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# Catalysis via Sol–Gel Acid Silicas: An Important Chemical Technology for 2nd Generation Biorefineries

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Heterogeneously catalyzed processes using mesoporous acid silicas selectively afford many valued products from biomass components. The versatile nanochemistry of the sol–gel process allows to shape materials with catalytically attractive morphologies, as well as to further functionalize the inner mesoporosity with other active species affording nanocomposites suitable for consecutive reactions in one-pot. Using selected examples from recent chemical research, we identify an approach that will likely produce catalysts of enhanced performance, suitable for practical application.

## Introduction

First described by Kato and co-workers in Japan in 1990[1] and further developed two years later by Kresge's team in the United States,[2] mesoporous silicas with ordered amorphous pore walls and large specific surface areas are now a well-established class of functional materials with numerous chemical applications.[3]

Since the inception of the so named MCM-41 materials, synthesized via a self-assembled liquid crystal mechanism involving silicon alkoxides sol–gel precursors and ionic surfactants (which form a hexagonally packed rod-shaped micelle structure), other members of the M41S family of materials have been introduced including the cubic, MCM-48, and lamellar, MCM-50, forms.[4] These molecular sieves are generally obtained using long-chain alkyltrimethylammonium halides as structure-directing agents (SDA). The surfactant is eventually removed by extraction (or calcination) to afford the M41S mesoporous silicas with pore sizes from about 15 to 100 Å.

In 1998, Stucky and co-workers synthesized SBA-15 silicas with larger pore sizes (50–300 Å) made by using nonionic (triblock and star diblock) copolymers as templates.[5] Almost concomitantly, Ozin and co-workers reported the discovery of so-called periodic mesoporous organosilicas (PMO),[6] obtained starting from bridged organosilanes.[7]

Functionalization of the inner porosity of these solids with metal nanoparticles, functional organic molecules, base or acid groups, and polymers, affords functional materials that can be used as catalysts, sensors, controlled release materials,[8] as well as to make innovative optical and electronic devices.[3]

In 1998 Jacobs and co-workers described the preparation of sulfonic acid-containing MCM-41 or hexagonal mesoporous silica (HMS), and their use as catalysts for condensation and esterification reactions.[9] Acid catalysis is such a significant area of catalysis[10] that progress in the field was so rapid that Wilson and Clark (in 2000),[11] and Davis (in 2002),[12] were already able to summarize the achievements with related silica-supported sulfonic acids for catalytic esterification, dehydration, acetalization, cyclization, etherification, and aldol reactions. Sol–gel silicas are true molecular sponges adsorbing and concentrating reactants at their surface, whose inner mesoporosity (pore diameter $<20$–$100$ Å) favors diffusion of a broad variety of molecules to the entrapped acid moieties resulting in effective solid-acid catalysis in liquid-phase.

In 2002 Clark referred to heterogeneous catalysis over acid silicas as an emerging green chemistry synthetic methodology with large applicative potential.[13] For example, Kanabe and Hölderich in 1999 identified[14] 127 petrochemical industrial processes (such as alkylation, isomerization, amination, cracking, etherification, etc.) using some 180 different solid catalysts (zeolites, oxides, complex oxides, phosphates, ion-exchange resins, clays, etc.). Applied to organic synthesis in liquid-phase mesoporous acid silicas would play a role similar to that played by acid zeolites in gas phase petrochemistry. Yet, zeolite use is limited by the small pore sizes ($<15$ Å) and often require high temperatures, which makes them generally poorly suitable for reactions involving most substrates of interest in synthetic organic chemistry.

Today a number of sol–gel acid silicas of tunable acid strength are commercially available at large scale, generally supplied either as xerogel irregular microparticles or as spherically shaped microparticles, typically from 45–70 μm to a few μm with pore diameters in the 60–150 Å range. For example, Canada's SiliCycle commercializes silica-supported propyl sulfonic acid and silica-entrapped tosic acid, which is a strong solid acid used both under batch and flow conditions;[15] while

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Europe's PhosphonicS manufactures similar acid silicas along with weaker encapsulated phosphonic acids, that recently showed promising results in the two-phase dehydration of fructose to 5-hydroxymethylfurfural (HMF).[16]

Since the reviews of Clark and Davis mentioned above, a number of thorough studies have appeared in the literature, addressing sol–gel sulfonic acid functionalized mesoporous silicas[17] and acid PMO.[18] A recent study of Lee elegantly describes the role of acid silicas in the heterogeneously catalyzed synthesis of biodiesel.[19] However, no study focuses on the role that these materials may play within the emerging context of biomass utilization for biorefineries for the production of organic chemicals. For instance, in 2010 Bozell revisited the US Department of Energy "Top 10" biobased products obtainable from biorefinary carbohydrates.[20] At least four of these products (levulinic acid, furans, sorbitol, and xylitol) are obtained by dehydration reactions with chemical catalysts; with the remaining bioderived compounds obtained via bioprocesses (with the exemption of glycerol).

Herein, we focus on the use of mesostructured acid silicas for biorefineries, namely multipurpose chemical plants that do not target the production of low value-added fuels from a single (and often edible) feedstock, rather the synthesis of high value-added chemicals and polymers starting from different (and preferably non-edible) biomass feedstocks.[21] Following a brief review of the chemical approach to the synthesis of these materials, we highlight selected conversions relevant to the new biorefinery, and conclude identifying a number of issues that remain to be addressed by future research.

## Mesostructured Acid Silicas

The original sol–gel synthesis first reported by Jacobs involves co-condensation of (3-mercaptopropyl)trimethoxysilane (MPTS) with tetraethylorthosilicate (TEOS) in the presence of hexadecyltrimethylammonium bromide ($C_{16}$TMABr) or *n*-dodecylamine.[9] The thiol functionalities are then oxidized into sulfonic acid groups by hydrogen peroxide followed by a final treatment with aqueous $H_2SO_4$.

Between 2000 and 2002, Wilson, Clark and co-workers extended the method by preparing a range of sulfonic acid-functionalized silicas by co-condensation of TEOS and MPTS with *n*-dodecylamine as SDA, first over the TEOS/MPTS molar ratio 9:1–1:1,[22] and then 19:1–1:1.[23]

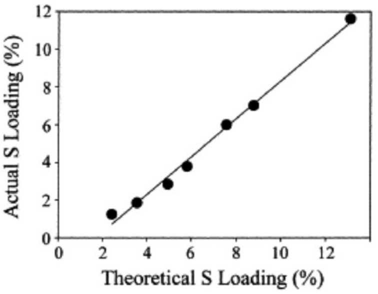

**Figure 1.** Correlation of actual and theoretical sulfur loading in sulfonic acid silicas. [Reproduced from Ref. [23], with kind permission].

The new synthesis did not generate any acid waste stream because the acid functionality was now generated by mild oxidation of the resulting thiol-functionalized silicas (after removal of the dodecylamine template by extraction in ethanol and drying of the powders at 70 °C) with an excess of concentrated $H_2O_2$ (70 wt%). High levels of MPTS incorporation (>90% efficiency) were achieved at all TEOS/MPTS ratios investigated (Figure 1), affording high loadings of $-SO_3H$ groups, up to 4.7 mmol$\,g^{-1}$. Remarkably, independent of the sulfonic acid loadings, the surface acid strength as determined by Hammett indicators was around $H_0 = -3$ for all of the materials. The team successfully employed the resulting strong acid materials in esterification and condensation reactions with enhancement of the resulting catalytic performance, ascribed to the high active site density achievable via the one-pot co-condensation, namely a maximum sulfur loading of 12 wt% vs. 2 wt.%. of post-grafting method.[24]

Many other researchers, including Pérez-Pariente,[25] Stein,[26] and Inagaki[27] pioneered the field of sol–gel acid silicas; including Stucky and co-workers who developed SBA-15-type mesoporous sulfonic acid silica silicas with ordered 2-dimensional hexagonal channel mesostructure (p6mm symmetry).[28] In general, the elegant chemistry of the sol–gel process can be designed to not only provide different degrees and types of acidity, but to tune the reaction selectivity by the "chemistry of form" of sol–gel porous silicas.[29] Furthermore, compared with the low surface area and thermally unstable sulfonated polymer resins, such as sulfonated polystyrene Amberlyst-15 and perfluorinated sulfonic acid Nafion-H, the new sol–gel entrapped Brønsted acid catalysts generally afford superior performance with higher conversions at lower temperatures, are compatible with any organic or aqueous solvent, and are stable up to 120 °C under most conditions.[28]

Unlike polymeric acid catalysts, mesostructured silicas do not swell, are versatile (effective for a wide range of acid-catalyzed processes) and selective (little or no side-product formation or coloration of products).[22,23] As a result, mesostructured silica supported sulfonic acids are proposed as effective catalysts to replace both homogeneous and conventional heterogeneous acid catalysts, capable to reduce waste and offer significant savings.[30]

In the following we focus on the application of some of these materials in the valorization of biomass components, starting from cellulose, the most abundant biomass product.

## Valorization of Cellulose

Depolymerizing cellulose into platform sugar molecules is a key (or "entry", to paraphrase Schüth)[31] step in developing the concept of an integrated biorefinery.[32] This reaction was traditionally catalyzed by either enzymes or homogeneous mineral acids, both presenting serious drawbacks. For example, during the last years of World War II, Germany built a number of large facilities that produced sugars for ethanol using the process developed by Bergius in 1930 that used concentrated hydrochloric acid (fuming acid, 42 wt% HCl) to make sugars from biomass. The sugars were then be fermented into ethanol fuel using yeast. The process is highly damaging to the environment and was abandoned after the war.[33]

Almost one century later, with the price of oil having reached unprecedented high levels, heterogeneous catalysts capable of cleanly affording high yields of the sugars contained in lignocelluloses remain highly desirable. Even more attractive would be the development of direct routes to platform chemicals of purity comparable with corn sugars, directly from the biopolymer, namely combining depolymerization with a selective dehydration, hydrogenation, or hydrogenolysis step.

In 2012 Wu and co-workers showed that acid heterogeneous hydrolysis and hydrogenation/hydrogenolysis reactions can indeed be combined for catalytic conversion of cellulose into renewable $\gamma$-valerolactone and sorbitol by using two heterogeneous catalysts in one-pot: sulfonic acid ($-SO_3H$) functionalized mesoporous silica (MCM-41) and Ru/C.[34] In detail, after hydrolysis and filtration of the acid mesoporous silica the hydrolysis products glucose and levulinic acid are hydrogenated over the Ru/C catalyst respectively yielding alkanediols (propylene glycol and ethylene glycol), sorbitol, and $\gamma$-valerolactone. Remarkably, the above hydrolysis products of cellulose are directly used in the hydrogenation reaction, without further purification. Under such conditions, the lifetime of the catalyst system was extended up to 6 times the original durability of the acid-functionalized silica.

Most recently, a team led by Hou in China expanded this approach by developing a multifunctional catalyst made of sulfonic acid silica further functionalized with Ru nanoparticles ($Ru/SiO_2-SO_3H$) for the hydrogenolysis of cellulose in one-pot, in neutral water medium.[35] The catalyst showed high yield of sorbitol, up to 61.2%, after 10 h reaction in water at 150 °C under 4 MPa $H_2$ pressure (Figure 2). The sulfonic acid groups and metal sites in adjacent positions actively interact, enhancing the yield of sorbitol. In addition, the catalyst could be reused five times with only a slight decrease in yield of sorbitol in the consecutive recycles, which is highly promising in light of future practical applications.

For comparison, when a commercial sulfonated silica gel is employed in similar xylan hydrolysis in plain water under relatively mild temperature and pressure (120 °C and 10 bar) conditions, the combined yield of xylose and arabinose noticeably decreases after the first recycling.[36] This indicates that loosely bound sulfonic groups leach into solution, whereas those that are strongly bound inside the pores remain available for catalysis. These outcomes clearly show that the inner porosity of mesoporous silicas plays a crucial role in ensuring better selectivity and higher catalyst stability (sustained catalytic performance).

Another remarkable example is the sulfonated (arenesulfonic) mesoporous silica, SBA-15-$SO_3H$, employed in the high-yield synthesis of butyl levulinate from furfuryl alcohol and *n*-butanol with high selectivity (Figure 3).[37] Butyl levulinate is of particular interest as solvent, flavoring agent, and fragrance with a value of about 10 \$ $lb^{-1}$ (1 lb = 454 g). Furfuryl alcohol, in turn, is a valued derivative of furfural typically obtained from corn-cob and sugar cane bagasse. Similarly biobutanol (1-butanol) is rapidly emerging as a valued fuel and chemical feedstock that can be advantageously produced by cellulosic biomass fermentation.[38]

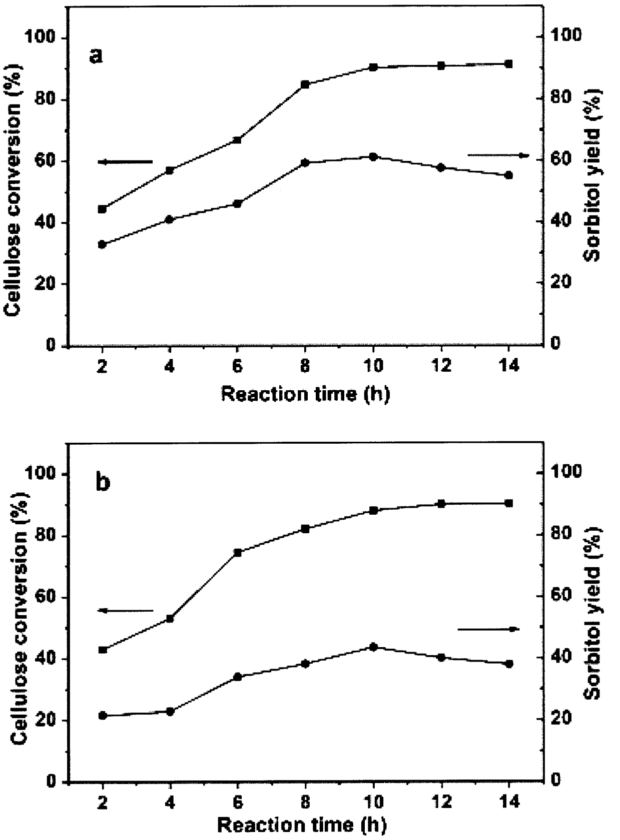

**Figure 2.** Changes in product yields with reaction time during the cellulose hydrogenolysis in water using a) $Ru/SiO_2-SO_3H$ and b) the mechanical mixture of $SiO_2-SO_3H$ and $Ru/SiO_2$ at 150 °C. [Reproduced from Ref. [35], with kind permission].

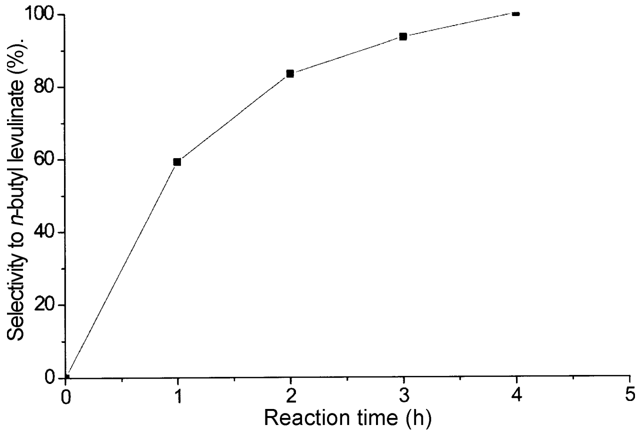

**Figure 3.** Long-range ordered sulfonic acid-functionalized SBA-15 mediates the complete conversion of furfuryl alcohol and *n*-butanol into intermediates in only 15 min. After 4 h the reaction is complete with 96% selectivity towards *n*-butyl levulinate. [Reproduced from Ref. [37], with kind permission].

The acid silica catalyst outperformed the state-of-the-art phosphotungstate acid catalyst, as well as several commercial and as-synthesized solid-acid catalysts, affording a remarkable 96% yield (and 100% selectivity) of butyl levulinate in 4 h at 110 °C. Furthermore, catalytic testing before and after a hot filtration confirmed that the active catalytic species do not leach into the solution; even though (see below) the catalyst is not recyclable.

## Valorization of Sugars

Another significant challenge for new biorefineries is the development of solid-acid catalysts to produce HMF via fructose dehydration.[39] HMF is a platform chemical ideally suited for the manufacture of polyester polymers. In this field, Dumesic and his team recently introduced a highly efficient (and recyclable) new composite catalyst made impregnating the amphiphilic polymer polyvinylpyrroldine (PVP) onto commercial silica spheres modified with propylsulfonic acid groups (PVP-p$SO_3$H-SS).[40] The polar aprotic polymer molecules dissolve and disentangle in water, hydrogen binding through the pyrrolidone carbonyl groups to the surface Si-OH groups. The entrapped PVP molecules were then cross-linked using benzoyl peroxide and irradiation in order to prevent dissolution and leaching.

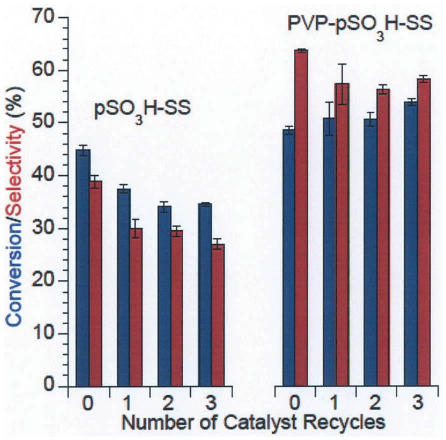

**Figure 4.** Effect of PVP-p$SO_3$H-SS catalyst recycle on fructose conversion and HMF selectivity at 130 °C in 4:1 THF/$H_2O$ (w/w). After each batch reaction, the catalysts were recovered, washed, dried and reused. [Reproduced from Ref. [40], with kind permission].

Under batch reaction conditions, recycled p$SO_3$H-SS lost activity with each reuse, whereas the composite PVP-p$SO_3$H-SS showed stable activity with only a minor decrease in selectivity after the first use (Figure 4). The catalyst was easily recovered from the reaction mixture and the product was readily isolated from the low-boiling solvent system. The PVP in the confined space of the nanochannels acts as a polar aprotic solvent in the confined mesopore microenvironment, increasing the stability of the furanose tautomers and resulting in increased HMF selectivity approaching levels (87% selectivity in HMF at 52% fructose conversion) previously achieved only with expensive ionic liquids and high-boiling aprotic organic solvents.

It is also relevant, in the context of HMF production, that in 2005 Fukuoka and co-workers reported that mesoporous benzene-silica with crystal-like pore walls (Ph-PMO) functionalized with propylsulfonic acid sites (Ph-PMO-Pr$SO_3$H) employed in the hydrolysis of sucrose and starch, are catalytically much more active and stable in water than Amberlyst-15, Nafion-silica, and HZSM-5 catalysts.[27] This is also true in comparison to sulfonated periodic mesoporous silicas such as SBA-$SO_3$H, MCM-$SO_3$H, or HMS-$SO_3$H, and was ascribed to reduced solvation and leaching of the active sites from the phenyl-modified PMO.

Jérôme and co-workers recently advanced these findings reporting enhanced activity and stability of sulfonated mesoporous benzene and biphenylene bridged PMOs in the dehydration of fructose to HMF in biphasic system (water and MIBK/2-butanol).[41] In detail, a 44 wt% aqueous solution of fructose was heated to 160 °C in the presence of the solid-acid catalyst (16 wt% related to the amount of fructose) and of MIBK/2-butanol (70/30). The material PMO-**1a** prepared by co-condensation of 1,4-bis(triethoxysilyl)benzene and MPTMS (Figure 5) with the highest $H^+$ loading (1.11 mmol $g^{-1}$) affords the a maximum 59% yield in HMF at 96% substrate conversion, retaining and even increasing its activity (TOF from 520 $h^{-1}$ to 650 $h^{-1}$) during the second run. The team revealed that an optimal hydrophilic/lipophilic balance, and proton loading and dispersion of sulfonic acid sites on the PMO surface, is required to assure an efficient dispersion of sulfonated PMO in the aqueous

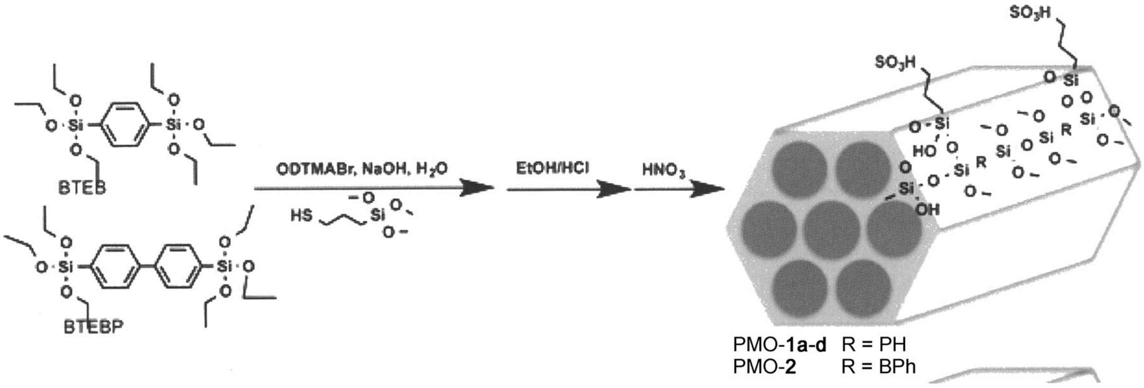

**Figure 5.** Schematic representation of sulfonic acid functionalized PMO materials used in fructose dehydration by Jérôme and co-workers. [Reproduced from Ref. [41], with kind permission].

phase, while favoring an optimal adsorption of fructose. Decreasing the proton loading from 1.11 mmol$g^{-1}$ (PMO-**1a**) to 0.36 mmol$g^{-1}$ (PMO-**1c**) the reaction TOF increased from 520 $h^{-1}$ to 945 $h^{-1}$; whereas a dramatic decrease to the TOF was observed when phenyl bridges were replaced by a more hydrophobic moiety (TOF = 350 $h^{-1}$), such as biphenyl (PMO-2). The activity of PMO-**1a**, however, irreversibly drops after the second catalytic cycle, suggesting that irreversible structural changes occur in the used catalyst.

## Valorization of Glycerol

In the last decade Melero and co-workers in Spain achieved highly promising results in glycerol valorization via etherification and esterification of the triol over SBA-15-type acid silicas. In 2008, the team reported the enhanced etherification of glycerol with isobutylene to yield *tert*-butylated derivatives.[42] Under optimized conditions (5 wt% of catalyst, isobutylene/glycerol molar ratio = 4:1, 75 °C) the mesostructured arenesulfonic acid catalyst Ar-SBA-15 led to complete glycerol conversion in 3 h, with a combined selectivity towards di-*tert*-butylglycerols (DTBG) and tri-*tert*-butylglycerol (TTBG) up to about 90%. The di- and tri-ethers of glycerol are the most desirable products, and the catalyst Ar-SBA-15 gives the highest yield of DTBG and TTBG, whereas the amount of the undesirable mono-*tert*-butyl glycerol MTBG decreased to 5 wt% after 4 h of reaction.

These ethers show good performance as component for biodiesel formulation. To achieve the best performance the presence of non-desired impurities should be reduced, such as diisobutylenes and unreacted acetic acid.[43] If the SBA-15 acid catalyst is used, no formation of undesirable isobutylene oligomers could be observed, which is important, as the isobutylene oligomers must be removed from the fuel additive before use.

In non-food applications, the esterification of acids with glycerol is commercially achieved using homogeneous catalysts, such as sulfuric and *p*-toluene-sulfonic acid. Melero and his team have shown that these homogeneous processes can now be replaced by heterogeneously catalyzed continuous conversions in which sulfonic-functionalized mesostructured silicas incorporated into a packed-bed continuous-flow reactor yield acetylated compounds in high yield,[44] simplifying product separation, purification, and dramatically reducing waste generation.

In detail, optimal conditions ($T$ = 125 °C and acetic acid/glycerol molar ratio of 9:1, 4 h reaction time) for reaction over sulfonic-modified SBA-15 afforded glycerol conversions above 90% and combined selectivities toward di- and triacetylglycerol in excess of 85%. The use of a high acetic acid excess to push the equilibrium towards right simultaneously enhances glycerol conversion and selectivity toward the most important di- and triacetylated derivatives. The catalyst activity, after a mild solvent-washing step, remarkably remains constant in consecutive catalyst recycles (Figure 6). The acidic strength of the sulfonic acid sites is the crucial factor determining the catalytic effectiveness of these materials. Stronger acid centers, such as those in arenesulfonic- and fluorosulfonic-modified mesostructured materials, in general improve performance both in glycerol conversion and selectivity. Comparing yields after 2 h of reaction suggests the participation of beneficial confinement effects when a sulfonic acid group is supported over a mesostructured material. Indeed, despite the high acid capacity (20.4 $mmol_{H^+}g^{-1}$) of $H_2SO_4$ and that it is soluble under reaction conditions, its catalytic behavior is not as good as that of Ar-SBA-15 and F-SBA-15.

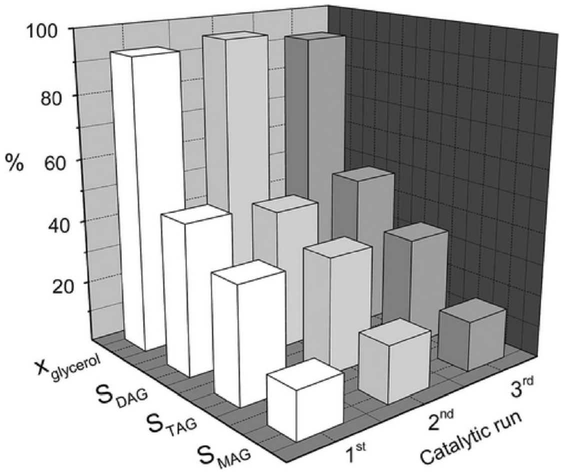

**Figure 6.** Catalyst reuse: Glycerol conversion and selectivity to MAG, DAG, and TAG after 4 h, in three consecutive catalytic runs reusing catalyst Ar-SBA-15. Reproduced from Ref. [44], with kind permission].

Both etherification and esterification reactions of crude glycerol obtained from production of fatty acid methyl esters (FAME) over the mesostructured silica catalysts were investigated at a Repsol plant in Spain.[45] The long-term stability of SBA-15 and related catalysts were thoroughly evaluated, owing to the high hygroscopicity of glycerol. The results confirmed the practical potential of the methods, even though they have not yet been scaled up.

## Catalytic stability

Besides the leaching of functional species, even more severe consequences for the catalytic activity can be expected by the collapse of mesoporous silica structure. Mokaya has thoroughly investigated the reasons for the low hydrothermal stability of MCM-41 silicas in aqueous solutions,[46] which are due to the easy access of water through the material's large inner mesoporosity where the water molecules cause silicate hydrolysis with consequent collapse of the pore walls and loss of mesoporosity and surface area.

SBA-15 materials and PMOs are much more hydrothermally stable, and indeed often show stable catalytic activity (Figure 6). Yet, in the case of highly oxygenated biomass components, the strong adsorption of intermediate or final reaction products may cause polymerization and or carbonyl formation, with consequent pore blockage and catalyst deactivation. This is the case, for instance, of the sulfonated (arenesulfonic) mesoporous silica SBA-15-$SO_3H$ employed in the butyl-levulinate synthesis,[35] in which the white catalyst powder after a single run turns into a brown powder that cannot not be recycled even after extensive washing in hot water or following prolonged sonication in distilled water.

Similarly, while studying bifunctional catalysts in the conversion of cellulose into sorbitol and other valued feedstocks, Cardona Martinez and co-workers found that Ru supported on arenesulfonic acid-functionalized mesoporous silica (Ru/SBA-15S) is more hydrothermally stable than SBA-15,[47] even though it loses a significant fraction of its surface area, acidity, and activity after prolonged exposure to water at 483 K. In general, strategies to afford mesoporous silicas of enhanced hydrothermal stability aim to the strengthen pore walls, to maximize the degree of condensation of the silica precursors, and to minimize micropore formation.[48] For instance, if SBA-1, SBA-3, SBA-15, MCM-41, or MCM-48 are added to an acidic medium the material's resistance for against acidic media is linked to a critical wall thickness-pore diameter threshold, with mesopores being partially collapsed or blocked, following initial proton attack of the micropore surface.[49]

Recently, a simple surfactant-free method to prepare acidic mesoporous sulfonated silica from TEOS and $ClSO_3H$ has been reported.[50] The new process affords sulfonated silica of large surface area with a narrow range of mesoporosity and good thermal stability, that show remarkable reusability in the butylation of phenol as well as in hydrolysis reactions.[49] Again, however, the re-use of the resulting acid catalysts in condensation, hydrolysis, esterification or etherification reactions of hydrophilic oxygenate substrates such as those of the biorefinery may be limited by irreversible reaction between the entrapped acidity and intermediate reaction products.

## Perspectives and Conclusions

Four important examples discussed in this account that show the large potential of mesoporous acid silicas and their nanocomposite derivatives applied to the conversion of biomass components to efficiently afford valued products.

- The one-pot depolymerization and hydrogenation of cellulose to afford valued sugars, glycols, and carbonyls in several consecutive reaction cycles.
- The selective esterification and etherification of glycerol, again with excellent catalyst stability.
- The high yield synthesis of HMF from fructose in water.
- The efficient synthesis of butyl levulinate from biobutanol and furfuryl alcohol.

Introduced in the late 1990s mesoporous acid silicas and their nanocomposite derivatives are beginning to play a significant role in the manufacturing of fine and specialty chemicals.[51] Their use has indeed further widened and intensified, and is now finding application within the emerging biorefinery. Chemists developing new acid silicas of enhanced catalytic performance are targeting materials with the right morphology and surface properties,[52] and new nanocomposites.

For example, the versatile chemistry of the sol–gel process using templates allows to control the shape and morphology beyond the original hexagonal architecture of the first mesoporous silicas.[29] Stucky and co-workers, for instance, demonstrated in 1999 that is sufficient to add an organic co-solvent to the surfactant-assisted sol–gel polycondensation of TEOS to obtain mesostructured cellular foams (MCF) composed of uniformly sized, large interconnected silica pores,[53] that are ideally suited for enhanced heterogeneous catalysis.[54]

Indeed, most recently Calvino-Casilda's team has shown that one such MCF modified by MPTMS followed by the usual $H_2O_2$ treatment can afford high yields of solketal (an important solvent, plasticizer, surfactant, flavor enhancer, and pharmaceutical intermediate) via the acetalization of glycerol with acetone at 40 °C with 97 % selectivity at 80 % glycerol conversion.[55] The open structure of the MCF cells size (around 220–420 Å) enhances the diffusion of the reactants and provides room for bigger molecules, whereas after reaction the water anchored within the MCF structure can be removed simply by drying the material to be reused later in a new cycle of reaction.

In the complementary nanocomposite approach, researchers can further functionalize the inner mesopores with polymer molecules or metal nanoparticles to obtain catalysts of enhanced selective activity, or even multifunctional materials that can be applied to mediate an acid-catalyzed process followed by one or more subsequent selective reactions.

In conclusion, renewably sourced chemicals manufactured in economically viable biorefineries will have to compete on price, performance, and customer satisfaction, as there will now be a "green premium" for bio-based products.[56] The route to a successful biorefinery-based economy will, therefore, either go through the creation of specialized plants where higher-margin products are manufactured;[57] or via developing a highly integrated, multipurpose refinery capable of handling multiple feedstocks (starting from the most abundant, namely lignocellulosic biomass) catalytically processing them in multiple ways and producing multiple valued products. Acid mesoporous silicas developed along the lines discussed in this study hold a great potential to start making soon a practical impact in the emerging, economically and environmentally viable biorefineries (as summarized in Table 1).

**Table 1.** State-of-the-art acid silica catalyst for selected acid-catalyzed processes in the biorefinery.

| Process | Catalyst | Ref. |
|---|---|---|
| cellulose hydrogenolysis | $Ru/SiO_2$-$SO_3H$ | [35] |
| butyl levulinate synthesis | SBA-15-$SO_3H$ | [37] |
| hydrolysis of sugars | HMM | [27] |
| fructose dehydration to HMF | PVP-p$SO_3H$-SS | [40] |
| solketal synthesis from glycerol | MCF-$SO_3H$ | [55] |
| glycerol etherification | SBA-15-$SO_3H$ | [42] |

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**Keywords:** acid catalysis · biorefinery · heterogeneous · mesoporous silica · sol–gel

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