Significant enhancement on selectivity in silica supported sulfonic acids catalyzed reactions†

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Thanks to strong hydrophilic interactions between reaction products and the catalyst surface, mesoporous silica supported sulfonic sites were found to be much more selective than homogeneous and common solid acid catalysts.

Silica immobilized molecular catalysts (SIMCs) has become a very promising tool for catalysis since recent researches showed a clear synergistic effect between the immobilized catalytic entities and the siliceous support.[1] Based on this strategy new and fascinating concepts recently emerged which gave access to multifunctional catalysts,[2] stabilisation of metal nanoparticules,[3] chiral materials[4] or the preparation of molecularly imprinted polymers.[5] However, the catalytic performance, activity and selectivity, of these SIMCs is usually lower than that of the corresponding homogeneous molecular catalysts. This lower catalytic activity is mainly due to a poorer accessibility of the catalytic sites caused by the steric hindrance and/or the high hydrophilicity of the inorganic solid support. In order to circumvent these issues, few strategies were developed such as the use of mesoporous silica framework with high specific areas[6] or the silica surface derivatization.[7] However, even if these promising methods succeded to increase the catalytic activities of the resulting SIMCs, they do not allow to improve their selectivity. Zeolites are one of the most spectacular examples of siliceous heterogeneous catalysts able to reach higher selectivity than homogeneous catalysts thanks to their shape selectivity.[9] However, their small pore openings limit their applications to weakly sterically hindered organic substrates. More recently, reported studies showed that silica supported nanoparticles[3] or ionic liquid films[8] can also afford selective processes but their long term stability on the solid support still remain a difficult challenge.[3]

Here we wish to report that the hydrophilicity of mesoporous SIMCs, usually considered as a drawback for the diffusion of organic substrates, can be favorably used to perform highly selective processes starting from unprotected polyfunctional organic derivatives. To our delight, mesoporous silica supported sulfonic groups were able to block a side polymerization process affording monomers with (i) selectivity higher than homogeneous and usual solid acid catalysts and (ii) high catalytic activity. The consideration of the hydrophilicity of mesoporous SIMCs allowed us to selectively and easily (no chemical modification of the silica surface) synthesize in an one step process various polyfunctional derivatives not accessible by conventional catalytic or organic routes.

Selective esterification of fatty hydroxylated carboxylic acids with glycerol was first studied as a model reaction for this purpose. This reaction is of great importance for supramolecular chemistry since the esterified products exhibit a broad polymorphism.[10] The selectivity here is the main problem since a rapid polymerisation reaction between reactants can occur making difficult the formation of the targeted amphiphilic monoesters with high yield. First, esterification of glycerol with 16-hydroxyhexadecanoic acid (juniperic acid) was studied at 110 °C in the presence of 2.5 mol% of *p*-toluene sulfonic acid (PTSA) as reference homogeneous catalyst. As expected, using PTSA, the resulting amphiphilic monomer was obtained with yield lower than 35% because of a rapid polymerization of the reactants (Fig. 1).

In order to increase the selectivity of this reaction, we immobilized sulfonic groups over three different kinds of mesoporous silica. These porous materials are known to be highly polar[11] and strong hydrophilic interactions between the silica framework and glycerol are expected to favor a rapid desorption of the targeted amphiphilic monomer from the catalytic surface avoiding thus the polymerization reactions.

Synthesis of mesoporous silica-supported sulfonic groups, with different pore diameters, was carried out according to known procedures using tri-block P123 and hexadecylamine as templates for mesoporous silica SBA-SO_3H and HMS-SO_3H respectively.[11]

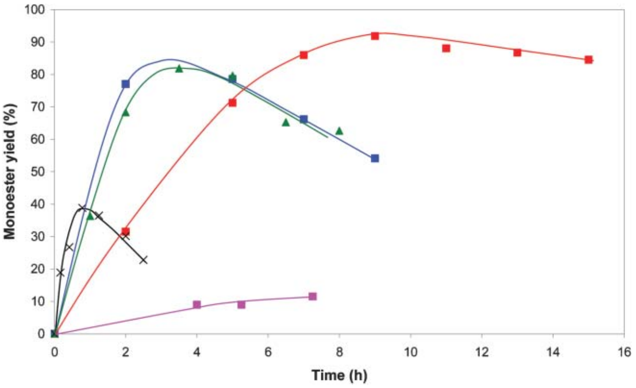

Fig. 1 Comparison of kinetic profiles between (blue) SBA-15-SO_3H, (green) HMS_1–SO_3H, (red) HMS_2–SO_3H, (×) PTSA and (pink) blank. From heterogeneous catalysts, maximum yields are obtained at 95% conversion of carboxylic acid. In the case of PTSA the maximum monomer yield is reached at only 75% conversion.

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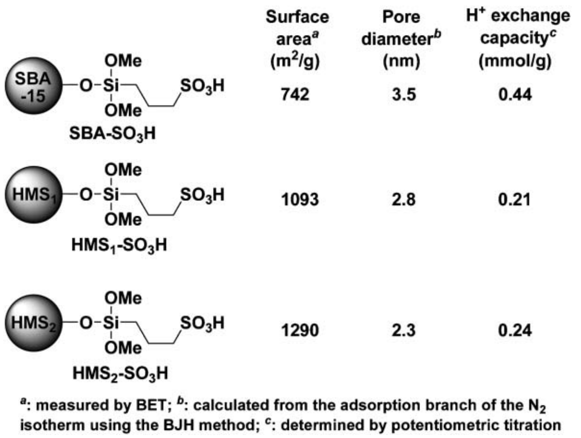


	Surface area[a] (m^2/g)	Pore diameter[b] (nm)	H$^+$ exchange capacity[c] (mmol/g)
SBA-SO$_3$H	742	3.5	0.44
HMS$_1$-SO$_3$H	1093	2.8	0.21
HMS$_2$-SO$_3$H	1290	2.3	0.24

[a]: measured by BET; [b]: calculated from the adsorption branch of the N$_2$ isotherm using the BJH method; [c]: determined by potentiometric titration

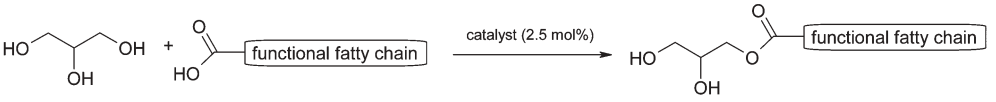
Scheme 1 Physicochemical properties of prepared acid SIMCs.

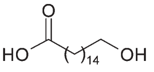
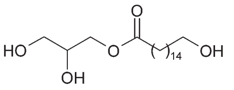
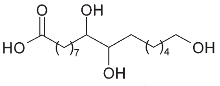
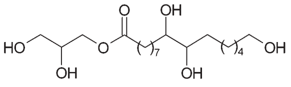
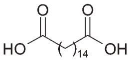
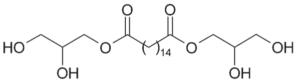
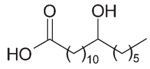
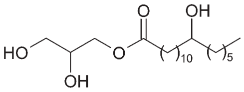
HMS$_1$-SO$_3$H and HMS$_2$–SO$_3$H differ each other from the initial oganosilane/TEOS molar ratio (see Electronic Supplementary Information†). Physico-chemical properties of these materials are given in Scheme 1.

To our delight, mesoporous SBA-SO$_3$H and HMS$_1$–SO$_3$H materials with pore diameters of 3.5 nm and 2.8 nm respectively appeared to be much more selective than homogeneous PTSA affording more than 81% yield into the desired amphiphilic monomer (Fig. 1). As we expected, in neat glycerol, the great affinity of the silica framework for this hydrophilic triol allowed a rapid desorption of the monoester from the catalyst surface limiting thus the formation of polymers as it was the case with PTSA. After total consumption of the starting carboxylic acid, the monomer yield drops due to intermolecular transesterification between two monomer units (Fig. 1). Using mesoporous silica catalyst with smaller pore opening such as HMS$_2$–SO$_3$H (2.3 nm), the reaction rate decreased due to a poorer accessibility of the catalytic sites but interestingly the yield into the desired amphiphilic monomer was increased from 81% to 92% (Fig. 1). This selectivity improvement is probably due to a synergistic effect between the siliceous hydrophilicity and the significant steric hindrance of HMS$_2$–SO$_3$H. This effect was also clearly illustrated at the end of the reaction since after total consumption of the starting carboxylic acid, the monomer yield remains quite stable for more than 8 h (Fig. 1).

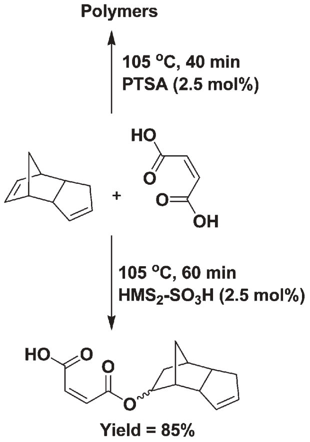
The scope of this method was then studied by conducting it starting from different functional carboxylic acids (aleuritic, thapsic and 12-hydroxystearic acid) and the efficiency of HMS$_2$–SO$_3$H was compared to other known solid acid catalysts such as cation exchange resin (A119), zeolite (HFAU) and sulfonated carbon (Carb-SO$_3$H) prepared as described elsewhere.[12] Whatever the starting functional carboxylic acid, the HMS$_2$–SO$_3$H was found to be the more selective solid catalyst affording the ester derivatives with selectivity of 86–99% range at conversion levels higher than 80% (Table 1). Replacement of the siliceous support by a carbonaceous or polystyrene framework led to a dramatic drop of the different targeted esters yield from 77–92% range for HMS$_2$–SO$_3$H to 25–77% range for A119 and 17–59% range for Carb-SO$_3$H pushing forward the great contribution of the siliceous hydrophilicty on the reaction selectivity (Table 1). HFAU zeolite is the less selective solid acid catalyst affording ester derivatives with only 12–68% yield (Table 1). The greater selectivity obtained with HMS$_2$–SO$_3$H by comparison to the siliceous HFAU is probably due to an easier diffusion of reactants whithin the HMS$_2$ porous netwok (HFAU pore opening = 0.74 nm *vs* 2.3 nm for HMS$_2$–SO$_3$H) and to the stronger acidity of sulfonic groups. These results clearly evidenced that the mesoporous siliceous framework

Table 1 selective esterification of various polyfunctional carboxylic acids over HMS$_2$–SO$_3$H



Acid	Catalyst	Product	Time/h	% Conversion	% Yield	% Selectivity
 juniperic[a]	HMS$_2$–SO$_3$H		15	99	91	92
	A119[d]		18	97	25	26
	HFAU[e]		25	95	12	13
	Carb-SO$_3$H[f]		28	90	17	19
 aleuritic[b]	HMS$_2$–SO$_3$H		4	94	92	98
	A119[d]		4	93	77	83
	HFAU[e]		6	90	68	75
	Carb-SO$_3$H[f]		26	80	59	75
 thapsic[a]	HMS$_2$–SO$_3$H		6	100	86	86
	A119[d]		7	100	44	44
	HFAU[e]		5	95	25	26
	Carb-SO$_3$H[f]		7.5	99	59	59
 12-hydroxystearic[c]	HMS$_2$–SO$_3$H		6	80	77	99
	A119[d]		11	80	62	77
	Carb-SO$_3$H[f]		15	83	39	47

[a] Carboxylic acid (1 mmol), glycerol (6 mmol), 110 °C, 2.5 mol% of supported sulfonic groups. [b] Carried out at 70 °C. [c] In the presence of 10 mol% of cetyltritylammonium bromide as a phase transfer agent. [d] Cation exchange resin, H$^+$ exchange capacity = 4.2 mmol/g. [e] Zeolite HFAU with total framework Si/Al ratio of 20, 10 wt%. [f] H$^+$ exchange capacity = 0.3 mmol g^{-1}.



Scheme 2 Selective addition of maleic acid to dicylopentadiene over $HMS_2–SO_3H$.

hydrophilicity of SIMCs can be favorably used to closely control the selective and direct transformation of unprotected polyfunctional carboxylic acids. Moreover, it is noteworthy that this selectivity improvement was not to the detriment of the catalytic activity as it is generally the case since $HMS_2–SO_3H$ exhibits similar and, even in some cases, higher catalytic activities than other solid acid catalysts.

In order to demonstrate that the consideration of the silica hydrophilicity of SIMCs was not only applicable to the selective esterification of functional carboxylic acids with glycerol, we then moved on to the reaction of dicyclopentadiene with maleic acid as another model reaction. Direct and selective nucleophilic addition of functional carboxylic acids to diene instead of alkyl halide is an attractive salt free method for organic chemists especially for the synthesis of monomer for polyester resins.[13] When maleic acid was heated at 105 °C in the presence of three times excess of dicyclopentadiene and 2.5 mol% of PTSA, the maleic acid was totally consumed in less than 40 min (Scheme 2). However, in these conditions, the formation of the targeted 10-membered ring ester was not produced and a rapid gelification of the reaction media was observed suggesting a polymerization of reactants. When PTSA was replaced by $HMS_2–SO_3H$ (2.5 mol% of supported sulfonic groups), the selectivity of the reaction was considerably improved since, even using three times excess of dicyclopentadiene, the starting maleic acid is totally converted into more than 85% of monoester adduct in less than 1 h (Scheme 2).

In conclusion we report here that acid mesoporous SIMCs are more selective than homogeneous or usual solid acid catalysts for the direct transformation of unprotected polyfunctional substrates. This remarkable selectivity improvement is due to the natural hydrophilic nature of their siliceous framework which allows a rapid desorption of the reaction products from the catalyst surface inhibiting thus polymerization reactions. Moreover, in the particular case of mesoporous acid SIMCs with pore diameter of 2.3 nm, a synergystic effect between the steric hindrance of the porous network and the siliceous hydrophilicity is observed affording acid solid catalyst able to reach unprecedented selectivity.

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