Introducing catalytic activity in helical nanostructures: microwave assisted oxathioacetalisation catalysed by Al-containing helical mesoporous silicas†

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Al-containing helical mesoporous silicas have been synthesized and characterised by different techniques, showing outstanding activities (comparable to those obtained with sulfuric acid) in the oxathioacetalization of cyclohexane.

Size and shape selectivity in porous inorganic structures plays a pivotal role in a wide range of industrial and biological applications involving molecular transport, adsorption, separation and catalysis.[1]

The preparation of helically nanostructured materials has attracted great attention due to their potential applications including chiral selective separation and recognition,[2a,b] and enantioselective catalysis.[2c] Although helical mesoporous silica materials were originally synthesized using chiral anionic surfactants,[3a] similar morphologies have been recently reported using non chiral templates under concentrated ammonia solutions.[3b] However, the lack of active sites is one of the main limitations of helical silica-based mesostructured materials.

Different strategies have been investigated to introduce catalytically active sites into mesoporous silicas including co-condensation of active species during mesoporous material synthesis or post-synthesis methods such as ion exchange.[4a,b] The isomorphous substitution of silicon by other elements has also been the subject of extensive studies.[4c]

Acetalisation reactions are generally utilised as protecting protocols for carbonyl groups in multi-step processes.[5] O/O-acetals are relatively sensitive in acidic conditions, while S S^{-1}- and mostly O/S-acetals (due to their ease of removal compared to the former) are frequently employed as acyl anion equivalents for C–C bond formation[6] and/or carbonyl protecting groups.[6,7]

O/S-acetals and ketals have been prepared from carbonyl compounds *via* acid catalysis, using a variety of solid acids including metal triflates,[8a] silica supported acids,[8b] clays[8c] and more recently sulfonated carbonaceous materials.[8d]. However, reported protocols to date involve hazardous and environmentally unfriendly reagents and/or catalysts, high temperatures and long reaction times (3–12 h), lacking thus far of a facile, efficient and clean methodology for the production of such compounds.

Herein, we report the first—to the best of our knowledge—methodology for the *in situ* incorporation of catalytic quantities of Al into helical mesostructured silica materials. Using this strategy, highly active catalysts with acid properties were prepared and investigated in the microwave-assisted oxathioacetalisation of cyclohexanone. In a one-step approach, a metal precursor is solubilised in the surfactant template micelles immediately prior to silica polymerisation. Subsequent template removal leads to metal containing helical mesoporous silica with high surface areas. In this method, the metal is brought directly into the pore walls and is expected to be highly accessible to the reactants.

Al-containing helical mesoporous silicas were prepared using a facile one-pot method. In a typical synthesis procedure, 0.96 g cetyltrimethylammonium bromide (CTABr) (Fluka, ≥ 96.0%) was dissolved in 300 mL of aqueous ammonia solution (Sigma-aldrich, 30 wt%) at 40 °C. 4.8 mL of tetraethoxysilane (Aldrich, 98%) and different quantities of $AlCl_3{\cdot}6H_2O$ (Sigma-aldrich, 99%) were then added to the solution. The molar composition of the synthesis gel was $1SiO_2 : 0.12CTABr : 110NH_4OH : 490H_2O : xAlCl_3{\cdot}6H_2O$, where x varied from 0.005 to 0.01, which in turn corresponds to Si/Al molar ratios of 95 and 190, respectively. The final mixture was then reacted at 40 °C for 3 h under stirring (600 rpm), followed by aging at 100 °C for 24 h in a Teflon lined stainless steel autoclave. Upon cooling at room temperature (RT), the solid product was thoroughly washed (first with water and then with ethanol), filtered off, and dried overnight. The surfactant was finally removed by calcination at 550 °C for 8 h (2 °C min^{-1}) under static air atmosphere. Materials were denoted as Al-HMM, where HMM stands for helical mesoporous materials.

Helical materials with homogeneous metal incorporation were obtained for Al contents up to molar ratios of Si/Al = 95 (Si/Al molar ratios of 70 and below rendered non helical mesostructures).

Representative TEM micrographs of the Al-HMM with a molar ratio Si/Al = 190 are shown in Fig. 1. TEM tilt series from −30° to +30° at an interval of 10° as well as a SEM image of the sample that support the helicity claim have been included in the ESI.†

The incorporation of Al in the framework of helical mesoporous silica does not significantly alter their adsorption

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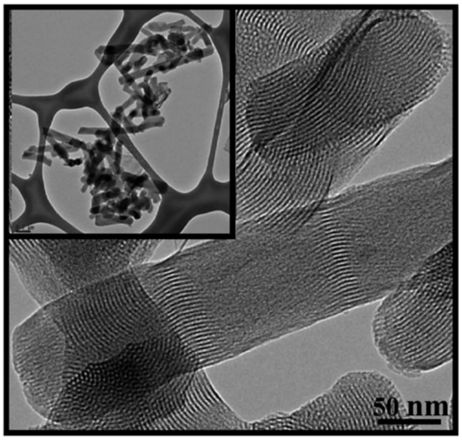


Fig. 1 TEM micrographs of Al-HMM (Si/Al = 190) at two different magnifications. Scale bar in the inset = 0.2 μm.

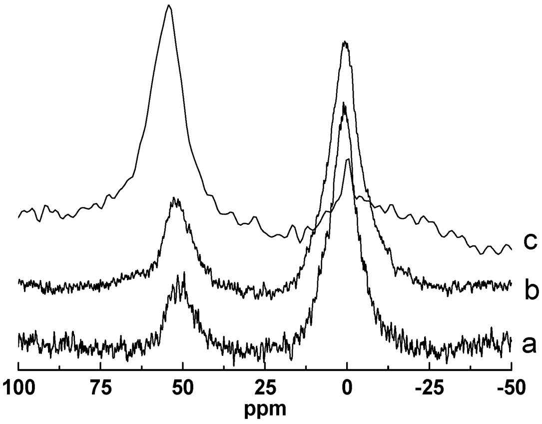


Fig. 2 ^{27}Al MAS NMR offset spectra of Al-HMM and Al-MCM samples with different quantities of Al^{3+}. The nominal Si/Al ratio of the metal in each sample is (a) Al-HMM (Si/Al = 190), (b) Al-HMM (Si/Al = 95) and (c) Al-MCM (Si/Al = 60). Spectra for (b) and (c) samples are vertically offset for clarity.

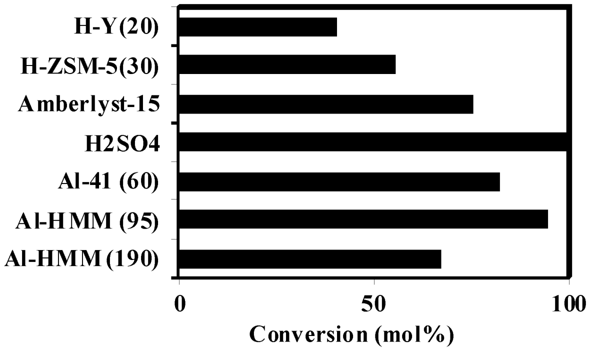
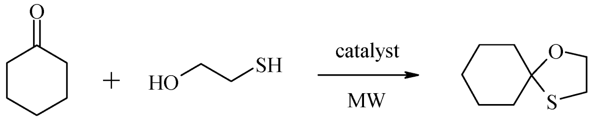


Fig. 3 Catalytic activity of various acid catalysts in the oxathioacetalisation of cyclohexanone with 2-mercaptoethanol under microwave irradiation. Reaction conditions: 5 mmol cyclohexanone, 10 mmol 2-mercaptoethanol, 0.05 g catalyst, microwaves, 300 W, 2 min, 70 °C (maximum temperature achieved). Carbon balance of products found was >99% of the starting materials.



Scheme 1 Microwave-assisted oxathioacetalisation of cyclohexanone with 2-mercaptoethanol.

properties, as evidenced by the virtually identical HMM isotherms with or without Al in their structure (ESI†).

Al-HMM also maintains a 2-D hexagonal mesopore arrangement, showing the three distinctive (100), (110), and (200) X-ray diffractions peaks characteristic of a hexagonally ordered mesopore structure (ESI,† see also Table 1).

Solid-state ^{27}Al MAS spectra of calcined Al-HMM samples show two signals at 50 and 0 ppm assigned to tetracoordinated and octahedrally coordinated Al^{3+}, respectively (Fig. 2).[9] Interestingly, Al was found to be partly in octahedral coordination (contribution at 0 ppm) which might be related to the presence of extra framework species that can have an influence on the properties of the materials.[10]

Infrared spectra also showed a shift of the band at *ca.* 1040 cm^{-1} towards higher wavenumbers for Al-containing materials. This is consistent with the metal incorporation into lattice positions of the helical silica materials (ESI†).[11]

The catalytic properties of Al-HMM materials were subsequently investigated. An acid-catalysed process (oxathioketalisation of cyclohexanone with 2-mercaptoethanol, Scheme 1) was chosen as a model reaction to test the activity of the materials. Recent literature reports show the reaction can be carried out at RT in a few hours (2–6 h).[6,8a]

Microwave protocols have been extensively employed in catalysis and organic synthesis as they can significantly speed up rates of reactions as well as often improving the selectivity to certain products.[12] Catalytic tests under optimised conditions were performed as follows: 5 mmol cyclohexanone, 10 mmol 2-mercaptoethanol and 0.05 g catalyst were placed on a microwave CEM-Discover reaction vessel and microwaved for 2 min at 300 W (pressure controlled, ESI†). The final mixture was then extracted and analysed by GC and GC–MS (ESI†).

Al-HMM exhibited excellent activities in the investigated reaction, providing quantitative conversion of starting

Table 1 Textural parameters of Al-HMM materials as compared with the parent helical material (HMM)

Sample	d_p[a]/nm	a[b]/nm	b_d[c]/nm	A_{BET}[d]/m^2 g^{-1}	V_{pore}[e]/cm^3 g^{-1}
HMM	2.7	4.7	2.0	880	0.8
Al-HMM (Si/Al = 190)	2.7	4.7	2.0	1077	1.0
Al-HMM (Si/Al = 95)	2.7	4.6	1.9	1020	1.0

[a] Average pore diameter from the adsorption branch according to the BJH method. [b] Unit cell parameter from XRD measurements. [c] Estimated wall thickness obtained from $b_d = a - d_p$. [d] BET surface area estimated by using multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.30. [e] Mesopore volume calculated from the adsorption branch of the nitrogen isotherm using the BJH method.

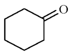
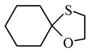
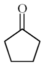
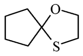
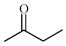
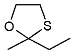
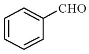
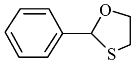
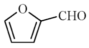
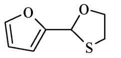
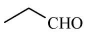
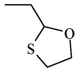
material in very short times of irradiation (typically 2 min). A complete selectivity to the oxathioacetal was also observed.

Blank runs (without catalyst and with the parent silica helical material) gave virtually no conversion of starting material after 15 min of microwave irradiation. Interestingly, the catalytic activities of Al-HMM (Si/Al = 95) were comparable to those of sulfuric acid and significantly superior to those obtained with related solid acids including zeolites and acidic resins (Fig. 3). Al-HMM (Si/Al = 95) also gave slightly higher conversions under the investigated conditions when compared to a commercial Al-MCM-41 even with higher Al content (Al-41, Si/Al = 60) (Fig. 3). These interesting findings may imply the helical mesostructure can slightly affect the activity in the materials for particular applications.[2] Another explanation for this unusual activity might as well be related to the observed Al in octahedral coordination. Al in Oh coordination has been shown to have excellent catalytic properties in different acid catalysed processes.[10]

The scope of the protocol was also extended to other substrates to prove the usefulness of the most active Al-HMM catalyst under the investigated conditions.

Table 2 shows the system was amenable to a range of carbonyl compounds (from aromatic to aliphatic ketones and aldehydes) with almost quantitative conversions of starting material and complete selectivities to the target product obtained in a few minutes of reaction (typically 2–5 min). Most importantly, Al-HMM were also highly reusable under the investigated reaction conditions, preserving over 90% of their initial activity after 4 uses (ESI†).

Table 2 Catalytic activity of Al-HMM with a Si/Al = 95 in the oxathioacetalisation of carbonyl compounds with 2-mercaptoethanol under microwave irradiation[a]

Entry	Substrate	Product	Time of reaction (min)	Conversion (mol%)
1			2	94
2			5	89
3			5	96
4			2	99
5			2	90
6			2	99

[a] 5 mmol substrate, 10 mmol 2-mercaptoethanol, 0.05 g catalyst, microwaves, 300 W (60–80 °C maximum temperature reached). Carbon balance of products found was >99% of the starting materials.

In conclusion, we have reported the introduction of catalytic sites on helical mesoporous silicas and their use as highly active and reusable materials in important acid catalysed reactions, such as the oxathioacetalisation of carbonyl compounds, for a wide variety of substrates. We envisage these materials to be applicable to related acid and/or redox catalysed processes. These reactions, including oxidations of alcohols and Friedel–Crafts alkylation and acylations, are currently under investigation in our laboratories.

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