of residual disulfide species coming from incomplete oxidation of thiol moieties has been checked by means of ^{13}C MAS NMR. Hence, the oxidation conditions must be properly tuned to achieve selective sulfonic-acid formation. Figure 1 briefly schematizes the three above-mentioned strategies of synthesis comprising the subsequent oxidation of thiol groups.

Following these pioneering works, the postoxidative synthesis strategy has been expanded to the use of other different surfactants and synthesis conditions. Pérez Pariente et al.[24] reported the synthesis of well-ordered SBA-2 materials containing mercaptopropyl groups using gemini surfactants (CH_3-$(CH_2)_{15}$-$N(CH_3)_2$-$(CH_2)_3$-$N(CH_3)_3$-$(Br)_2$) in basic medium. The SBA-2 mesophase[25] consists of a complex set of narrow channels interconnecting the large cavities.[26] However, the corresponding oxidized materials containing $-SO_3H$ groups showed poor catalytic activity and selectivity in the esterification of fatty acids with glycerol. The same research group described the synthesis of sulfonic-modified MCM-41 materials by means of postoxidation of thiol-modified materials synthesized using a mixture of cationic surfactants (C_{16}TAB and C_{12}TAB) and tetramethoxysilane (TMOS) as the silica source in basic conditions with tetramethylammonium hydroxide (TMAOH) instead of NaOH.[27] The authors postulated that this novel method allowed the synthesis of highly ordered mesostructured materials in comparison with that using just C_{16}TAB as surfactant. Following the same hypothesis, the cationic C_{12}TAB surfactant was substituted by a neutral surfactant such as *n*-dodecylamine.[28] The authors proposed that formation of mixed micelles with both surfactants allows a more efficient packing of the hydrophobic core, resulting in a better ordering of the channels arrangement. It is important to note that the narrowing of the pore size distribution, approaching a unique pore size as in the case of zeolites, might induce changes in the selectivity of certain reactions. In fact, in the above-mentioned works the authors found a significant improvement of activity for esterification reactions as compared with the standard materials using single-surfactant procedures.

The use of low molecular weight amphiphilic surfactants leads to functionalized materials with pore sizes below 20 Å, and therefore, type I nitrogen adsorption isotherms corresponding to microporous solids are obtained. Even though these pore sizes may be able to favor stereoselection, further research has been performed in order to increase the pore size of these sulfonic-functionalized mesostructured materials using nonionic surfactants. Stucky and co-workers[29] employed a triblock copolymer (poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide), Pluronic 123, $EO_{20}PO_{70}EO_{20}$) under acidic conditions to create a thiol-containing mesoporous material. Organic loadings from 1.5 to 2.9 mmol/g were found by thermogravimetric analysis, incorporating ca. 90% of the organic functionality during synthesis. The materials were subsequently oxidized with hydrogen peroxide with varying oxidation times. Proton exchange capacities of 0.5−1.2 meq of H^+/g of silica were determined and found to be dependent on the oxidation conditions. Increased oxidation times enhanced the number of acid sites but reduced the structural order. Nevertheless, the resultant sulfonic-modified materials showed unreacted thiol groups.

Pérez-Pariente et al. prepared[30] a variety of mesostructured silicates modified with propylsulfonic moieties from gels containing nonionic surfactants using the postoxidative procedure. Poly(ethylene oxide)-based surfactants such as Pluronic 123 ($EO_{20}PO_{70}EO_{20}$), Brij 76 ($C_{18}EO_{10}$), and Triton X-114 ($CH_3C(CH_3)_2CH_2C(CH_3)_2(C_6H_4)(EO)_7OH$) were used in acidic medium. The results revealed poor ordering of the mesostructured materials and in the case of Triton X-114 only an amorphous material without evidence of ordered

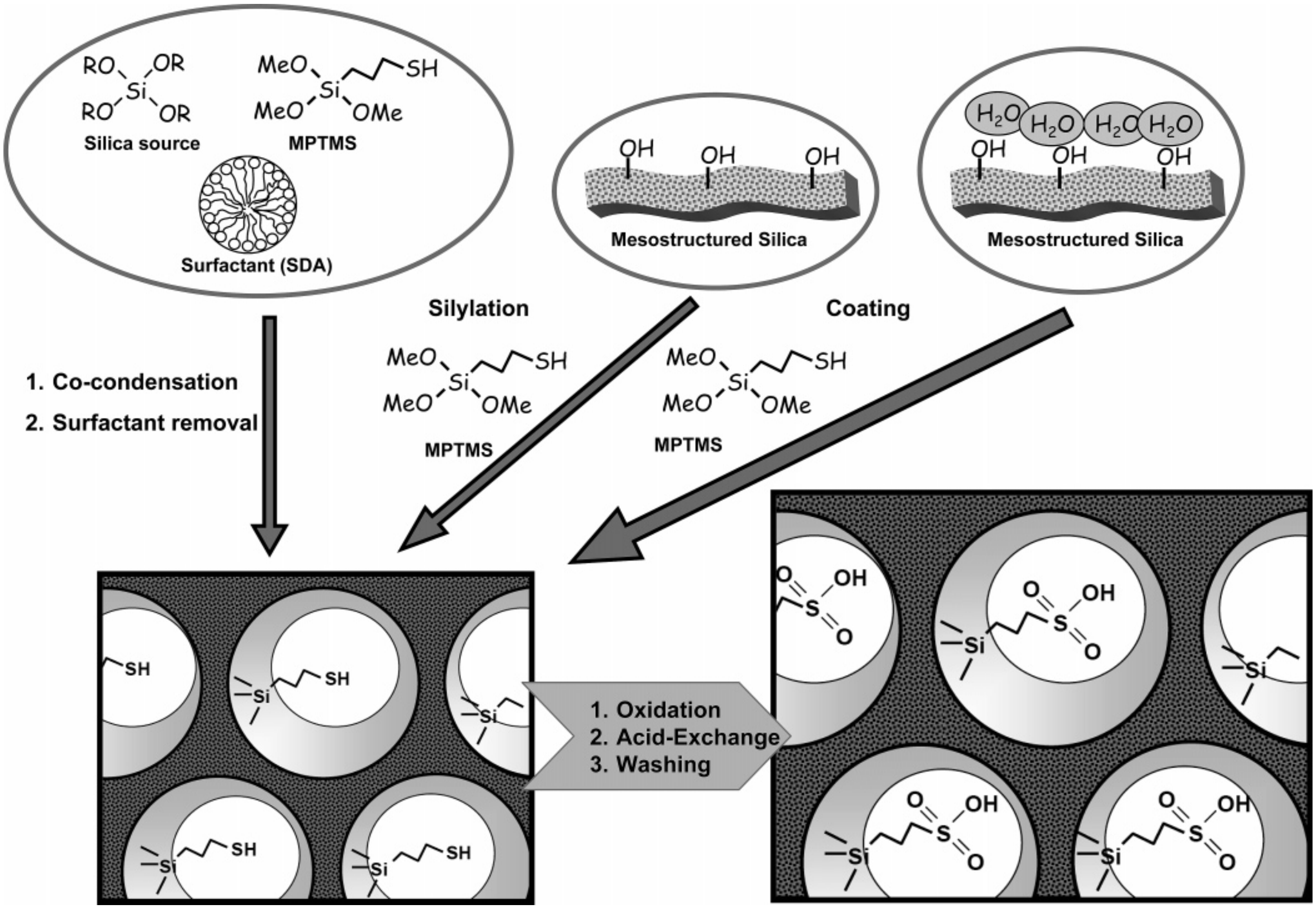


Figure 1. Postoxidative synthesis strategy for the preparation of sulfonic-acid-modified mesostructured materials (Van Rhijn, W. M.; De Vos, D. E.; Sels, B. F.; Bossaert, W. D.; Jacobs, P. A. *Chem. Commun.* **1998**, 317. Reproduced by permission of The Royal Society of Chemistry).

mesopores was obtained, probably due to the lack of a prehydrolysis step for TEOS before adding the MPTMS.

2.2. In-Situ Oxidation of Mercaptopropyl Groups by a Direct Synthesis Procedure

This two-step synthesis strategy (thiol incorporation and postoxidation) has serious drawbacks. Materials prepared in this way have yielded XRD patterns with lower scattering intensities that indicate relatively poor long-range ordering in comparison to the starting material containing the thiol groups.[20,21,29] Moreover, a decrease in the surface area and pore volume after oxidation of thiol groups incorporated by posttreatment strategy is clearly observed and reduces the potential application of these catalysts. Despite the large excess of oxidant used in the process, in most of cases the postoxidation step does not allow quantitative reaction of thiol groups, and in some cases, leaching of sulfur species is clearly evidenced. The presence of unoxidized sulfur species might have a negative effect on the catalytic performance of these materials.

A step forward was achieved by Stucky and co-workers in the preparation of sulfonic-modified mesostructured materials.[29] They improved the direct synthesis method to create periodic ordered sulfonic-functionalized mesostructures with pore sizes up to 70 Å and high acid-exchange capacities (1−2 meq H^+/g SiO_2) using triblock copolymer species (Pluronic 123; $EO_{20}/PO_{70}/EO_{20}$) as the templating surfactant in acid medium. This new procedure involved a one-step synthetic strategy based on the co-condensation of TEOS and MPTMS in the presence of Pluronic 123 species and H_2O_2 in HCl aqueous solutions (Figure 2). This approach allows in-situ oxidation of the thiol groups and acid exchange of the resultant sulfonic-acid groups. The one-step synthesis using acid catalysis in the presence of Pluronic 123 produced SBA-15-modified materials with greater oxidation efficiency (100% vs 25−77% in postsynthetic treatments) with larger (up to 70 Å) and more uniform pores, higher surface areas (700−800 m^2/g), and good long-range order in contrast to postoxidative methods (see Figure 3). Moreover, this outcome was achieved under milder and simpler synthetic conditions utilizing less time and less material (in-situ oxidation with a stoichiometric amount of oxidant and acid exchange). The net result was a sulfonic-mesostructured material with acid capacities several times greater than those achieved with postoxidative methods and thermal stability up to 450 °C in air. Finally, one of the most interesting features of the in-situ syntheses was the observed enhancement of the long-range order found in the mesoporous products. In-situ formation of sulfonic-acid moieties apparently introduces variations that promote microphase separation of the PEO−PPO−PEO copolymer blocks and thus increasing mesoscopic ordering.

Solid-state ^{29}Si NMR confirmed the presence of organofunctionalized moieties as part of the silica wall structure for the sulfonic-acid organically modified mesostructured materials (Figure 3). Distinct resonances can be clearly observed for the siloxane [$Q^n = \mathrm{Si}\,(\mathrm{OSi})_n\text{-}(\mathrm{OH})_{4-n}$, $n = 2{-}4$; Q^3 at −100 ppm; Q^4 at −110 ppm)] and organosiloxane

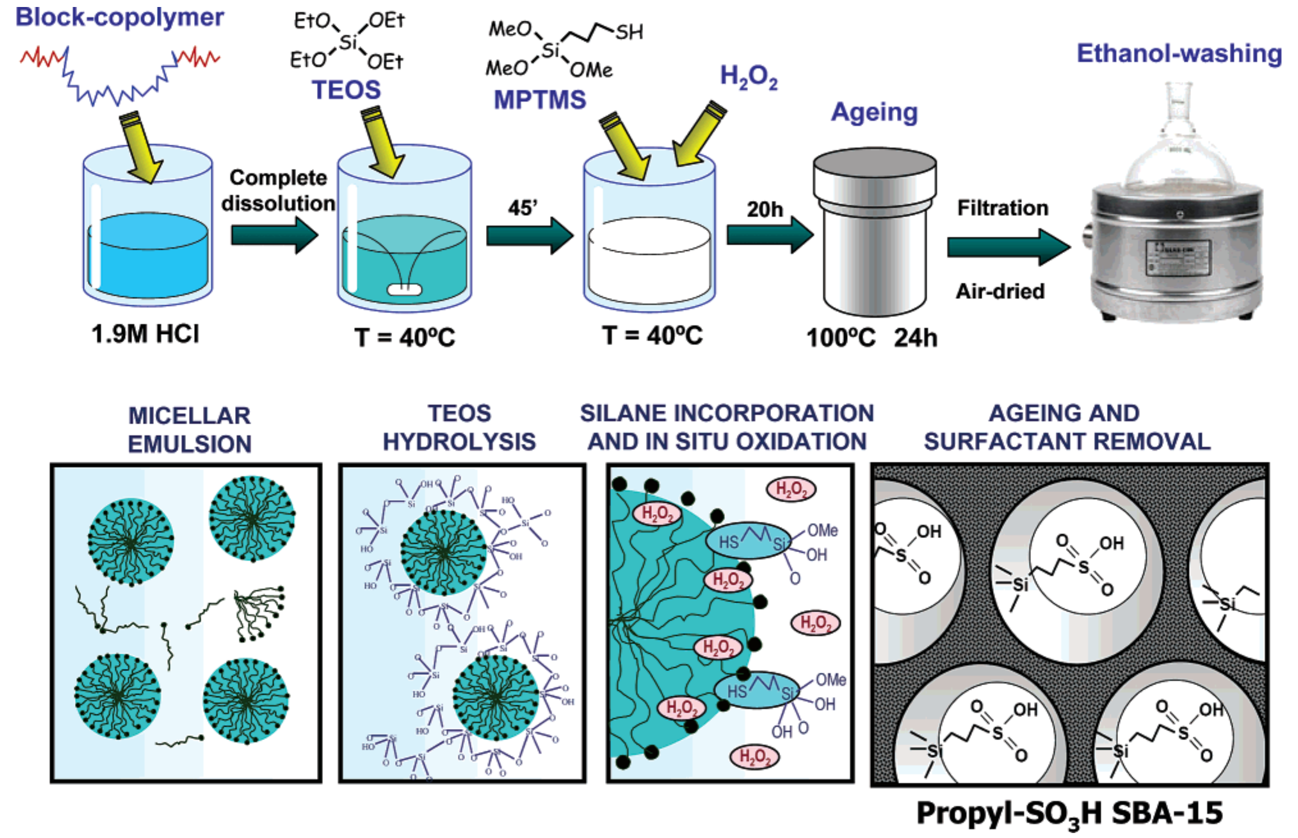


Figure 2. In-situ oxidation synthesis strategy for the preparation of sulfonic-acid-modified mesostructured materials.

[T^m = RSi $(OSi)_m$-$(OH)_{3-m}$, $m = 1-3$; T^3 at −65 ppm; T^2 at −57 ppm] units. The relative integrated intensity of the organosiloxane (T^m) and siloxane (Q^n) NMR signals (T^m/Q^n) allows calculation of the incorporation degree of organic moieties. Additionally, the organic nature of the ordered sulfonic materials has been investigated by ^{13}C CP MAS NMR. Propylsulfonic-modified mesostructured materials show three clear signals (Figure 3) with NMR shifts of 11.4 (C^I carbon), 18 (C^{II} carbon), and 54 (C^{III} carbon), which are consistent with those calculated for molecular 1-propanesulfonic acid. In postoxidative methods other signals are also relevant in ^{13}C CP MAS NMR coming from unreacted thiol groups or partially oxidized disulfide species (i.e., organic moieties containing sulfur to sulfur bonds, −R−S−S−R−).[20,21,31,32] The presence of these disulfide species has been attributed to a nonrandom distribution of S-containing groups during condensation, which seem to cluster upon the surface and are not removed after the subsequent oxidation step. Formation of these nonacidic species explains the difference between sulfur loading and proton exchange capacity measured by titration described in some works (i.e., the H^+/S ratio is always lower than 1).[20,21,31,32] In contrast, the in-situ oxidation method avoids residual unreacted thiol groups and/or the presence of other sulfur compounds arising from incomplete oxidation as confirmed by ^{13}C CP MAS NMR (Figure 3) and H^+/S ratios close to 1. The in-situ oxidation of thiol groups in an acid environment seems to promote full oxidation of potential formed disulfide species. However, K. Wilson et al.[33] have not identified disulfide species by Raman spectroscopy in sol−gel sulfonic-acid silicas synthesized in the presence of dodecylamine under neutral synthesis conditions by means of a postoxidative method. These last two works[29,33] seem to indicate that basic conditions favor formation of disulfide species.

Finally, ^{31}P MAS NMR measurements of adsorbed triethylphosphine oxide on these propylsulfonic-modified SBA-15 materials suggested the presence of Brönsted-acid sites. The acid strength of these propylsulfonic SBA-15 mesoporous materials was compared with conventional acid catalysts: Al−MCM-41 with different aluminum content (Si/Al = 30 and 14), H-USY zeolite, and sulfonic resin (amberlyst-15).[29] In mesoporous Al-MCM-41 most of the acid centers showed a signal at 66 ppm with strong acid sites showing relatively weak intensities at 73 and 83 ppm. In addition, the SBA-15 mesoporous material anchored with alkylsulfonic groups presented a higher acid strength than the Al-MCM-41 samples (shift of over 70 ppm). Finally, this functionalized SBA-15 material was compared with a sulfonic resin (amberlyst-15). Though the mesoporous material shows a lower acid strength, the homogeneity of the acid centers noted in the ^{31}P NMR results and its higher thermal stability provides this material processing latitude not present with Amberlyst-15.

Later, Van Grieken et al.[34] expanded the in-situ oxidation procedure developed by Stucky for the preparation of sulfonic-modified hexagonally mesostructured materials using nonionic surfactants other than Pluronic 123 (PL64, $EO_{13}/PO_{30}/EO_{13}$; Brij 56, $C_{16}EO_{10}$; Brij 76, $C_{18}EO_{10}$). Materials with high mesoscopic ordering were obtained in contradiction to those results previously reported by means of postoxidation processes.[30] The same group tailored the pore size of these sulfonic mesoporous materials conveniently modifying the synthesis conditions using Pluronic 123 as template and acid conditions.[34] Addition of swelling agents such as trimethylbenzene (TMB) and *n*-decane to the mixture slightly expanded the pore size in high contrast with the effect occurring for pure silica-based mesoporous materials.[9] However, enlargement of the hydrothermal treatments and

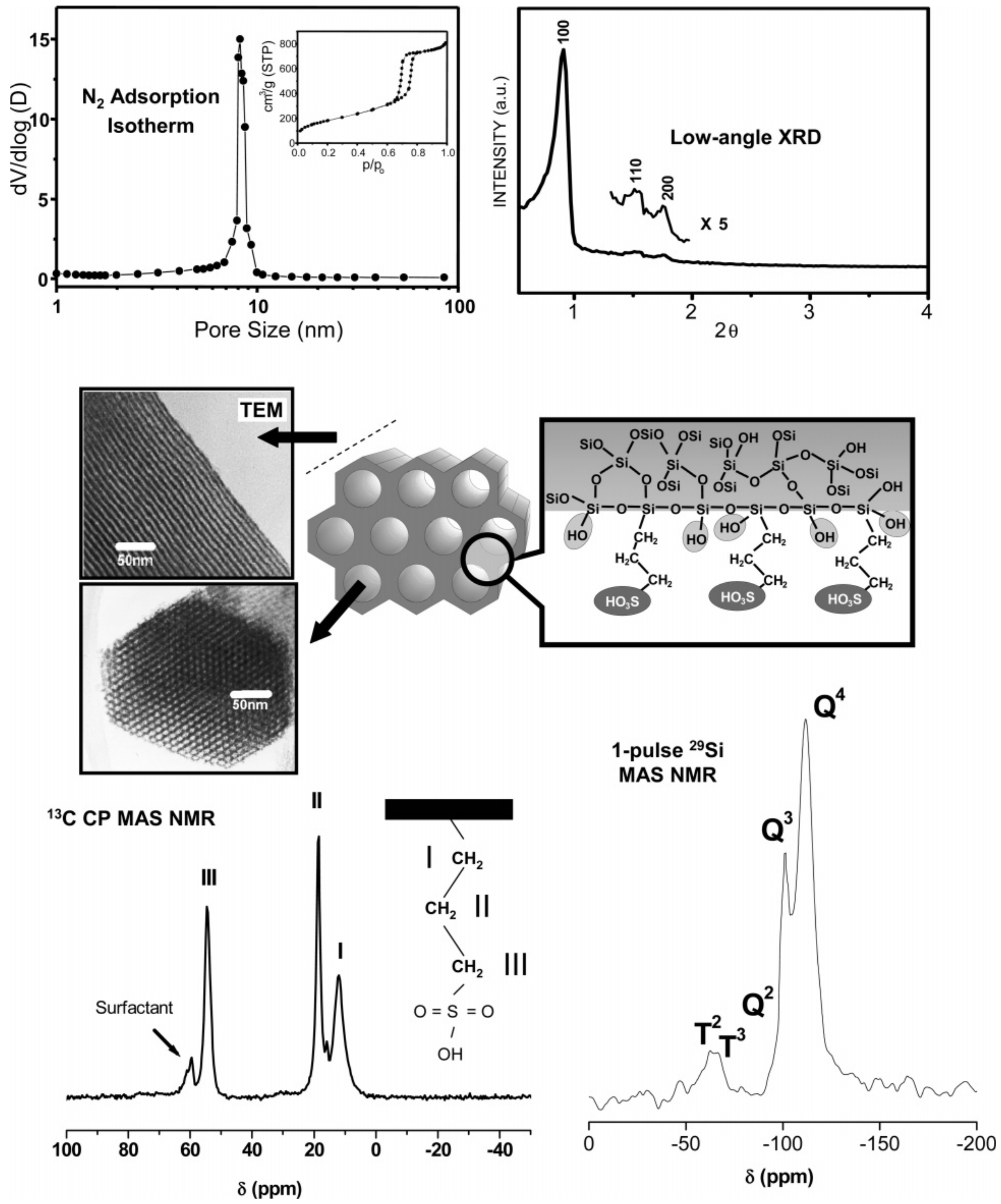


Figure 3. Propylsulfonic-acid-modified SBA-15 material synthesized by means of an in-situ oxidation procedure.

temperature promotes higher pore sizes. Upon different hydrothermal aging treatments and in the presence of swelling agents the pore size was tailored from 30 to 110 Å.

3. Propylsulfonic-Modified Mesostructured Materials as Catalysts for Acid-Catalyzed Reactions

This section will focus on pioneering applications of this novel propylsulfonic-modified mesostructured material in diverse acid-catalyzed reactions and their advantages in comparison to conventional homogeneous and heterogeneous acid catalysts.

3.1. Preparation of Monoglycerides through Esterification Reactions

Monoglycerides are valuable chemical products with wide application as emulsifiers in food, pharmaceutical, and cosmetic industries. European consumption of these esters can be estimated in 1 × 10^5 t per year. There are two industrial routes for the synthesis of monoglycerides:[35,36] transesterification of triglycerides with glycerol at high temperatures in the presence of basic catalysts (glycerolysis) and direct esterification of glycerol with fatty acids (Figure 4). Approximately 80% of the manufacturing processes use conventional acid catalysts such as sulfuric, phosphoric, or organosulfonic acids. The main drawback of these processes is that mixtures of mono-, di-, and triglycerides are generally obtained, so additional separation steps are needed. Another disadvantage of the processes is generation of chemical waste due to catalyst removal. Hence, development of appropriate solid acid catalysts and selection of favorable reaction conditions are highly desirable to improve the monoester selectivity.

Zeolites have been widely tested in this reaction with the purpose of increasing selectivity toward the monoderivative compound, taking advantage of the shape selectivity effect. This type of catalyst has been shown to be efficient for relatively small substrates, but its performance with bulky fatty acids is poor.[37] Even large pore 12-membered ring zeolites have shown lower activities than those expected.[38−40] Synthesis of sulfonic-modified mesostructured materials containing Brönsted-acid sites and large and uniform pores allowed a systematic exploration of their performance as catalysts for fatty acid esterification of glycerol. The first report on the use of these novel materials for polyol esterification stressed the benefits of this new type of catalyst on conversion and selectivity, specifically in the esterification of sorbitol with lauric acid.[22]

Jacobs et al.[41] reported the synthesis of monolaurin via direct esterification of glycerol with lauric acid over propylsulfonic-acid MCM-41 and HMS materials prepared by means of different strategies of synthesis (grafting, coating, and co-condensation). Sulfonic-modified mesostructured materials were far more active than H-USY zeolite and even more active than commercial sulfonic-acid resins, such as Amberlyst-15, in the esterification of glycerol with lauric acid (385 K, glycerol:lauric acid = 1:1, 5 wt % catalyst). Moreover, these materials gave the highest monoglyceride yield as compared with H-USY zeolite, Amberlyst-15, and homogeneous *p*-toluenesulfonic-acid catalysts. The mesostructured catalyst was reused, and conversion and selectivity to monoglyceride remained indistinguishable from those of the fresh catalyst. These results demonstrated beyond any doubt that the observed activity was not a contribution of leached sulfonic-acid groups. They concluded that sulfonic-modified mesostructured materials offered a unique combination of high activity and selectivity not achievable with homogeneous or traditional heterogeneous catalysts. Likewise, using the same catalysts they tested various polyols (1,2-propanediol, 1,3-propanediol, meso-erythritol) and acids (lauric and oleic acid). It is important to note that glycerol and lauric acid are immiscible, and their mutual selectivities are low. As soon as the esterification reaction gives enough emulsifying monoglycerides, an emulsion is formed. Therefore, the hydrophobicity of the catalyst is an important factor since its distribution between phases leads to preferential formation of products.

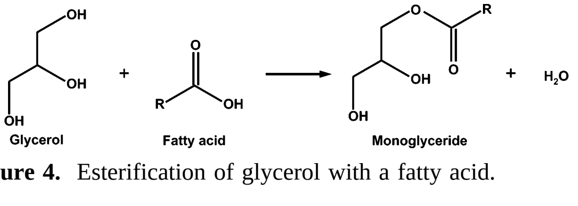


Figure 4. Esterification of glycerol with a fatty acid.

Pérez-Pariente et al. extensively studied the same esterification reaction over optimized propylsulfonic-modified mesoporous materials.[24,27,28,30] The authors showed that propyl-SO_3H-MCM-41 materials synthesized using mixtures of cationic surfactants[27] improved the selectivity toward monoglycerides in the esterification of glycerol with fatty acids as compared with standard materials due to the better pore arrangement of these catalysts. Furthermore, the same research group investigated the catalytic activity of propylsulfonic-modified MCM-41 materials synthesized using mixtures of cationic and neutral surfactants[28] in the esterification of glycerol with lauric acid. The catalyst exhibited an acid conversion of 90% with selectivity to the monoester of 75% after 24 h of reaction. In contrast, the propyl-SO_3H MCM-41 synthesized in the absence of amine gave selectivity as low as 40% with an acid conversion of 96%. Both works clearly showed that a judicious mixture of surfactants provides sulfonic-acid-bearing MCM-41 catalysts with clear improved catalytic properties for the esterification reaction as compared with the conventional single-surfactant synthesis process.

Due to the relatively bulky molecules involved in the esterification process, Pérez Pariente et al. proposed the use of other mesoscopic structures with a larger pore size than MCM-type materials for this reaction.[24,30] Particularly, SBA-15 structure[8,9] has a hexagonal arrangement of channels with pore sizes much larger than MCM-41, which makes this material attractive for fatty acid esterification with glycerol. Additionally, structures having intersecting channels such as SBA-12[42] and SBA-2[26] topologies would be desirable also with the purpose of enhancing the diffusion of reactants and products. Accordingly, these mesoscopic structures were functionalized with propylsulfonic-acid groups by means of a postoxidation procedure and tested in the esterification of glycerol with oleic acid.[24,30] The catalytic results showed that the turnover number (TON) for MCM-41 materials is higher than those corresponding to the new topologies. For SO_3H-SBA-15, the low TON value was attributed to the presence of sulfonic groups located in structural micropores of the silica walls whose occurrence has been reported by several authors.[43−46] In this case, the esterification reaction would be extremely hindered as it occurs when using zeolites, influencing on the overall TON. Low activity in SO_3H-SBA-12, even lower than that observed in SBA-15 material, was related to the small size of the windows that interconnect the large cavities. Finally, SBA-2 topology showed close activity to the blank reaction. This result was consistent with the severe pore blocking of the structure as a consequence of the high population of stacking faults detected in this material.[25,26] Besides, the pore size of SBA-15 and SBA-12 seems to be too large for significant shape-selectivity effects in the esterification reactions.

Shanks et al. further investigated the catalytic performance of propylsulfonic-modified mesoporous materials in the esterification of free fatty acid in oil with methanol to produce methyl esters.[47] The goal of the research was the use of such catalysts for the esterification of free fatty acids present in oil feeds used as raw materials for the manufacturing of biodiesel fuel. The high content of free fatty acids in the feed to be transesterified needed to be reduced up to 0.5 wt % to avoid subsequent processing problems. The authors studied the catalytic behavior of propyl-SO_3H SBA-15 and HMS materials in the esterification of palmitic acid with methanol in a model mixture containing 15 wt % of this acid in a refined soybean oil. The catalytic activity was compared with commercial catalysts such as sulfuric acid (homogeneous) and sulfonic resins (Nafion NR 50 and Amberlyst-15). Catalytic studies were carried out at 85 °C with a methanol to palmitic acid weight ratio of 20:1 and catalyst concentration of 10 wt % (except 5 wt % for H_2SO_4). Among the functionalized mesoporous silicas, propyl-SO_3H SBA-15 (acid capacity of 1.4 meq H^+ per gram and mean pore diameter of 35 Å) catalyst gave higher catalytic activity than propyl-SO_3H HMS (acid capacity of 0.6 meq H^+ per gram and mean pore diameter of 22 Å) with palmitic acid conversions of 85% and 55%, respectively, after 3 h of reaction. The higher activity of propyl-SO_3H SBA-15 was consistent with larger number of acid sites and pore diameter. In contrast, despite its high acid capacity Amberlyst-15 gave a conversion of only 40% and Nafion yielded a conversion of 70%. Hence, propyl-SO_3H SBA-15 afforded higher removal of palmitic acid than sulfonic resins, although less than with the homogeneous H_2SO_4 catalyst (almost complete conversion after 3 h of reaction).

Work described in the literature clearly indicates that propylsulfonic-modified mesostructured materials can be used as active catalysts for the selective esterification of glycerol with fatty acids with comparable and even superior catalytic performances to those observed in conventionally used homogeneous and heterogeneous acid catalysts.

3.2. Condensation and Addition Reactions

Several works have reported use of these propylsulfonic-modified mesostructured materials in condensation and addition reactions. In this section a review of the most remarkable results will be presented.

The catalytic properties of these materials have been tested in the synthesis of 2,2-bis(5-methylfuryl)propane (DMP) by hydroxyalkylation−condensation of methylfuran (MF) with acetone (Figure 5).[20,22] MCM-type materials functionalized with alkylsulfonic-acid groups combined a remarkable DMP selectivity (in most cases up to 95%) with outstanding acetone conversion. No formation of products coming from aldol condensation of acetone was detected, and electrophilic aromatic substitution of the highly reactive MF with acetone prevailed. These materials surpassed the DMP yield of H-beta zeolite and sulfonic-modified nonordered amorphous silica.

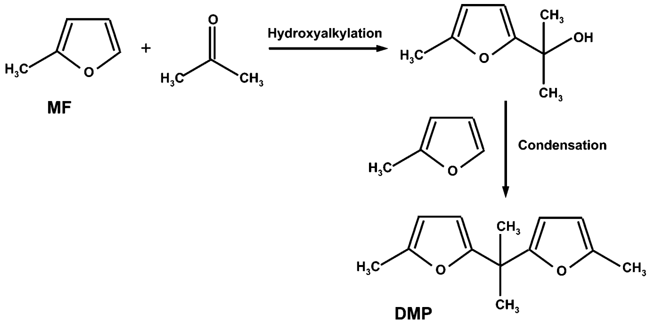


Figure 5. Synthesis of 2,2-bis(5-methylfuryl)propane (DMP) by hydroxyalkylation−condensation of methylfuran (MF) with acetone.

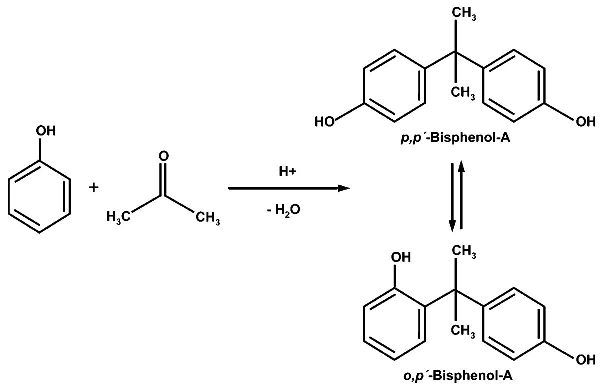


Figure 6. Synthesis of Bisphenol A.

Table 1. Synthesis of Bisphenol A for Different Catalysts (Data Adapted from *J. Catal.*, *223*, Das, D.; Lee, J. F.; Cheng, S., p 152, Copyright 2004, with Permission from Elsevier)[a]

catalyst	T, °C[b]	Si/Al	acid capacity, mmol H^+ [g sample]$^{-1}$	X_{Ph}[c]	$S_{p,p'-Bisphenol A}$[d]
blank	70				
H-beta	70	50		5.2	52.8
HY	70	11		6.8	
HZSM-5	70	80		2.7	9.9
propyl-SO_3H-MCM41	70		1.1	29.6	91.7
propyl-SO_3H-MCM41[e]	70			17.0	90.0
propyl-SO_3H-MCM41	100		1.1	35.3	88.6
propyl-SO_3H-MCM41	125		1.1	38.2	84.5
propyl-SO_3H-MCM41	150		1.1	38.6	81.4
amberlite-120	70		4.4	35.3	89.2
amberlite-120	100		4.4	38.0	85.0

[a] Reaction time 24 h, and phenol to acetone molar ratio of 5. [b] Reaction temperature. [c] Phenol conversion (maximum achievable conversion of 40%). [d] Selectivity toward *p,p*′-Bisphenol A. [e] Incomplete oxidation of thiol sites determined by XANES.

Sulfonic-acid-functionalized mesoporous MCM-41 silica has been also used as a convenient catalyst for Bisphenol A synthesis.[48,49] Bisphenol A is a very important raw material for the production of epoxy resins and other polymers industrially manufactured through the acid-catalyzed condensation reaction of phenol and acetone (Figure 6). Conventional exchange resins are used worldwide to produce this product, whereas use of mineral acid catalysts is avoided due to their corrosive nature. Sulfonic-modified ion-exchange resins, like Amberlyst-15, yield good activity with selectivities to the desired *p,p*′ isomer of about 90%.[50] However, low thermal stability and loss of active species in the reaction medium are serious problems. Therefore, important research efforts are addressed to develop solid and thermally stable catalysts for Bisphenol A synthesis.

Solids catalysts such as heteropolyacid ($H_3PW_{12}O_{40}$) encapsulated in MCM-41 were reported to be active for Bisphenol A synthesis.[51] However, these catalysts needed temperatures of over 120 °C, and hence, formation of byproducts such as alkylated phenols and chroman was favored, leading to a decrease of selectivity toward Bisphenol A. Likewise, these materials have shown heteropolyacid leaching for high loaded samples. In this context, Das et al.[48] first reported that acid-functionalized MCM-41 materials were very effective for Bisphenol A synthesis at a relatively low reaction temperature. Table 1 compares the catalytic activity of a propylsulfonic-modified MCM-41 material with different microporous acid zeolites and a commercial sulfonic-acid resin Amberlite-120 in the synthesis of Bisphenol A at 70 °C.[49] Acidic zeolites showed negligible conversion due to pore-size constraints, which also lead to formation of undesired oligomeric products. Propyl-SO_3H MCM-41 yielded about 30% of phenol conversion with more than 90% selectivity toward the desired isomer. Although Amberlite-120 gives apparently higher phenol conversion (ca. 35%), its acid capacity is four times that of the mesostructured

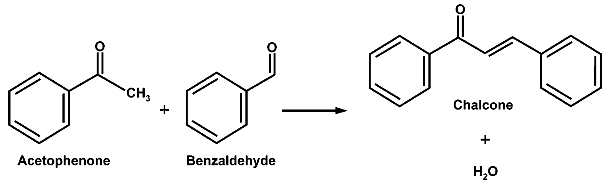


Figure 7. Condensation reaction of benzaldehyde and acetophenone.

material. Both catalysts are close to the maximum achievable phenol conversion (40%) at a phenol/acetone molar ratio of 5. Moreover, over propyl-SO_3H MCM-41 just the *p,p* isomer was detected, the presence of byproducts such as chroman and trisphenols being negligible. Increasing the reaction temperature up to 150 °C yielded a phenol conversion of ca. 39%, almost the maximum value achievable. However, selectivity toward the *p,p′*-Bisphenol A dropped continuously with temperature as a consequence of byproduct formation. Interestingly, at 100 °C phenol conversion of propyl-SO_3H MCM-41 and Amberlite-120 are very close. Elemental analysis of the used sulfonic-modified mesostructured catalysts showed that leaching of sulfur species during the course of reaction was negligible, evidencing the high stability of acid sites. The authors also reported that optimization of thiol oxidation in the preparation of sulfonic-modified materials is essential to achieve high catalytic activities. Samples with incompletely oxidized sulfur species such as sulfides and disulfides yielded much lower activities (see data in Table 1). In conclusion, propylsulfonic-acid MCM-41 materials are active and selective catalysts for the synthesis of *p,p′*-Bisphenol A at relatively low reaction temperatures.

The versatility of these sulfonated mesostructured catalysts has been also explored in the Claisen−Schmidt condensation of acetophenone with benzaldehyde, which is conventionally catalyzed by HCl, $AlCl_3$, or BF_3 (Figure 7). Wilson et al.[33] reported acetophenone conversions over propyl-SO_3H HMS materials superior to those observed in zeolites in similar reaction conditions (150 °C and equimolecular amounts of reactants). The acetophenone conversion for SO_3H HMS catalyst was ca. 30% after 6 h, significantly higher than that obtained using HY zeolite as catalyst, which offered only 12% conversion in similar reaction conditions but using a higher catalyst-to-substrate ratio. Moreover, the organosulfonic mesostructured materials led selectively to formation of chalcone without evidence of undesired byproducts.

Propylsulfonic-functionalized FSM-16 mesoporous silica (SO_3H−FSM) has been also tested in the acetalization of carbonyl compounds with ethylene glycol.[52] SO_3H FSM material was more effective than conventional acid solids such as SiO_2-Al_2O_3, acid zeolites, montmorillonite, and Amberlyst-15 in the acetalization of acetophenone with ethylene glycol. The rate per acid site for SO_3H FSM catalyst was ca. 10 fold higher than that of the sulfonic-acid resin and large-pore zeolites and 2 orders of magnitude higher than medium-pore size acid zeolites. The high catalytic performance of the sulfonic-acid mesostructured material was attributed to the presence of strong Brönsted-acid sites, determined by NH_3 calorimetric adsorption at 150 °C, which are located on mesopores with relatively low hydrophilicity where both reactants and products can smoothly access the acid sites. The authors expanded the method for the acetalization of a wide range of ketones and aldehydes with ethylene glycol, obtaining high conversions and yields of the corresponding 1,3-dioxolane (Table 2). Likewise, the SO_3H FSM catalyst was stable during the reaction without evidence of leaching and deactivation of sulfonic-acid sites and reusable several times.

3.3. Alcohols Coupling to Ethers

Kinetic analysis suggests that the mechanism of alcohol coupling is a S_N2 pathway involving competitive adsorption of reactants on proximal Brönsted-acid sites.[53] Thus, a large-pore silica material with internal strong acid sites, high surface area, large void space, and thermal stability is expected to effectively catalyze ether formation. Therefore, Klier et al. prepared alkylsulfonic-acid SBA-15 materials and used them in the synthesis of unsymmetrical ethers (Figure 8).[54] The catalytic tests were carried out in a continuous down-flow reactor at a temperature range from 115 to 250 °C, with a methanol:isobutanol molar ratio varying from 1 to 2 and total pressure from 101.3 to 4.2×10^3 kPa. The reaction products after reaction were methyl isobutyl ether (MIBE, a high cetane compound), secondary ethers such as dimethyl ether (DME) and methyl *tert*-butyl ether (MTBE), and butenes (mainly isobutene but also including *n*-butene and *cis*- or *trans*-2-butene).

The catalytic tests over propyl-SO_3H SBA-15 materials under different reaction conditions were carried out for 8−12 h, and no deactivation was observed in long-term tests of several hundred hours. The rate of product formation is enhanced with increasing temperatures, but selectivity toward butenes formation rapidly increased at higher temperatures, leading to lower ether selectivity (MIBE and DME), as presented in Table 3. SO_3H SBA-15 catalyst at 125 °C yielded a clear enhancement of MIBE formation as compared with conventional acid solid catalysts such as SiO_2/Al_2O_3 or montmorillonite. Furthermore, butenes were not detected over SO_3H SBA-15 at 125 °C as compared with the significant amounts obtained for SiO_2/Al_2O_3, montmorillonite and ZrO_2/SO_4 catalysts. Although SO_3H SBA-15 catalyst was superior among the different inorganic acid catalysts in ether formation, its catalytic activity was lower than that of polymeric acid resin catalysts (Amberlyst-35 and Nafion-H). However, SO_3H SBA-15 catalyst showed selectivity to ether formation of close to 100% (MIBE and DME) below 125 °C, appreciably higher than that observed for the sulfonic-acid resins (66−79% ether selectivity) at the same temperature. Furthermore, among the ether products, SO_3H SBA-15 catalyst favored MIBE formation at 115 °C, whereas sulfonic-acid resins favored formation of DME compound in special Amberlyst-35 resin catalyst.

Propylsulfonic-acid groups bonded onto SBA-15 mesoporous silica effectively catalyzes the alcohol coupling reaction toward MIBE and DME with high selectivities to the former for temperatures below 125 °C and moderate pressures. The material exhibited superior catalytic performance over inorganic acid solid catalysts and polymeric sulfonic-acid resins. The propylsulfonic-acid groups anchored on the pore walls are stable and maintain their activity and selectivity after prolonged reaction times.

The same research group further investigated the catalytic performance of these acid materials in this particular reaction,

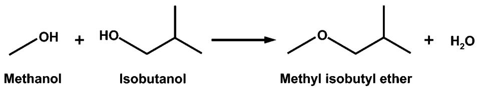
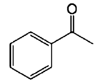
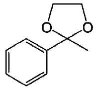
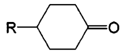
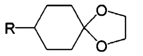
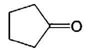
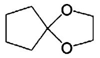
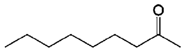
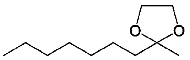
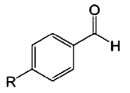
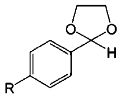
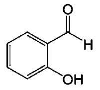
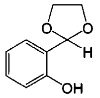
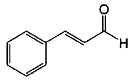
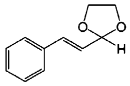
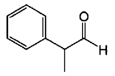
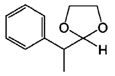
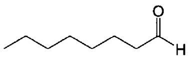
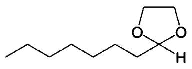
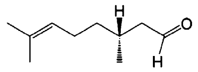
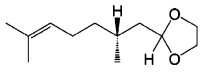


Figure 8. Coupling of methanol and isobutanol to methyl isobutyl ether.

Table 2. Catalytic Results of the Acetalization of Carbonyl Compounds over SO_3H FSM Catalysts (Data Reprinted from *J. Catal.*, *231*, Shimizu, K.; Hayashi, E.; Hatamachi, T.; Kodama, T.; Higuchi, T.; Satsuma, A.; Kitayama, Y., p 131, Copyright 2005, with Permission from Elsevier)[a]

Entry	Substrate	Time	Product		Conversion[b] (%)	Yield[c] (%)
1 2		10		R = H	96	93
3 4		3 1		R = H R = Bu^t	99 98	90 89
5		3			99	88
6		3			91	91
7 8 9		1 1 12		R = H R = Cl R = OCH_3	99 98 97	90 94 80
10		12			77	74
11		8			84	81
12		2			99	99
13		3			99, 98[d], 99[e], 98[f]	99, 97[d], 98 [e], 96[f]
14		1			93	88

[a] The reaction was performed by refluxing the mixture of carbonyl compound (5 mmol) and ethylene glycol (6 mmol) in toluene (5 mL) with a catalyst (0.1 mol %, 7 mg) in air. [b] Conversion of carbonyl compounds determined by GC using internal standard method. [c] Yield of acetals determined by GC. [d] Second cycle. [e] Third cycle. [f] Fourth cycle.

Table 3. Catalytic Results of the Etherification of Isobutanol with Methanol over SO_3H SBA-15 Catalyst (Data Adapted with Permission from Ref 54. Copyright 2002 American Chemical Society)[a]

catalyst	T, °C[b]	production, mol (kg cat)$^{-1}$ h^{-1} MIBE	DME	MTBE	butenes	ethers selectivity (%)
SO_3H SBA-15	115	0.014	0.006			100
Nafion-H	115	0.058	0.040		0.026	79
Amberlyst-35	115	0.082	0.337	0.009	0.218	66
SO_3H SBA-15	125	0.020	0.009			100
$SiO_2-Al_2O_3$	125	0.011	0.007	0.001	0.028	40
montmorillonite	125	0.008	0.008		0.008	67
ZrO_2/SO_4	125	0.020	0.006	0.003	0.067	30
SO_3H SBA-15	150	0.023	0.013		0.053	40
SO_3H SBA-15	175	0.033	0.018		0.125	29
SO_3H SBA-15	200	0.041	0.026		0.198	25
SO_3H SBA-15	225	0.053	0.037		0.322	23
SO_3H SBA-15	250	0.074	0.067		0.551	20

[a] Molar ratio of methanol to isobutanol of 1 with flow rates of 3.4 and 16 mol (kg cat)$^{-1}$ h^{-1} for alcohols and carrier gas at 101.3 kPa of total pressure. [b] Reaction temperature.

probing the mechanistic pathway and reaction intermediates involved in the condensation/dehydration of mixtures of alcohols to form ethers and olefins.[55] The authors concluded that low temperatures and elevated pressures should be used for enhancement of ether formation. Low reaction pressures preferentially favor adsorption of isobutanol on the acid sites, yielding predominantly isobutene by dehydration. As the pressure increased, adsorption of methanol and production of ethers are enhanced at the expense of isobutene formation.

4. Hydrophobicity Control of Pore Surface in Organosulfonic-Modified Mesostructured Materials

The hydrophilic/hydrophobic character of the catalyst's surface should have interesting effects on the adsorption and diffusion of reactants and products within the mesopores and ultimately on controlling the surface reactivity of these acid materials. Moreover, most solid acids are poisoned by water in reactions where this highly polar molecule is involved as reactant, product, or even solvent. Thus, the hydrophobitization of the acid sites microenvironment is an important challenge to reduce poisoning by water molecules. One can expect that the adjustment of sulfonic-modified catalyst hydrophobicity to that required for balancing the differences in polarity of the reactants and products will probably have strong implications in the catalytic performance.

Stucky et al.[29] found that their innovated in-situ oxidation process was suitable for the simultaneous incorporation of sulfonic-acid groups along with other organic moieties (Figure 9, Route a). For example, sulfonic-acid mesoporous surfaces mixed with benzyl and methyl groups were prepared; the co-incorporation of both functionalities did not modify the acid capacity, similar to that of the monofunctionalized sulfonic-acid material. XRD and nitrogen adsorption analyses showed that the hybrid mesoporous materials exhibited a good mesoscopic order.^{13}C CP/MAS NMR of the bifunctional materials confirmed the presence of both sulfonic-acid groups and benzyl or methyl moieties. No catalytic results were reported.

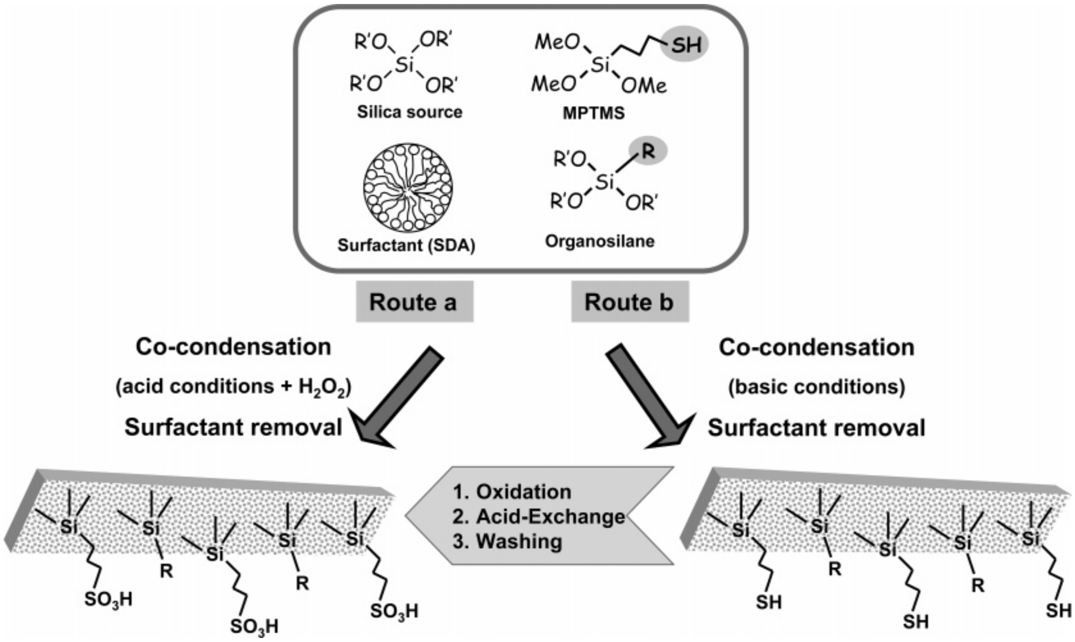


Figure 9. Co-incorporation of organic functionalities with sulfonic groups on the silica surface.

Table 4. Catalytic Activity and Selectivity of Methylated SO_3H MCM-41 Materials in the Esterification of Fatty Acids with Glycerol (Data Reprinted from *Appl. Catal., A: Gen., 242*, Díaz, I.; Mohino, F.; Pérez-Pariente, J.; Sastre, E., p 161, Copyright 2003, with Permission from Elsevier)[a]

	lauric acid, 100 °C				oleic acid, 120 °C			
sample	TON	X^b	$S_{ML}{}^c$	$S_{50ML}{}^d$	TON	X^b	$S_{MO}{}^c$	$S_{50MO}{}^d$
S-1[e]	6.0	85	59	77	5.0	89	40	65
S-2[f]	3.8	45	77	76	2.0	30	74	60

[a] LA: lauric acid. OA: oleic acid. [b] Fatty acid conversion after 8 h of reaction. [c] Selectivity to monoglyceride (wt %) after 8 h of reaction. [d] Selectivity to monoglyceride (wt %) at 50% conversion of fatty acid. [e] Methyl and sulfonic groups in the same silicon atoms. [f] Methyl and sulfonic groups in independent silicon atoms.

Sastre et al.[31] also reported the synthesis of well-ordered MCM-41 materials simultaneously containing alkyl and mercaptopropyl groups by hydrothermal treatment of gels containing a mixture of dodecyl- and hexadecyltrimethylammonium surfactants (Figure 9, Route b). Subsequently, the materials were oxidized with hydrogen peroxide to obtain the corresponding combined alkylsulfonic MCM-41 material. They explored a wide range of synthesis conditions with the purpose of optimizing the alkyl/mercaptopropyl ratio of the solid product, preserving mesoscopic ordering and achieving a maximum content of methyl groups of up to 4.5 meq per gram of material upon removal of the surfactant and oxidation of thiol groups. This research group has extensively explored the surface modeling of these hybrid sulfonic-acid catalysts with the purpose of enhancing the activity and selectivity toward monoglyceride derivate in the esterification reaction of glycerol with fatty acids.[32,56,57] Esterification of glycerol with fatty acids involves interaction of molecules with very different polarities on the catalyst's surface; tuning the hydrophobicity of the sulfonic-acid mesoporous materials should have a significant influence on the catalytic performance. Pérez-Pariente et al. tested methyl-modified SO_3H MCM-41 materials in the esterification of glycerol with lauric and oleic acids.[56] The amount of water adsorbed in the samples clearly decreased as the content of methyl groups became higher, indicating an increase of hydrophobicity. Conversions of lauric acid higher than 90% were obtained after 24 h for samples with the highest methyl content, while less than 20% conversion is attained in the absence of catalyst at the tested reactor temperature. A comparison of the catalysts on the basis of turnover number (TON) after 8 h of reaction clearly indicated that the activity increased by a factor of 3 as the methyl concentration of the catalyst approaches to 2 meq per gram and remains constant for higher contents. Moreover, incorporation of methyl groups enhanced not only the activity but also the selectivity toward the monoglyceride compound. Monolaurin yields of 60% were obtained for the most active and selective materials with acid conversions of ca. 95%, whereas the amount of triderivative was almost negligible. A similar catalytic behavior was obtained for oleic acid, although in this case the selectivity to mono-olein was lower. Combination of propylsulfonic-acid moieties as active centers and methyl groups as hydrophobicity regulators led to catalysts showing outstanding performance in the esterification of glycerol with lauric and oleic acids. They also checked the nature of the alkyl group anchored to the silica surface, either methyl or propyl, on the catalyst activity and selectivity.[56] Catalytic results showed that TONs for both catalysts were very similar, in agreement with their similar hydrophobic character. Nevertheless, the methylated catalyst was more selective toward the monoderivative than propyl-containing material. Following tuning the hydrophobicity character of the sulfonic-modified MCM-41 materials, the same research group synthesized materials with both methyl and sulfonic-acid groups anchored to the same silicon atom using methylmercaptopropyl silane as precursor in the presence of the amino-acid leucine as a co-structuring agent.[57] The presence of leucine enhances the oxidation of thiol groups but reduces the average pore size. The new methylated SO_3H MCM-41 catalyst obtained upon mild oxidation of thiol groups was tested in the esterification of glycerol with lauric and oleic acids (Table 4). The catalytic results showed that the turnover of the catalyst containing the new functionalized silane (S-1 sample in Table 4) is higher than that of the samples containing methyl and sulfonic-acid groups on independent Si atoms (S-2 sample in Table 4). The authors attributed the improvement of the catalytic activity to the presence of the hydrophobic group ($-CH_3$) bonded to the silicon atom where the propylsulfonic-acid group was also anchored, which leads to better adsorption of reactants on the catalyst. In contrast, this hydrophobic effect is lower in S-2 sample, since the methyl groups in this material are not randomly distributed over the pore surface, probably due to segregation phenomena during the co-condensation of organosilane precursors.[31]

The appropriate surface modification allows catalyst's design to meet the requirements of the esterification reaction (adequate lipophilic−hydrophilic balance). The presence of different functional groups to alter the hydrophobicity of the cavity surrounding the sulfonic-acid sites enormously expands the capabilities of the catalyst for this particular reaction and future catalytic applications.

5. Tuning the Acid Strength of Anchored Sulfonic-Acid Sites: Expanding the Catalytic Applications of Organosulfonic-Modified Mesostructured Materials

Heterogeneously catalyzed chemical reactions are dramatically influenced by the strength of acid sites, which determines the rate of the reaction and in some cases the feasibility of the catalytic process. The chance to tune the acid strength of sulfonic-acid groups by close attachment of different functionalities might enlarge the potential catalytic applications of this type of material.

5.1. Arenesulfonic-Acid Groups Anchored onto Mesostructured Materials

The presence of electron-withdrawing species close to the sulfonic group is expected to increase the acid strength of the acid sites in comparison to other low-electron-withdrawing environments such as methylene groups. In this sense mesostructured materials functionalized with arenesulfonic groups similar to those found in commercial sulfonated Amberlyst-15 resins have been reported.[58−60] Lindlar et al.[58] reported the synthesis arenesulfonic-modified MCM-41 materials with pore diameters up to 60 Å using swelling agents. The synthesis strategy was based on grafting of phenyl groups to the silica surface and subsequent sulfonation with chlorosulfuric acid. The postoxidative treatment clearly damaged the textural properties of the material, leading to a clear reduction of the surface area. No catalytic studies were reported in this work.

In a similar approach, Singh and co-workers[59] functionalized mesoporous zirconium hydroxide (Zr−TMS) with benzylsulfonic-acid groups using a postsynthesis route without destroying the mesoporous structure (Figure 10). Solids with acid capacities up to 1.2 mmol per gram, determined by ammonia adsorption/desorption studies in the temperature range 30−200 °C, were obtained with high mesoscopic ordering. The catalytic activity of the synthesized materials was examined in the benzoylation of diphenyl ether (DPE) with benzoyl chloride (BC) to yield 4-phenoxybenzophenone (4-PBP) at 160 °C using nitrobenzene as solvent. Sulfonic-modified Zr−TMS catalyst showed DPE conversion of ca. 60% along with 100% selectivity toward 4-PBP after 0.5 h of reaction time starting from an equimolar mixture of DPE and BC. At identical reaction conditions, amorphous sulfonated zirconia yielded only 5% of DPE conversion.

Due to the good results obtained in the preparation of periodic ordered alkanesulfonic-functionalized mesostructures using the one-step direct synthesis with in-situ oxidation previously reported,[29] Melero et al.[60] used the same route for the preparation of ordered SBA-15 materials containing arenesulfonic-acid groups. The synthesis strategy involved the co-condensation of TEOS and 2-(4-chlorosulfonylphenyl)-ethyltrimethoxy silane (CSPTMS)) using Pluronic 123 as template under acidic conditions. Hydrolysis of the chlorosulfonyl groups ($-SO_2Cl$) to the corresponding sulfonic-acid groups is achieved under acidic condensation conditions. Direct synthesis procedure allowed the effective anchoring of arenesulfonic groups on the pore surface of SBA-15 mesostructured materials (Figure 11). The resultant materials showed large uniform pore sizes (ca. 60 Å) with large surface areas (ca. 650 m^2/g), good mesoscopic ordering, and thick walls, leading to hydrothermally stable materials. The acid centers displayed excellent thermal resistance and significant stability against leaching in aqueous and organic medium. No disulfide species were detected, as confirmed by ^{13}C CP MAS NMR (Figure 11). Solid acidity of the synthesized arenesulfonic-acid material was characterized by means of ^{31}P NMR of chemisorbed triethylphosphine oxide and compared with other acid solids. The arenesulfonic SBA-15 material presented ^{31}P NMR signal shifts toward higher values in comparison to those obtained for alkylsulfonic-acid sample, confirming enhancement of the acid strength due to the presence of an electron-withdrawing substituent adjacent to the sulfonic-acid groups, such as the benzene ring.

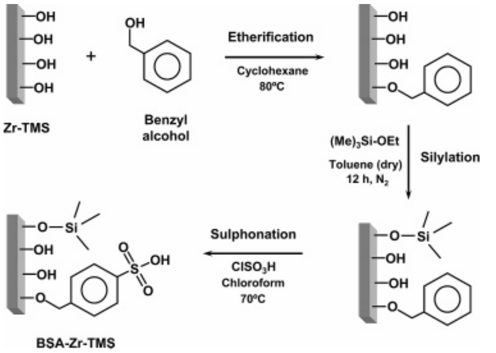


Figure 10. Preparation of mesostructured benzylsulfonic-functionalized Zr−TMS materials (Reprinted from *Catal. Today*, *97*, Parambadath, S.; Chidambaram, M.; Singh, A. P., p 233, Copyright 2004, with permission from Elsevier).

The catalytic benefit of arenesulfonic-modified SBA-15 with respect to propylsulfonic-modified SBA-15 and other acid catalysts has been readily demonstrated in some reactions. Shanks et al.[47] reported that the apparent reactivity (defined as the average turnover rate per total number of acid sites) of arenesulfonic-modified SBA-15 materials in the esterification of fatty acids with methanol to produce methyl esters was significantly higher than that shown by Nafion and propylsulfonic-functionalized SBA-15 and comparable to the homogeneous sulfuric acid. Furthermore, several examples already illustrate the potential of the arenesulfonic-modified SBA-15 materials for catalytic applications in the production of fine chemicals which usually demand higher strength of acid sites.

5.1.1. Friedel–Crafts Acylation of Aromatic Compounds

Friedel−Crafts acylation is one of the most important reactions in organic chemistry for synthesizing aromatic ketones, which are important intermediates for the production of fine chemicals. The conventional stoichiometric catalysts

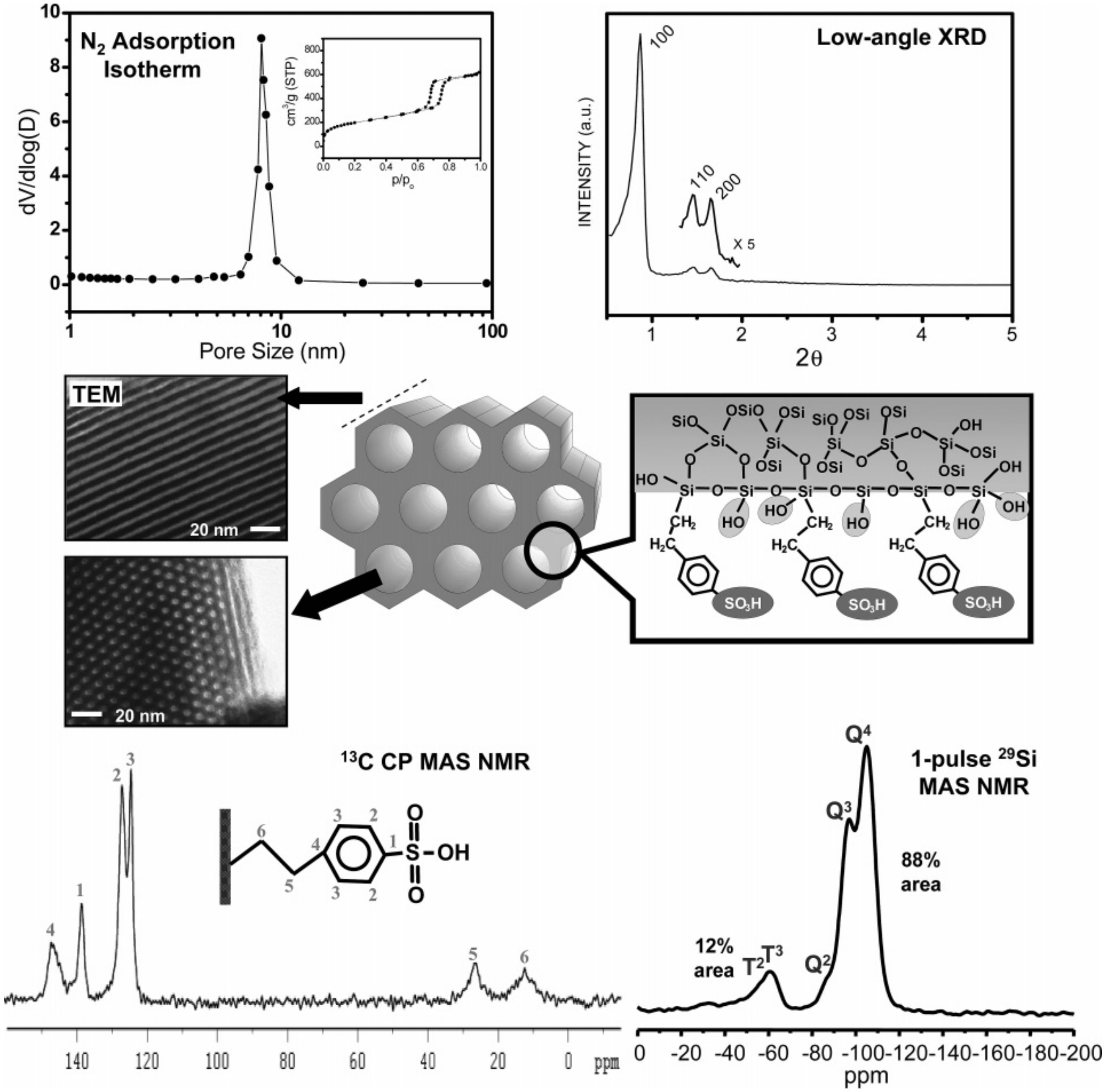


Figure 11. Physicochemical properties of arenesulfonic-acid-modified SBA-15.

traditionally used, e.g., $AlCl_3$, BF_3, or HF, have serious drawbacks. In this context, heterogeneous catalysts seem to be an attractive alternative to the homogeneous catalytic reaction. Mainly zeolites, exchanged clays, Nafion/silica composites, and even graphite have been tested as heterogeneous acylation catalysts over different substrates and using a wide range of acylating agents.[61]

Melero et al. recently described the catalytic performance of arenesulfonic-modified SBA-15 materials (Ar$-SO_3H$) for acylation processes.[62] The activity of this material has been compared with other conventional acid solid catalysts as well as with propylsulfonic-modified SBA-15 materials (Pr$-SO_3H$) in the acylation of anisole in the presence of anhydride acetic as acylating agent in solventless conditions (Figure 12). Table 5 summarizes the catalytic results obtained with the different catalysts tested.

Arenesulfonic-containing SBA-15 showed higher absolute anisole conversion than that obtained with conventional acid zeolites. Specific catalytic activity (TON values) for Ar$-SO_3H$ SBA-15 was superior to that found for Amberlyst-15, which could be related to the low accessibility of the acid sites arising from the low specific surface area of the latter. Propylsulfonic-modified SBA-15 materials gave low activity, evidencing the crucial role of the aromatic ring attached close to the sulfonic-acid group to reach the necessary acid strength for this particular reaction. *p*-Toluenesulfonic-acid homogeneous catalyst evidenced very poor activity as compared to its heterogeneous counterpart. Confinement of the arenesulfonic-acid groups within the mesoporous structure of the SBA-15 material led to enhancement of the activity of the acid sites as compared with the homogeneous catalyst. The authors also demonstrated the

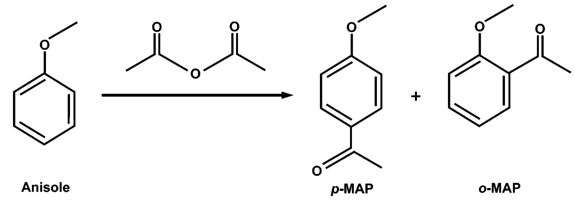


Figure 12. Reaction scheme of anisole acylation with acetic anhydride.

Table 5. Acylation of Anisole at 125 °C and Solventless Conditions (Data Adapted from *Catal. Commun.*, *5*, Melero, J. A.; van Grieken, R.; Morales, G.; Nuño, V., p 131, Copyright 2004, with Permission from Elsevier)[a]

catalyst	acid capacity, mmol H^+ [g sample]$^{-1}$	Si/Al	X_{anisole},[b] %	TON[c]	*p*-selectivity,[d] %
SBA-15	0.0		0.0	0.0	
Ar-SO_3H SBA-15	1.1		24.0	79.0	95.2
Ar-SO_3H SBA-15	1.7		35.0	77.0	95.5
Pr-SO_3H SBA-15	1.0		1.0	2.7	95.4
Amberlyst-15	4.8		57.8	43.0	95.7
beta-zeolite		100	16.2		100.0
H-ZSM-5		30	17.2		97.1
homogeneous[e]				0.1	100.0

[a] Reagents: anisole (185 mmol), acetic anhydride (196 mmol), and catalyst (0.5 g). [b] Absolute anisole conversion after 3 h. [c] Turnover number defined as mmol of converted anisole per mmol of sulfonic group after 3 h of reaction. [d] Selectivity toward *p*-methoxyacetophenone. The other product detected in the liquid phase was the *o* isomer. [e] *p*-Toluenesulfonic acid.

high activity and accessibility of acid sites for these arenesulfonic-modified mesostructured materials even with relatively high acid capacities close to 1.7 mmol H^+ per gram of catalyst. Recently, Shingh et al.[63] immobilized propylsulfonic-acid groups over amorphous silica at different concentrations and tested the resultant catalyst in the acylation of anisole at 100 °C. Catalytic data showed a maximum conversion of ca. 15% over 40% sulfonic-acid-containing catalyst after 48 h of reaction. Under similar conditions Melero et al.[62] achieved an anisole conversion of ca. 13% in just 3 h of reaction over arenesulfonic-modified SBA-15 with a significantly lower amount of acid centers. This comparison clearly evidences the requirement of relatively strong acid centers to carry out the acylation reaction and the benefit of using mesostructured materials as support.

Melero et al. also reported a complete deactivation of the arenesulfonic-modified SBA-15 materials after 3 h of reaction. Elemental analysis of the catalyst after reaction indicated an increase of carbon content, and therefore, this loss of activity was attributed to catalyst poisoning by strong adsorption of *p*-methoxyacetophenone and polyacylated compounds, as previously reported for zeolites.[64] No leaching of sulfur species during the reaction was detected.

The same research group also studied the catalytic performance of these arenesulfonic-modified SBA-15 materials in the acylation of bulkier aromatic compounds such as 2-methoxy-naphthalene (2MN).[62] This acid-catalyzed reaction yields mainly four isomers:1-acetyl-2-methoxynaphthalene (1), 8-acetyl-2-methoxynaphthalene (2), 3-acetyl-2-methoxynaphthalene (3), and 6-acetyl-2-methoxynaphthalene (4) (Figure 13). Acylation of 2MN (82 mmol) in the presence of acetic anhydride (AA) (molar ratio AA/2MN of ca. 2) at 125 °C in solventless conditions over Ar−SO_3H SBA-15 yielded a substrate conversion of ca. 89% in 3 h with a selectivity value toward isomer 1 of 95%.

The authors concluded that arenesulfonic-modified mesostructured materials possess high activity in acylation processes as compared with other homogeneous and heterogeneous sulfonated acid catalysts. Moreover, this activity is accompanied with negligible leaching of sulfur species. This novel material could constitute a competitive alternative to traditional homogeneous systems conventionally used as catalysts in acylation processes. Moreover, such materials can be interesting alternatives to commercially available sulfonated resins (Amberlyst-15 and Nafion), which have low surface areas and poor thermal stability and are also used in acylation processes. Nevertheless, the catalyst's deactivation limits the reusability of the catalytic system. Finally, their use as catalyst for the acylation of lesser activated aromatic compounds to settle its potential industrial applicability was proposed.

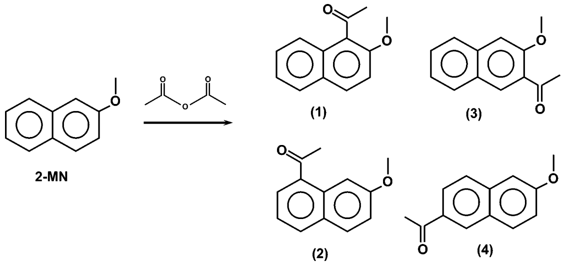


Figure 13. Reaction scheme of 2-methoxynaphthalene acylation with acetic anhydride.

5.1.2. Fries Rearrangement of Phenyl Acetate

The selective Fries rearrangement of aromatic alcohol esters serves as a valuable synthesis step in the production of industrial pharmaceuticals, dyes, and agrochemicals.[65] This reaction involves acylium ion intermediates that are generated from the ester by interaction with an acid catalyst. More specifically, the Fries rearrangement of phenyl acetate (PAc) yields *o*- and *p*-hydroxyacetophenones (*o*-HAP and *p*-HAP), which are valuable precursors in the pharmaceutical industry (Figure 14). *p*-HAP is widely used for the synthesis of paracetamol (4-acetoaminophenol).[66] *o*-HAP is a key intermediate for producing 4-hydroxycoumarin and warfarin, which are both used as anticoagulant drugs in the therapy of thrombotic disease,[67] and it has also been used for the synthesis of flavonones.[68,69]

Conventional homogeneous catalysts such as Lewis acids ($AlCl_3$, complexed BF_3) or mineral acids (HF or H_2SO_4) have been widely used in overstoichiometric amounts for this reaction. HF, which acts as catalyst and solvent simultaneously and is very toxic, corrosive, and volatile (bp 15 °C). Aluminum trichloride is also corrosive and reacts violently with water. Boron trifluoride is very toxic and corrosive and gives a strong reaction with water. Furthermore, the reaction mixture has to undergo a hydrolysis step where contaminated salts and corrosive gases are generated. In this step the conventional homogeneous catalysts are destroyed and cannot be recycled. Replacement of these conventional catalysts by heterogeneous reusable acid catalysts has promoted an important effort in heterogeneous catalysis research, mainly in the field of zeolites. Zeolites[70−75] and other acid heterogeneous catalysts such as the sulfonic-acid resin Nafion[76] have been studied as catalytic systems in the Fries rearrangement of phenyl acetate. Rapid deactivation observed in zeolites, either in the gaseous or liquid phase, evidences the need for a greater size pore system. On the other hand, sulfonic-acid resins such as Nafion or Amberlyst have limited specific surface areas and relatively low thermal

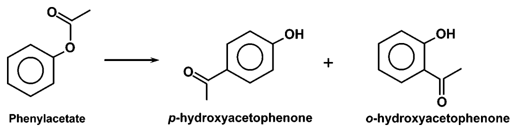


Figure 14. Main reaction products from Fries isomerization of phenylacetate.

Table 6. Fries Rearrangement of Phenyl Acetate over Different Acid Solid Catalysts (Data Adapted from *Appl. Catal.*, *289*, van Grieken, R.; Melero, J. A.; Morales, G., p 143, Copyright 2005, with Permission from Elsevier)[a]

catalyst	acid capacity, mmol H^+ [g sample]$^{-1}$	Si/Al	HAP's production[b] 4 h	HAP's production[b] 24 h	*p*-HAP/ *o*-HAP[c]
Ar-SO_3H SBA-15	1.1		14.8	22.9	2.5
Pr-SO_3H SBA-15	1.0		1.3	2.3	1.2
Ar-SO_3H SiO_2	0.8		4.0	6.4	1.0
Amberlyst-15	4.8		5.8	7.8	2.6
USY-zeolite		3.5	1.7	1.7	1.5
homogeneous[d]	5.3		0.7	4.0	0.3

[a] Reaction conditions: temperature 150 °C; 30 g of PAc; 0.5 g of catalyst; PAc/phenol mass ratio of 3. [b] Millimoles of produced HAP's per mmol of acid center after 4 and 24 h of reaction. [c] Molar ratio of isomers after 4 h of reaction. [d] *p*-Toluenesulfonic acid.

stabilities due to their organic nature. Supporting these sulfonic resins over silica materials with high specific surface has been tested also.[70] Likewise, heteropoly-acid $H_3PW_{12}O_{40}$ has been shown as a novel efficient reusable catalyst for Fries rearrangement of phenyl acetate in homogeneous or heterogeneous liquid-phase systems,[77,78] evidencing the importance of a catalyst with high acid strength to carry out this reaction. Efforts have also been addressed in the field of homogeneous catalysis: methanesulfonic acid[79] has been evaluated as an environmentally friendly catalyst due to its biodegradability, but the high amount of required catalyst (>80 wt %) to obtain acceptable conversion and selectivity reduces the chance of this process to arise as the final alternative.

In this context, Melero et al. described the catalytic behavior of organosulfonic-modified SBA-15 materials in the liquid-phase Fries rearrangement of phenyl acetate using phenol as solvent at 150 °C[60,80] (Table 6). Arenesulfonic-acid SBA-15 catalyst displayed the best performance, reaching a maximum value of 23 mmol of produced HAP's per acid center after 24 h, almost 2.8 times the production obtained with Amberlyst-15 and more than 10 times that obtained with propylsulfonic-acid SBA-15. The apparently limited catalytic behavior displayed by the sulfonic-acid resin might be explained in terms of lower accessibility of the sulfonic-acid sites as well as the possible thermal degradation of its structure. Again, the benefit of arenesulfonic-modified SBA-15 compared to propylsulfonic-modified SBA-15 was readily demonstrated. The acid strength of propylsulfonic-acid groups does not appear to be enough to effectively catalyze the Fries rearrangement of phenyl acetate. Interestingly, Ar−SO_3H SiO_2 showed six times less activity per acid site than Ar−SO_3H SBA-15 sample though both possess similar arenesulfonic-acid groups. It is clear that the mesoscopic ordering favored diffusion of reactant and product molecules in the liquid-phase rearrangement of phenyl acetate. Activity per acid center of homogeneous *p*-toluenesulfonic acid was very low in these conditions. Confinement of the arenesulfonic-acid groups within the mesoporous structure of the SBA-15 material led to an enhancement of the activity of the acid site as compared with the homogeneous catalyst. The authors also reported a catalytic performance for arenesulfonic-acid SBA-15 comparable to that obtained with $H_3PW_{12}O_{40}$ supported on silica.[80]

Clear evidence of catalyst deactivation for all heterogeneous samples after 4 h of reaction was reported. Nevertheless, this activity decay was less pronounced for arenesulfonic-acid SBA-15 material. In the case of zeolite, deactivation occurs after just 1 h of reaction, which confirms that microporous size promotes faster deactivation processes. However, the authors observed that use of dichloromethane as solvent over arenesulfonic-modified SBA-15 material promoted an enhancement of HAP's production and more importantly with slower catalyst's deactivation. Use of dichloromethane for this particular reaction opens a new field of research to be further explored with the purpose of obtaining higher yields on HAP's compounds and increasing the lifetime of the catalyst.

5.1.3. Beckmann Rearrangement

The Beckman rearrangement of cyclohexanone oxime to ϵ-caprolactam is an important reaction in the manufacturing of nylon fibers and resins.[81] Commercial processes use sulfuric acid as catalyst, which has a serious environmental impact. Great efforts in developing solid acids to replace liquid acid processes have been carried out. Cheng et al.[82] studied the catalytic performance of arenesulfonic-acid SBA-15 materials in the liquid-phase rearrangement of cyclohexanone oxime to ϵ-caprolactam (Figure 15).

The authors compared the catalytic activity of Ar−SO_3H SBA-15 using chlorobenzene as solvent with other acid−solid catalysts including Pr−SO_3H SBA-15, zeolites, and aluminum-containing SBA-15 and MCM-41. Both sulfonic-modified materials yielded the highest conversions (ca. 40% after 24 h of reaction at 130 °C), but the selectivity toward ϵ-caprolactam was close to 90% for arenesulfonic-modified sample and just 40% for propylsulfonic-acid SBA-15 catalyst. The arenesulfonic-acid SBA-15 catalyst also yielded better selectivity to the lactam compound than Al−MCM-41 and Al−SBA-15 materials, which gave selectivities of only 13% and 19%, respectively. The authors attributed the significant difference in the selectivity to the high acid strength of the Ar−SO_3H SBA-15 sample. The catalytic performance of the arenesulfonic-acid SBA-15 was further investigated in this particular reaction with different acid loadings. Catalytic results showed similar TON values, revealing that acid sites were homogeneously dispersed on the SBA-15 support and hence highly accessible to the oxime molecules. No leaching of sulfonic-acid species was reported.

5.2. Cooperative Effect of Close Sulfonic-Acid Groups for Enhancement of Acid Strength

Davis and Dufaud[83] prepared catalytic materials bearing multiple sulfonic-acid functional groups positioned at varying distances on the surface of SBA-15 materials, and they explored the effects of the spatial arrangement of active sites on catalytic activity and selectivity. Organosiloxane precursors containing dimeric sites were synthesized (Figure 16) in comparison to the isolated ones present in conventional precursors (MPTMS and CSPTMS).

Starting from the symmetrical dipropyl disulfide (precursor A, Figure 16), two alkylsulfonic-acid groups in close proximity to each other can be produced after cleavage of disulfide linkages using reducing agents and oxidation under mild conditions. This treatment did not allow a quantitative

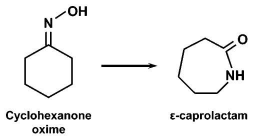


Figure 15. Reaction scheme of Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam.

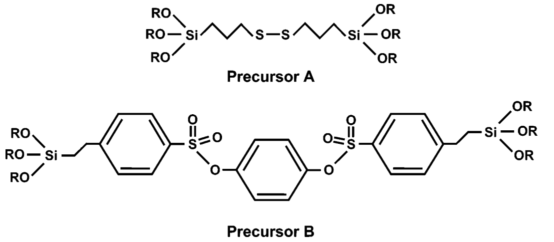


Figure 16. Nonconventional precursors for the synthesis of sulfonic-modified mesostructured materials.

oxidation of thiol groups, and partially oxidized disulfide species were detected by ^{13}C CP MAS NMR. The catalytic activity of this material containing two organic alkylsulfonic-acid groups in close proximity on the silica surface was tested in the condensation of phenol and acetone to yield Bisphenol A and was compared with that of conventional alkylsulfonic-modified SBA-15 materials and the homogeneous counterpart (1-propanesulfonic acid). This novel alkylsulfonic-modified SBA-15 material exhibited a double activity per acid site as compared with conventional alkylsulfonic-modified SBA-15 and homogeneous system and also a high regioselectivity as compared with the latter. The authors concluded that the enhancement of the activity might be due to the cooperation between two proximal alkylsulfonic-acid groups on the silica surface, but they did not discard the active role of nonacidic sites coming from incomplete oxidation as postulated by other authors.[84]

From bis(arylsulfonate) ester (precursor B, Figure 16) two close arenesulfonic-acid groups can be generated after removal of the phenyl spacer by means of hydrolysis in aqueous solution of sulfuric acid at 60 °C overnight. The materials obtained showed a poor quality, and generation of sulfonic-acid sites was very limited with an acid capacity lower than 0.1 mmol of H^+ per gram of silica. Because of these values, the materials were not used in catalytic tests.

5.3. Anchoring of Perfluorosulfonic-Acid Sites onto Mesoporous Materials

Perfluorinated sulfonic-acid resins such as Nafion have been used in a wide range of organic reactions including alkylation, acylation, nitration, etherification, and esterification. The presence of electron-withdrawing fluorine atoms in the structure significantly increases the acid strength of the terminal sulfonic-acid groups, which becomes comparable to that of pure sulfuric acid. However, these polymeric catalysts present low surface areas. To overcome this limitation of the ion-exchange resins, a group of researchers developed Nafion−silica composites and tested them in different acid-catalyzed reactions.[70,85−87] These nanocomposite materials have large surface areas (150−500 m^2/g) and contain small (<100 nm) Nafion particles entrapped in a porous silica framework. However, the materials suffer from limited availability of the acid groups due to the imperfect dispersion of the resin within the silica pores.

Acid-site accessibility can be enhanced through an alternative grafting procedure. In this sense, Harmer et al. demonstrated how the attachment of perfluorosulfonic acid [$Si-(CH_2)_3-(CF_2)_2(O)(CF_2)_2SO_3H$] to silica surface generates a solid with an acid strength comparable to that shown by perfluorinated sulfonic-acid resins.[88] The presence of fluorine atoms significantly increases the acid strength of the sulfonic-acid group. However, the complexity of the preparation of the organosilane precursor [$(OEt)_3$-$Si-(CH_2)_3-(CF_2)_2(O)$-$(CF_2)_2SO_2F$] makes this material not very cost effective as compared with the use of MPTMS and CSPTMS as precursors. Moreover, the integrity of the silica framework as that of the tethered organic moieties could be not preserved during the S−F hydrolysis, leading to $Si-(CH_2)_3-(CF_2)_2$-$(O)(CF_2)_2SO_3{}^{-}M^+$, which requires drastic basic hydrolysis conditions.

This synthesis approach has been recently explored by Corma et al. for anchoring of perfluoroalkylsulfonic-acid groups analogous to Nafion over MCM-41 and SBA-15 solids.[89] The synthesis strategy was based on grafting of the precursor (1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid sultone, commercially available) over the silica surface (Figure 17). The precursor reacts with the surface silanol groups by opening up the sultanyl ring and forming a covalent bond. Hybrid materials with acid capacities up to 0.5 mmol of H^+ per gram of solid were obtained, and the anchoring process of active species retained the mesoscopic ordering and textural properties of the parent MCM-41 and SBA-15 materials. Covalent attachment of the perfluoroalkylsulfonic-acid group to the silica surface was confirmed by ^{19}F MAS NMR experiments. This synthesis strategy allows preparing hybrid organic−inorganic mesoporous silica catalysts functionalized with perfluorosulfonic-acid groups in a single step using a commercial precursor in comparison with the method first reported by Harmer.[88]

The catalytic performance of these catalysts was tested in the esterification of alcohols with long-chain aliphatic acids.[89,90] The hybrid mesoporous materials yielded twice the activity shown by the commercial Nafion silica composite and Nafion silica cogels despite the latter having higher amounts of sulfonic-acid groups. Additionally, these materials were reused repeatedly without any evidence of loss of activity, confirming the stability of the covalent bond. The same authors tested the catalytic performance of the perfluorosulfonic-modified mesostructured materials in a more demanding acid-catalyzed reaction such as the acylation of anisole with acetic anhydride.[90] The catalytic results show that acylation of anisole can be carried out over these hybrid mesostructured materials with good conversion and high selectivity to the para isomer and with catalytic activities per acid site 2.5 times higher than those of commercial SAC-13 (Nafion/silica composite material). However, catalyst

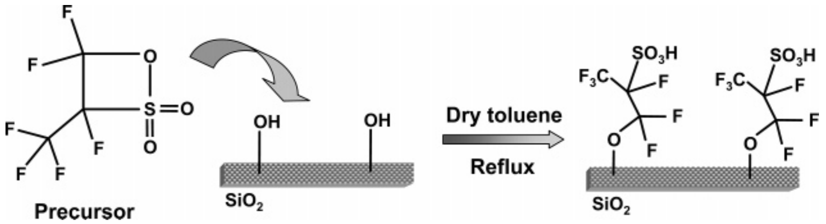


Figure 17. Perfluoroalkylsulfonic-modified mesostructured materials synthesized by the grafting technique (Alvaro, M.; Corma, A.; Das, D.; Fornés, V.; García, H. *Chem. Commun.* **2004**, 956. Reproduced by permission of The Royal Society of Chemistry).

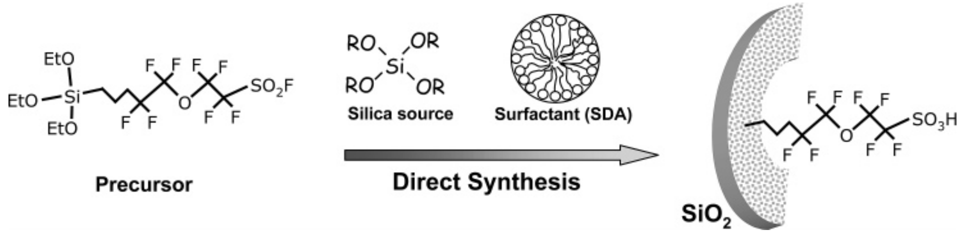


Figure 18. Preparation of perfluoroalkylsulfonic-modified mesostructured materials by direct synthesis.

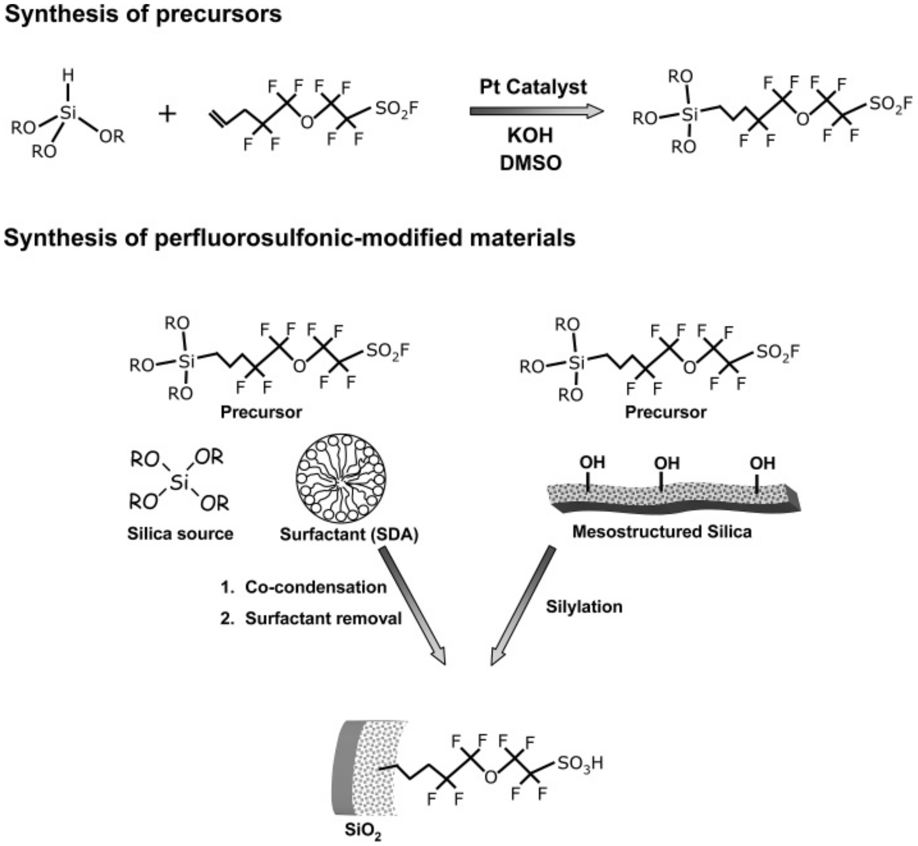


Figure 19. Synthesis of perfluorinated sulfonic-acid precursors by means of hydrosilylation processes.

deactivation limits its reusability as it was observed for arenesulfonic-modified SBA-15 materials.[62]

Harmer et al. prepared mesoporous silica-perfluorosulfonic-acid materials by a nonoxidative direct-synthesis procedure combining the advantages of the acid strength of Nafion with the excellent dispersion available with sol−gel-templated synthesis (Figure 18).[91] Materials were prepared by co-condensation of the corresponding silane (precursor of alkylperfluorosulfonic-acid group) and TEOS using *n*-dodecylamine as template. Final acid extraction of the template with 0.1 M H_2SO_4 leads directly to the sulfonic-acid product. Complete incorporation of silane was obtained, yielding a sulfonic acid loading of 0.2 mmol g^{-1} in the final material. The solid was tested in the Friedel−Crafts acylation of anisole with benzoyl chloride in solventless conditions. The catalyst showed a rapid acylation of anisole and provided high selectivity to the para isomer after 24 h of reaction at 100 °C. The perfluorosulfonic-modified material was also tested in the reaction of 2-methylfuran and acetone to give the bis-furan and was compared with propylsulfonic-modified MCM-41 and HMS solids. The activity of the perfluorosulfonic-acid site was 6 times higher than those obtained with propylsulfonic-modified mesostructured materials with selectivities toward bis-furan over 97%.

To modify the hydrophobicity of the microenvironment surrounding the perfluorosulfonic-acid sites, the same authors incorporated a propyl functional group (via incorporation of the appropriate triethoxysilane) during the synthesis. This material increased the reaction rate in Friedel−Crafts acylation and in the condensation reaction as compared with monofunctionalized perfluorosulfonic-acid sample. The authors attributed the catalytic difference of both materials to the decrease of the surface's polarity, aiding adsorption/desorption kinetics and thus speeding up reactions.

All the above-described results clearly indicate that tuning the acid strength of sulfonic-acid groups implies use of convenient precursors. However, not all the interesting precursors are commercially available. Hence, an important field of research in the future will be addressed to the synthesis of appropriate precursors containing electron-withdrawing species such as phenyl groups, F atoms, or a combination of both for the preparation of these sulfonic-modified mesostructured materials. One synthesis strategy could be preparation of the corresponding organosilane through a hydrosilylation procedure catalyzed by platinum catalysts (Figure 19)[92] and subsequent anchoring to the silica surface by means of co-condensation reactions or grafting method.

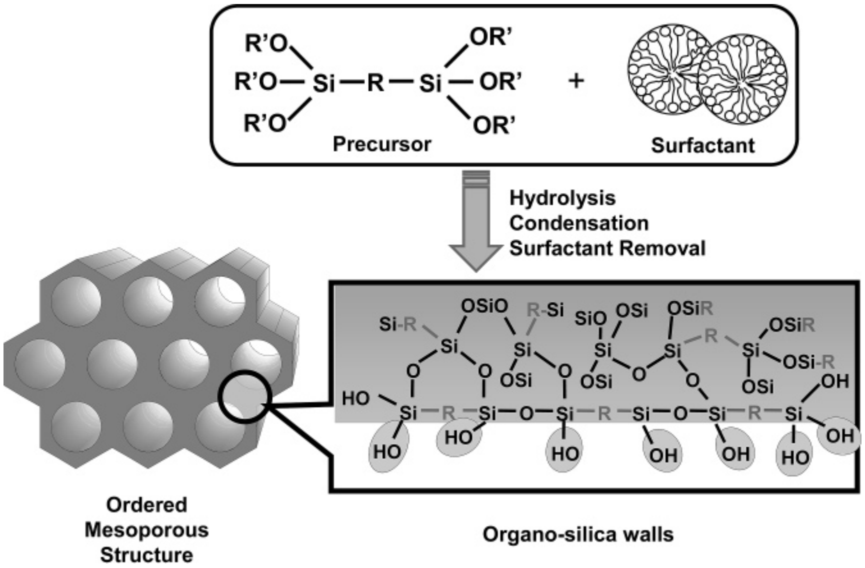


Figure 20. Strategy of synthesis for the preparation of PMO's materials.

6. Organosulfonic-Functionalized Periodic Mesoporous Organosilica

In the late 1990s mesoporous materials composed by hybrid inorganic−organic frameworks with ordered mesopores, designated as periodic mesoporous organosilicas (PMO's), were first synthesized.[93,94] These materials exhibited a homogeneous distribution of organic fragments and inorganic oxide within the framework accompanied by highly ordered structures and uniform pore size distributions. These novel materials offer serious advantages as compared to their inorganic counterparts associated with properties of organic polymers (structure rigidity and degree of hydrophobic character) but with improved accessibility of functional sites due to their open structure. Development of PMO's is a major breakthrough in the field of synthesis of porous materials, opening great opportunities for the tuning of framework properties by means of a judicious choice of the organic groups incorporated and the synthesis conditions employed. These properties are expected to be desirable for many applications, such as catalysis, separation, and advanced materials design.

The synthesis strategy of these materials is based on the condensation, in the presence of the corresponding surfactant, of organosilanes such as $(R'O)_3$-Si−R−Si−$(R'O)_3$ in which the organic moiety (−R−) is covalently attached to two trialkoxysilyl groups (−Si−$(R'O)_3$) (Figure 20). Under basic conditions and using cationic surfactants, ethane and ethylene moieties were first incorporated through direct synthesis within the framework of 2D and 3D hexagonal porous structure symmetries.[93−95] The authors reported high thermal stability of the structures. To date, synthesis of PMO materials has been extensively enlarged to other organic groups including methane,[96] benzene,[97,98] thiophene,[97] and biphenylene[99] and using cationic,[93,94] anionic,[100] neutral,[101] and nonionic oligomeric[102,103] surfactants from highly basic to strongly acid conditions. Furthermore, several recent papers have reported the synthesis of 2D hexagonal PMO's materials having well-ordered large pores using the triblock copolymer P123 as surfactant in acidic conditions.[104−106] Ha et al. prepared highly ordered three-dimensional PMO materials under strongly acidic conditions in the presence of inorganic salts using the triblock copolymer F127 (EO_{106}-$PO_{70}EO_{106}$) as surfactant and incorporating ethane groups within the silica walls.[107] Dai et al.[108] demonstrated a self-assembly synthesis of PMO materials using imidazolium-based surfactants. Finally, Kim et al.[109] recently synthesized highly ordered mesoporous organosilica materials with various mesostructures using gemini surfactants and under different controlled reaction conditions.

Remarkable advances have been already achieved in the preparation of mesostructured materials containing both bridging organic moieties within the silica framework and terminal organic groups anchored to the pores.[110,111] This approach provides PMO materials with additional functionalities. Furthermore, several authors have taken advantage of both surface and framework organic modification for the design of sulfonic-acid bearing organic−inorganic hybrid materials (SO_3H PMO) with potential use in acid-catalyzed applications.[112−116] The combination of both functionalities (acidic and hydrophobic) may result in interesting surface properties enhancing diffusion of reactants and products in acid-catalyzed reactions (Figure 21).

Inagaki et al.[98] reported the synthesis of periodic mesoporous benzene−silica with crystal-like pore walls having a surface structure with alternatively arranged hydrophobic benzene and hydrophilic silica layers with a periodicity of 7.6 Å (Figure 22). This group first described the direct sulfonation of a phenylene group located within the walls of mesoporous benzene−silica preserving both the meso- and molecular-scale ordered structures and the possibility of its use as a solid acid catalyst. The sulfuric-acid groups were located on the hydrophobic benzene layers in the hybrid material and retained to temperatures up to about 500 °C in air or nitrogen showing a high thermal stability. To improve the accessibility of sulfonic-acid centers, the same authors reported the synthesis of alternative sulfuric-acid-functionalized benzene−silica with propylsulfonic-acid groups attached on the hydrophilic silica layers[112] (Figure 23). In contrast with the former material, in this case catalytic acid sites and hydrophobic benzene sites are separate from each other on the mesoporous surface. Synthesis was accomplished by postoxidation of previously synthesized thiol-functionalized benzene−silicas using cationic surfactants and basic conditions. The degree of oxidation was lower than

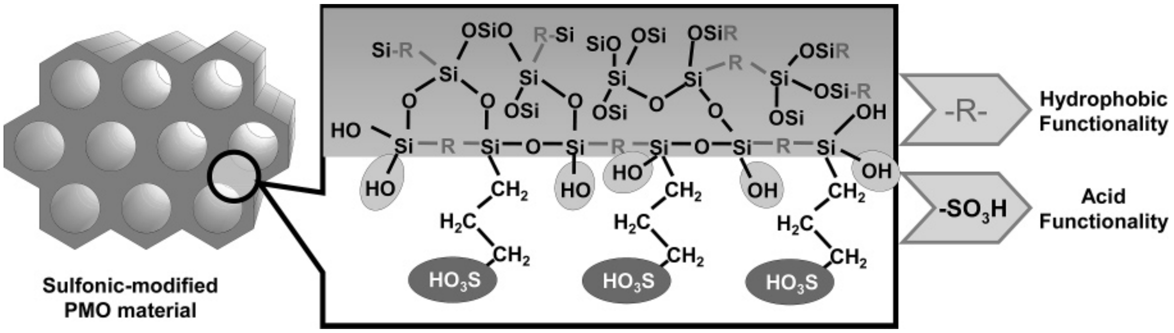


Figure 21. Sulfonic-modified PMO materials.

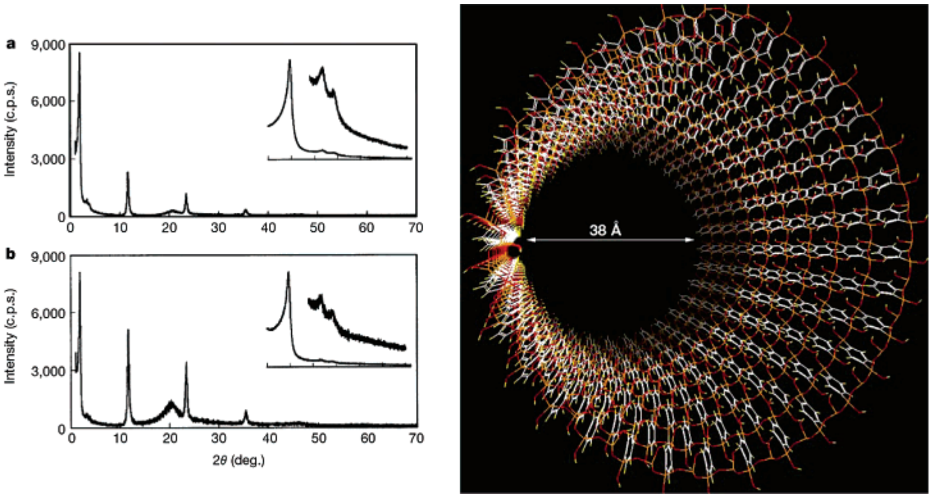


Figure 22. Model showing the pore surface of mesoporous benzene−silica: silicon, orange; oxygen, red; carbon, white; hydrogen; yellow. Powder X-ray diffraction (a) of as-made mesoporous benzene−silica and (b) after removal of surfactant (Reprinted with permission from ref 98 (http://www.nature.com). Copyright 2002 Nature Publishing Group).

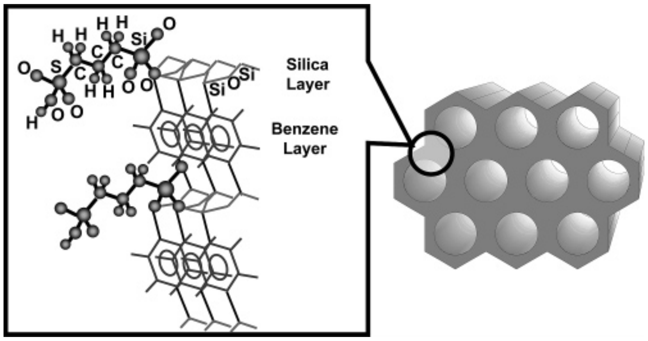


Figure 23. Structural model of periodic pore surface attached with propylsulfonic-acid groups (Reprinted with permission from ref 112. Copyright 2002 American Chemical Society).

60%, and the maximum acid capacity observed was 0.7 mmol of H$^+$ per gram of material.

In a similar approach Kaliaguine et al.[113] reported the synthesis of alkylsulfonic-acid-bearing ethane−silica mesostructured materials. Different loadings of functional groups (up to 32 mol %) were successfully incorporated into the hybrid mesostructured material, reaching acid capacities up to 0.7 mmol H$^+$ per gram, but also with poor oxidation efficiency of the thiol groups. Interestingly, the acidity of the sulfonic-acid sites was investigated by FTIR using pyridine as the probe molecule. The spectrum of the solids after pyridine adsorption and degassing at different temperatures showed absorbance bands at 1490, 1548, and 1640 cm^{-1}, attributed to interaction of the basic molecule with Brönsted-acid sites. Furthermore, these bands were still retained after evacuation at 100 °C, which indicates the existence of relatively strong acid sites. Additionally, these materials displayed appreciable proton conductivity at room temperature and in the presence of different water contents, which confers them a potential use as proton carriers in PEM fuel cell membranes. Kaliaguine et al.[115] also successfully synthesized periodic mesoporous ethane−silica materials functionalized with arenesulfonic-acid groups via the one-step co-condensation approach under acidic conditions and in the presence of P123 and Brij 76 as surfactants. The synthesized materials exhibited high surface areas (up to 1040 m^2/g), pores sized up to 6.5 nm, and uniformly organized worm-hole-like structure. The acid capacity was up to 1.4 mmol of H$^+$ per gram of material, higher than that reported by other authors.

Inagaki et al. also reported the synthesis of biphenylene-bridged bifunctional hybrid mesoporous materials functionalized with sulfonic-acid functionalities.[114] Materials were synthesized by co-condensation of 4,4′-bis(triethoxysilyl)-biphenyl precursor and 3-mercaptopropyltrimethoxysilane in basic medium using a cationic surfactant followed by an oxidation step. The authors claimed that the presence of biphenylene groups is a rather interesting system since it has an equimolar ratio of phenylene to silica, which provides the possibility to exert an enhanced hydrophobic character in the resulted PMO material. The materials afforded an acid capacity up to 1 mmol of H$^+$ per gram of material.

Nevertheless, no catalytic results were reported with these hybrid materials up to the work by Kim et al.[116] PMO catalysts were prepared with ethane moieties within the silica framework, functionalized with alkylsulfonic-acid groups and applied successfully to the alkylation of phenol with 2-propanol. Sulfonic-modified mesostructured materials (both PMO$-$SO$_3$H and MCM-41$-$SO$_3$H) showed higher activities than ZSM-5 catalysts. The authors observed that the activity of MCM-41$-$SO$_3$H gradually decreased over 10 h, whereas hybrid sulfonic-acid PMO catalyst exhibited constant activity. Moreover, they also evidenced that the mesoscopic structure of the MCM-41$-$SO$_3$H material was destroyed after reaction, in contrast with PMO$-$SO$_3$H whose structure did not change. In conclusion, the bridged moieties within the framework yielded materials with excellent catalytic and hydrothermal stability. After this pioneering work interesting catalytic applications of sulfonic-acid-functionalized periodic mesoporous organosilicas have been described in the literature.

Inagaki et al.[117] first reported the direct synthesis of sulfonic-modified mesoporous organosilicas with a high concentration of $-$SO$_3$H sites by co-condensation of ethane- or benzene-bridged organosilane with MPTMS in the presence of hydrogen peroxide and nonionic surfactants (Brij-76) in acid medium. The in-situ oxidation method allows obtaining a complete oxidation of thiol groups and materials with acid capacities up to 1.7 mmol of H$^+$ per gram of material, higher than those reported before.[113,114] These materials were efficient catalysts for the condensation reaction of phenol with acetone to yield Bisphenol A.

The first catalytic application of sulfonic-acid-functionalized hydrophobic benzene$-$silica with lamellar pore structure has been recently reported by Inagaki et al.[118] The authors prepared two different samples, first via co-condensation of 1,4-bis(triethoxysilyl)benzene and MPTMS under basic conditions, and second by grafting of thiol precursor on the periodic mesoporous benzene$-$silica. In both cases the oxidation of thiol ($-$SH) into sulfonic-acid ($-$SO$_3$H) group was accomplished by treatment with HNO$_3$ (65 wt %). Both catalysts were tested in the esterification of acetic acid with methanol and compared to the commercially available Nafion. Grafted materials exhibited higher catalytic activity than Nafion. The improved activity was attributed to the active role of crystal-like walls and unique surface structure as well as the rather different hydrophobic properties of the two materials which respond differently to hydrophilic substrates. However, direct incorporation of thiol groups during synthesis yields materials with lower activity although comparable to Nafion. This was attributed to the irregular distribution of active sites. Molnar and co-workers[119] further explored the catalytic properties of these benzene$-$PMO materials with anchored propylsulfonic-acid groups in both gas-phase and liquid-phase reactions. These materials were tested in different Friedel$-$Crafts-type reactions such as alkylation of toluene and benzene with benzyl alcohol, alkylation of phenol with isopropyl alcohol, and Fries rearrangement of phenyl acetate. The catalytic performance, in terms of activity and stability, of these PMO-based materials markedly exceeded those obtained with propylsulfonic-modified pure silica samples (MCM-41, HMS, and SBA-15). Interestingly, selectivities in Fries rearrangement of phenyl acetate over these PMO-based catalysts differed significantly from those corresponding to the homogeneous reaction (*p*-toluenesulfonic acid). PMO catalysts yielded enhancement of the para selectivity. Likewise, the catalytic performance of PMO materials functionalized with benzenesulfonic-acid groups within the silica framework (PMO$-$benzene$-$SO$_3$H), previously reported by Inagaki et al.,[98] was first studied and compared with that of alkylsulfonic-modified PMO$-$benzene materials. Both materials were tested in the dimerization of α-methylstyrene (AMS, Figure 24) and rearrangement$-$aromatization of ketoisophorone (KIP, Figure 25). PMO$-$benzene$-$SO$_3$H materials, containing stronger arenesulfonic-acid groups, preferentially yielded the cyclic dimer indan derivate (selectivities of 60%) in contrast with PMO$-$benzene$-$alkylsulfonic-acid catalyst which yielded mainly the isomeric pentenes (P1 and P2) with selectivities to indan lower than 10%. A similar picture was observed in the rearrangement$-$aromatization of KIP. PMO$-$benzene$-$SO$_3$H yielded 2,3,5-trimethylhydroquinone diacetate (HQAc), a reaction demanding stronger acid sites, with selectivities over 50% and higher reaction rates than PMO$-$benzene$-$alkylsulfonic-acid catalyst, which gave an enol monoacetate (enAc) selectivity close to 100% and negligible formation of HQAC.

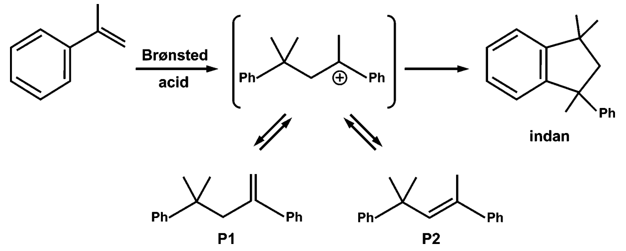


Figure 24. Dimerization of α-methylstyrene.

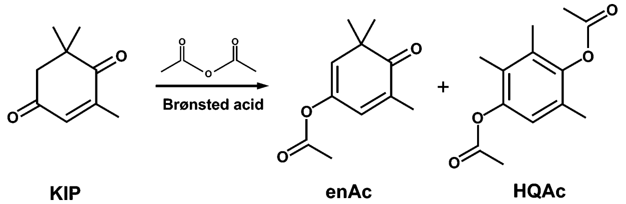


Figure 25. Rearrangement$-$aromatization of ketoisophorone.

Kaliaguine et al.[120] investigated the catalytic performance of sulfonated organosilica in the reaction of 1-butanol etherification. The sulfonic$-$organosilica material showed higher activity than sulfonic-modified pure silica for the direct production of dibutyl ether from 1-butanol. The authors claimed that the high activity of organosilica materials is related to the hydrophobic character of the ethane-containing silica, which reduces the acid site deactivation associated with adsorption of water generated by the reaction. In a similar way, Fukuoka et al.[121] tested the catalytic activity of sulfonated organosilica materials in water media reactions. The authors proved that these hybrid materials work effectively as recyclable water-tolerant solid acid catalysts in the hydrolysis of bulky sugar molecules (sucrose and starch) to yield the corresponding monosaccharides. The hybrid materials yielded higher conversion per acid site than that obtained with Amberlyst-15 and Nafion$-$silica. Sulfonic-acid ethane$-$silica degraded 80% of sucrose at 353 K after 4 h of reaction, and no decrease of activity was observed after three repeated catalytic runs. Furthermore, no reaction occurred after adding sucrose to the filtrate solution. Therefore, no leaching of active sites was evidenced and easy regeneration of the materials was obtained after washing with water.

Inagaki et al.[122] prepared sulfonic-acid-functionalized mesoporous organosilica with different concentrations of ethane groups in the silica framework [BTME/(BTME +

TMOS) molar ratio from 0 to 100%] by one-step condensation method with in-situ oxidation of thiol groups under acid conditions and using nonionic surfactants. The authors used tetramethyl orthosilicate (TMOS) instead of tetraethyl orthosilicate (TEOS) because the former has a faster hydrolysis rate and could match the hydrolysis of ethane-bridged precursor to favor formation of ordered mesostructure with uniform pore sizes and homogeneous distribution of active functionalities. X-ray diffraction studies along with nitrogen adsorption analyses reveal formation of well-ordered hexagonal mesoscopic structures in a wide range of $-CH_2CH_2-$ concentrations in the mesoporous framework. Hydrothermal stability of the samples is increased with incorporation of bridging ethane groups to the mesoporous network. The authors attributed the enhancement of hydrothermal stability to the increasing hydrophobic character of the materials upon incorporation of ethane groups in the mesoporous network. Moreover, the hydrophobic character of the samples was further investigated by water adsorption analyses. Adsorption results confirmed that the hydrophobic character of samples is enhanced with a gradual increase of ethane moieties within the silica framework. Finally, the catalytic performance of these materials was checked in the esterification of ethanol with acetic acid. The catalytic results evidenced that the catalysts with ethane moieties are more active compared to materials without bridging ethane groups, indicating that activity depends largely on the surface hydrophobic/hydrophilic properties of the sulfonic-acid-functionalized organosilicas.

Kondo et al.[123] recently described a novel chemical modification method for preparation of a new class of hybrid mesoporous solid acid catalysts with catalytic active sites on the surface of PMO material. The silica framework was functionalized with ethylene moieties through condensation of bis(triethoxysilyl)ethylene in the presence of Pluronic 123 in acid medium. The ethylene sites were successfully converted to phenylene−sulfonic-acid groups by Diels−Alder reaction with benzocyclobutene followed by sulfonation in concentrated H_2SO_4. The resultant acid hybrid material (Ph−SO_3H HME) possesses a surface area of ca. 500 m^2 g^{-1} with high mesoscopic ordering and an acid capacity of 1.4 mmol of H^+ per gram.

The catalytic performance of this material was first investigated in the esterification of acetic acid with ethanol and compared with perfluorinated sulfonic-acid resin (Nafion), sulfonated polystyrene resin (Amberlyst-15), and niobic acid. This novel material exhibited high activity for formation of ethyl acetate, much higher than that obtained with niobic acid and comparable to that for Amberlyst-15 and Nafion. Likewise, reuse of the catalysts four times did not evidence loss of activity or leaching of sulfonic-acid species. In the same contribution, the catalytic performance of this acid hybrid material was examined in the pinacol−pinacolone rearrangement and compared with several acid catalysts (Table 7). The conversion obtained was higher than that for homogeneous catalysts such as $HP_3W_{12}O_{40}$ and *p*-toluenesulfonic acid and comparable to that corresponding to concentrated H_2SO_4. This hybrid material also exhibited higher conversion than Nafion and Amberlyst-15.

Table 7. Conversion and Selectivity for Pinacol−Pinacolone Rearrangement in the Liquid Phase (Data Reprinted with Permission from Ref 123. Copyright 2005 Wiley-VCH)

catalysts	conversion, %	selectivity, %	
		pinacolone	2,3-dimethyl-1,3-butadiene
H_2SO_4	98.4	71.7	28.3
Ph-SO_3H HME	92.0	83.5	16.5
$H_3PW_{12}O_{40}$	70.5	90.8	9.2
Amberlyst-15	69.5	83.5	16.5
p-toluenesulfonic acid	42.8	74.4	25.6
nafion	42.2	88.2	11.8

[a] Reaction conditions: temperature, 130 °C; 42 mol of pinacol; 0.2 g of catalyst; no solvent; time, 1 h.

7. Summary and Outlook

Sulfonic-modified mesostructured materials with large and uniform pores, high surface area, and relatively strong acid sites represent an attractive alternative to the hazardous homogeneous acids with particular interest for reactions involving molecules that are too large to access the small cavities of acid zeolites. These materials have been already tested in a wide variety of acid-catalyzed reactions and in most of cases showing better catalytic performance than conventional homogeneous and other heterogeneous catalytic systems. Tuning of the acid strength as well as control of the hydrophobic/hydrophilic balance of the silica surface of this organosulfonic-modified mesostructured material will definitively open up new possibilities for preparation of acid−solid catalysts with potential applications in a wide range of industrial reactions with special interest in fine chemistry. Further work on the reusability of these sulfonic-modified mesostructured materials must be explored in the future. Commonly used thermal treatments for regeneration of the catalysts must be discarded in order to preserve the integrity of acid−organic groups, and efforts must be addressed to modify the reaction conditions (i.e., choice of an appropriate solvent may be crucial for increasing the lifetime of the catalyst) and optimize regeneration treatments.

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