

Sulfonic acid functionalised ordered mesoporous materials as catalysts for condensation and esterification reactions

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Mesoporous silicas were functionalised with sulfonic acid groups; the resulting materials are excellent catalysts for formation of bisfurylalkanes and polyol esters.

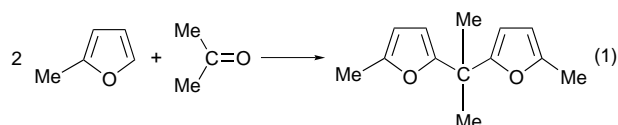
The discovery of mesoporous materials has raised the general expectation that the catalytic efficiency of microporous zeolites can be expanded to mesoporous dimensions.¹ It is necessary to introduce functionality into MCM or HMS structures, so surface modification techniques are enjoying a renewed interest, and it is clear that the pore walls of mesoporous materials are easily modified with either purely inorganic or with hybrid, semi-organic functional groups.^{2,3} Reports on Ti-MCM-41 prove that this oxidation catalyst can indeed handle voluminous substrates such as alkylated phenols.⁴ We recently illustrated the potential of a guanidine-functionalised MCM-41 in base-catalysed condensations.⁵ Progress in acid catalysis is lagging behind, largely because of the low acid strength of Al-substituted mesoporous silicas such as Al-MCM-41.⁶ As an alternative, we now propose the covalent attachment of alkylsulfonic acid groups to the surface of MCM and HMS molecular sieves, *via* secondary synthesis as well as *via* direct one-step synthesis. The resulting MCM-SO₃H and HMS-SO₃H materials perform well in typical strong-acid catalysed reactions. The hydrophobic nature of the active sites' environment can be exploited to perform reactions which are outside the reach of other inorganic solid acid catalysts.

The key precursor in the synthesis of alkylsulfonic acid functionalised mesoporous materials is 3-mercaptopropyltrimethoxysilane (MPTS). This molecule contains an SH group, a stable propyl spacer and a hydrolysable Si(OMe)₃ moiety. Hybrid mesoporous silicas were prepared either *via* silylation of preformed mesoporous silica, or *via* co-condensation of the primary building blocks.† First, MPTS and Si(OEt)₄ were hydrolysed together in the presence of an ionic or a non-ionic surfactant (*viz.* C₁₆NMe₃Br and *n*-C₁₂-amine), leading to MCM or HMS type materials, respectively (Scheme 1, route 1). Alternatively, secondary modification comprised the silylation of a vacuum-dried pre-existing MCM support with MPTS in dry toluene, or the coating of a partially hydrated support with an MPTS layer (Scheme 1, routes 2a and b).³ Both primary and

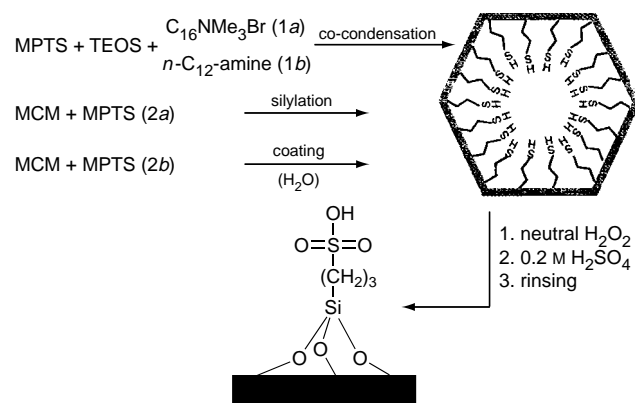
secondary syntheses lead to materials functionalised with largely intact SH groups, as is evidenced by an IR ν_{S-H} vibration of medium intensity at 2575 cm⁻¹, and by the solid state ¹³C NMR shifts [δ 11 (C₃), 27 (C₁, C₂)]. The MeO groups of the liquid MPTS spectrum are absent, while the CH₂(-Si) is slightly shifted downfield (from δ 8 to 11). These SH groups are easily converted into sulfonic acid groups by mild oxidation with neutralised H₂O₂, acidification and finally, thorough washing to remove all liquid acid. In view of the high loading of the material with functional groups, it is not surprising that some disulfide is observed in the final product (δ 41, 23). However, the major signals are observed at δ 54, 18 and 11. These are consistent with those calculated for *e.g.* propanesulfonic acid and give strong proof for the prevalence of (CH₂)₃SO₃H surface groups.

In ambient conditions, the water affinity of the material is remarkably low, as proved by thermogravimetric analysis (less than 1 wt% H₂O) and by the weakness of the IR δ_{OH} vibration (1638 cm⁻¹). Typical loadings, as measured by thermogravimetry or *via* titration of the SO₃H groups, vary between 1.0 and 1.5 mequiv. g⁻¹. Sorption characteristics depend strongly on the preparation method. For instance, an MCM-SH material prepared *via* silylation (route 2a) displays a BET surface of 740 m² g⁻¹ and a pore volume of 0.51 ml g⁻¹ with a radius between 2 and 4 nm (from the Kelvin equation and the BJH method). These data evidence the mesoporous nature of the material, even if the specific surface and mesoporous volume are somewhat lower than for a typical MCM-41. However, coating of the material with an MPTS layer (route 2b) leads to a reduction of BET surface (510 m² g⁻¹), average pore radius (< 2 nm) and pore volume (0.25 ml g⁻¹), as determined from T-plot analysis). Oxidation of the latter material to its sulfonic acid form leads to further minor changes of BET (399 m² g⁻¹) and pore volume (0.19 ml g⁻¹). Isolated silanol groups, which reportedly absorb at 3740 cm⁻¹,⁷ were not detected in the IR spectra of MCM-SO₃H upon evacuation at 373 or 473 K. The absorption between 3500 and 2700 cm⁻¹ may rather be assigned to hydrogen-bonded SO₃H groups. Summarising, the catalyst design leads to a hydrophobic mesoporous material, with uniform and well-characterized SO₃H groups.

The catalytic properties of the new materials were first tested in the synthesis of 2,2-bis(5-methylfuryl)propane (DMP). Bisfurylalkanes are relevant intermediates for macromolecular chemistry.⁸ DMP is produced from 2-methylfuran (MF) and acetone in a strong acid catalysed condensation [reaction (1)].



Zeolites may seem accomplished catalysts for such reactions. However, exposure of zeolites such as H-β or H-US-Y to furans leads to immediate formation of tarry oligomeric products, even for the substituted compounds such as MF.⁹ Addition of acetone



Scheme 1

Table 1 Solvent-free reaction of MF (1.8 g) with acetone (3.2 g) (molar ratio = 1:2.5) in the presence of 0.18 g acid catalyst (323 K, 24 h)

Entry	Catalyst	Conversion (%) ^a	Selectivity (%) ^b
1	—	0	—
2	H-β ^c	61	74
3	H-US-Y ^d	55	67
4	Al-MCM-41	5	95
5	MCM-SO ₃ H (coated) ^e	85	96
6	HMS-SO ₃ H (co-cond.; 10%) ^f	61	94
7	HMS-SO ₃ H (co-cond.; 20%) ^g	73	95
8	MCM-SO ₃ H (co-cond.; 20%) ^g	52	87
9	MCM-SO ₃ H (silylated) ^c	57	92

^a Conversion of MF. ^b Selectivity for DMP, based on MF. ^c Si:Al = 12.5 (PQ). ^d Si:Al = 22.5. ^e Prepared *via* secondary modification with MPTS. [†] Prepared *via* co-condensation of MPTS and TEOS (10:90). ^g As in *f*, with MPTS:TEOS = 20:80.

partially suppresses MF oligomerisation. As a result, catalyst deactivation is fast, and DMP selectivities are limited even at moderate conversions (Table 1, entries 2, 3). Moreover, the strong adsorption of DMP or other reaction intermediates in the relatively narrow zeolite pores leads to detectable secondary condensation products, which desorb with even greater difficulty than DMP itself. Such observations have led previous workers to use elevated catalyst concentrations;¹⁰ in our reaction conditions, the side-reactions impose an upper limit of 45% on the overall DMP yield. While the DMP selectivity is better on Al-MCM-41, the low acid strength causes an unsatisfactory MF conversion. In contrast, the sulfonic acid MCMs combine a remarkable DMP selectivity (often up to 95%) with elevated MF conversions (entries 5–9). Apparently the hydrophobic surface prevents a too strong MF adsorption and oligomerisation, while the larger dimension of the pores facilitates product desorption. The highest DMP yield on MF basis, a remarkable 82%, is obtained with an MCM-SO₃H prepared *via* the surface coating procedure (entry 5). Thus, polarity, rather than the activity, makes the sulfonic MCMs superior to zeolites for this particularly demanding reaction.

Another application of the new materials may be found in polyol esterification. These reactions produce valuable products such as emulsifiers, detergents or low-caloric fats. The use of (preferably heterogeneous) catalysts may allow lower reaction temperatures, but the intrinsic immiscibility of the polyol and fatty acid phases is a major problem. Thus, in the esterification of *e.g.* D-sorbitol with lauric acid, zeolites such as H-β reside exclusively in the polyol layer. The only reaction is sorbitol degradation, and the fatty acid conversion is zero even after prolonged reaction times (Table 2, entry 2). In contrast, the much more hydrophobic MCM-SO₃H readily effects formation of a small amount of monoacylated products, and because of the detergency of the latter, homogenisation of the reaction medium. Main products are monolaurylisorbide, which is an important detergent precursor,¹¹ or in a later stage, the isorbide diester (entry 3).

In conclusion, sulfonic acid functionalised MCM or HMS materials are new and worthwhile materials for reactions in which zeolites fail.

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Table 2 Esterification of D-sorbitol (3.64 g) with lauric acid (24.0 g) (molar ratio = 1:6) catalysed by an acid zeolite or by a mesoporous sulfonic acid catalyst (0.36 g) (385 K, 24 h)^a

Entry	Catalyst	Lauric acid conversion (%)	Product selectivity (%) ^b
1	—	0	—
2	H-β ^c	0	—
3	MCM-SO ₃ H (co-cond.; 20%) ^d	33	>95

^a Analysis with size-exclusion HPLC, ¹H-¹³C NMR and COSY. ^b Selectivity, based on lauric acid, for dilaurylisorbide. ^c Si:Al = 12.5 (PQ). ^d Prepared *via* co-condensation of MPTS and TEOS (20:80).

Notes and References

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† Preparation of MCM-SO₃H and HMS-SO₃H *via* co-condensation (Scheme 1, route 1): MCM-41 type materials were synthesized from a mixture of MPTS (20 mol%) and Si(OEt)₄ (TEOS, 80 mol%). The molar gel composition was 0.12 C₁₆NMe₂Br:0.5 NaOH:1.0 total siloxane:130H₂O (24 h, 293 K). An acid solvent extraction technique was used to remove the ionic surfactant. Mercaptopropyl-modified HMS was obtained from the following gel composition: 0.9 (or 0.8) TEOS:0.1 (or 0.2) MPTS:0.275 *n*-C₁₂-amine:8.9 EtOH:29.4 H₂O (24 h, 293 K). *n*-C₁₂-Amine was extracted with boiling EtOH (12 h, 3 times).

Silylation (Scheme 1, route 2a) was performed on a calcined and evacuated (393 K) MCM-41 (synthesised from Ludox), using excess MPTS in dry toluene (4 h, reflux), followed by Soxhlet extraction with Et₂O and CH₂Cl₂. For coating with an MPTS layer (route 2b), the MCM was refluxed in water (3 h), filtered and suspended in toluene. Part of the water was removed in an azeotropic distillation with a Dean-Stark trap. Further preparation followed route 2a.

Mercaptopropyl groups were oxidised with a three-fold excess of neutralised H₂O₂. After washing with H₂O and EtOH, and acidification in 0.2 M H₂SO₄, the powder was rinsed thoroughly with distilled H₂O and dried at 333 K.

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