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Low-temperature sol–gel transformation of methyl silicon precursors to silica-based hybrid materials

Veena Dhayal[a], Rakesh Bohra[a]* , Meena Nagar[a], Ajay Kaushik[b], Sanjay Mathur[c]* and Sven Barth[c]

Six new methyl silicon (IV) precursors of the type [MeSi{ON=C(R)Ar}$_3$] [when R = Me, Ar = 2-C_5H_4N (1), 2-C_4H_3O (2) or 2-C_4H_3S (3); and when R = H, Ar = 2-C_5H_4N (4), 2-C_4H_3O (5) or 2-C_4H_3S (6)] were prepared and structurally characterized by various spectroscopic techniques. Molecular weight measurements and FAB (Fast Atomic Bombardment) mass spectral studies indicated their monomeric nature. ^{1}H and ^{13}C{^{1}H} NMR spectral studies suggested the oximate ligands to be monodentate in solution, which was confirmed by ^{29}Si{^{1}H} NMR signals in the region expected for tetra-coordinated methylsilicon (IV) derivatives. Thermogravimetric analysis of 1 revealed the complex to be thermally labile, decomposing to a hybrid material of definite composition. Two representative compounds (2 and 4) were studied as single source molecular precursor for low-temperature transformation to silica-based hybrid materials using sol–gel technique. Formation of homogenous methyl-bonded silica materials ($MeSiO_{3/2}$) at low sintering temperature was observed. The thermogravimetric analysis of the methylsilica material indicated that silicon-methyl bond is thermally stable up to a temperature of 400 °C. Reaction of 2 and Al(OPr^i)$_3$ in equimolar ratio in anhydrous toluene yielded a brown-colored viscous liquid of the composition [MeSi{ON=C(CH_3)C_4H_3O}$_3$.Al(OPr^i)$_3$]. Spectroscopic techniques ^{1}H, ^{13}C{^{1}H}, ^{27}Al{^{1}H} and ^{29}Si{^{1}H} NMR spectra of the viscous product indicated the presence of tetracoordination around both silicon and aluminum atoms. On hydrolysis it yielded methylated aluminosilicate material with high specific surface area (464 m^2/g). Scanning electron micrography confirmed a regular porous structure with porosity in the nanometric range.

Keywords: functionalized oximes; TGA; hybrid material; single-source precursor; methylsilica; aluminosilicate; scanning electron micrograph; nanometric

Introduction

Since the discovery of the M41S mesoporous silica materials in 1992 by Mobile Corporation,[1] there has been a growing interest in the development of new mesoporous materials. Recently, a new class of materials, periodic mesoporous organosilica (PMOs), has been reported.[2] When compared with the first-generation periodic mesoporous silica materials, PMOs are unique because their channels contain both organic and inorganic substrates.

The presence of organic functional groups in the mesoporous framework allows the mechanical or optical properties of the bulk materials to be tuned, giving rise to a wide range of materials having potentially interesting electronic, optical and charge-transfer properties.[3] These can also modify the hydrophilicity/hydrophobicity of the surface and may change the surface reactivity of the materials for a particular application.

Furthermore, the presence of a heteroatom such as Al into the pore walls of hybrid mesoporous organosilicas offers the opportunity to introduce further functionalities, which are suitable for applications in catalysis and separation.[4]

It has been reported in the literature that organic group modified mesoporous silica materials with improved skeletal mechanical silica strength (Si–O–Si network) may be prepared under acidic conditions by the *in situ* co-condensation of organosilane precursors and tetraethyl orthosilicate in the presence of surfactants.[5]

It would be relevant to mention here that alkoxysilanes {$R_nSi(OR)_{4-n}$} are hydrolytically stable species which may undergo only acid- or base-catalysed hydrolysis reactions.[6a,b] Kessler *et al*.[6c] suggested that the sol–gel transformation is not a kinetically controlled hydrolysis-polycondensation, but a micellar self-assembly processes directed by surface interactions enhanced by the presence of introduced heteroligands.

Thus, the objective of the present work was to synthesize better precursor for the silica based hybrid materials. This led us to the synthesis and characterization of some methylsilicon(IV) oximates. Some of these have been used as single source molecular precursors for the preparation of homogenous methylsilica materials by the sol–gel technique at low sintering temperatures (100–300 °C). This appears to be a better method for the

* *Correspondence to: Sanjay Mathur, Leibniz-Institut für Neue Materialien gGmbH, Saarland University, GebäudeD2 2, 66123 Saarbrücken, Germany. E-mail: s.mathur@uni-wuerzburg.de*

a *Department of Chemistry, University of Rajasthan, Jaipur-302004, India*

b *Department of Chemistry, MLV Textile and Engineering College, Bhilwara, Rajasthan, India*

c *Leibniz-Institut für Neue Materialien gGmbH, Saarland University, GebäudeD2 2, 66123 Saarbrücken, Germany*

preparation of methylsilica materials as, during hydrolysis, the liberated oxime may act as a weak acid and can catalyze further hydrolysis reaction. A methylated aluminosilicate material was also obtained by the hydrolysis of a coordination compound, $[MeSi\{ON{=}C(CH_3)C_4H_3O\}_3.Al(OPr^i)_3]$, formed from the reaction of an equimolar mixture of $[MeSi\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_3$ (**2**) and $Al(OPr^i)_3$ by the sol–gel technique at low temperature($\geq$100 °C) without phase segregation (no formation of discreet silica and alumina regions). The thermal behavior of one of the precursors $[MeSi\{ON{=}C(CH_3)C_5H_4N\text{-}2\}_3]$ (**1**) as well as of a hybrid material, $MeSiO_{3/2}$, are also reported herein.

Results and Discussion

Metathetical reactions of $MeSiCl_3$ with internally functionalized oximes in 1 : 3 stoichiometry in the presence of triethylamine afford compounds of the type $[MeSi\{ON{=}C(R)Ar\}_3]$ in quantitative yields as depicted below:

$$MeSiCl_3 + 3\,HON{=}C(R)Ar + 3Et_3N \xrightarrow{Benzene} \underset{(\mathbf{1}-\mathbf{6})}{[MeSi\{ON{=}C(R)Ar\}_3]} + 3Et_3N{\cdot}HCl\downarrow$$

where R = Me, Ar = 2-C_5H_4N (**1**), 2-C_4H_3O (**2**) or 2-C_4H_3S (**3**), and where R = H, Ar = 2-C_5H_4N (**4**), 2-C_4H_3O (**5**) or 2-C_4H_3S (**6**).

All these derivatives are brown yellow solids or liquids (complex **1** is a pink liquid) and are soluble in common organic solvents except (**6**), which becomes insoluble on aging. Molecular weight measurements in freezing benzene (Table 2) and the FAB mass spectral studies of two of the derivatives (**1** and **4**; Table 2) indicate the monomeric nature of all these complexes. Elemental analyses correspond to the expected formulae (Table 1).

Spectral studies

IR spectra

The IR spectra of the reported compounds were interpreted by comparing with the spectra of the free oximes and related derivatives[7] (Table 3). The absence of vibrations corresponding to the hydroxyl group of oximes (3200–3400 cm^{-1}) together with the presence of a new strong intensity vibration in the region 790–852 cm^{-1} (assigned to ν Si–O) indicated deprotonation of the oxime and concomitant bond formation with silicon. Absorptions in the regions 923–963 and 749–770 cm^{-1} were assigned to ν (N–O) and ν (Si–C), respectively. The ν (C=N) absorptions appeared at slightly lower wave numbers (a shift of 13–30 cm^{-1}) in comparison to the free oxime,s indicating that the nitrogen atom of C=N group is not taking part in coordination with the central silicon atom.

NMR spectra

The ^1H and $^{13}C\{^1H\}$ NMR spectra of the complexes were interpreted by comparing them with those of the free oximes[7] (Table 4). The hydroxyl proton resonances of the free oximes (δ 8.58–9.23 ppm) were absent in all ^1H NMR spectra of the complexes, indicating deprotonation of the oximes and their bonding to silicon. Absence of any significant shift in the hetero aryl ring proton/carbon resonances in the $^1H/^{13}C\{^1H\}$ NMR spectra suggests that the heteroatom of the ring is not taking part in coordination with the central silicon atom. The chemical shift values of the C=N carbon resonance of the ligand moiety are almost unchanged in the $^{13}C\{^1H\}$ NMR solution spectra of the complexes, indicating the monodentate nature of the oximate moieties (Fig. 3). A single $^{29}Si\{^1H\}$ NMR absorption signal was observed in the region δ −24.2 to −25.4 ppm for all these derivatives, which falls within the expected range for tetra-coordinated methyl silicon atom, corroborating the proposed monomeric behavior of these complexes.[8] On the basis of the above data, a tetrahedral environment around the silicon atom is probable for all these complexes in the solution state (Fig. 1).

Thermal studies

Differential thermogravimetric analysis (TGA) of a representative precursor $[MeSi\{ON{=}C(CH_3)C_5H_4N\text{-}2\}_3]$ (**1**) revealed a two-step decomposition behavior (Fig. 2).

These TG steps are connected with exothermic events caused by the pyrolysis of organic by-products. The precursor decomposition process is accompanied by two major weight losses occurring in the temperature ranges 50–200 °C (32.2%) and 200–500 °C (48.0%). Minimal weight loss, which occurs gradually, at higher temperatures (>650 °C) corresponds to the partial elimination of methyl groups and continuous removal of organic residues.

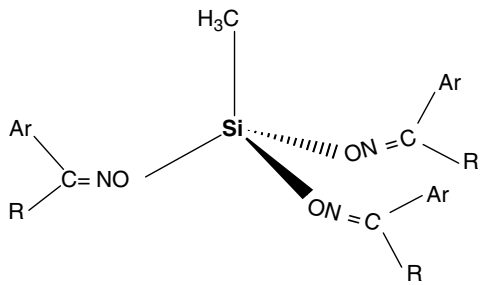

Figure 1. Proposed structures for $[MeSi\{ON{=}C(R)Ar\}_3]$.

Table 1. Physical and analytical data of monomethylsilicon(IV) complexes with internally functionalized oximes:-

Complexes	State/% yield	% Analysis Found (cal.) Si	C	H	N	Molecular weight Found (cal.)	M.P. (°C)
$[MeSi\{ON{=}C(CH_3)C_5H_4N\text{-}2\}_3]$ (**1**)	Viscous/98.8	6.20 (6.26)	58.49 (58.91)	5.19 (5.39)	18.63 (18.74)	435 (448.6)	–
$[MeSi\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_3]$ (**2**)	Solid/98.0	6.66 (6.76)	54.80 (54.93)	5.12 (5.09)	10.03 (10.11)	425 (415.5)	78
$[MeSi\{ON{=}C(CH_3)C_4H_3S\text{-}2\}_3]$ (**3**)	Viscous/98.2	5.95 (6.06)	49.00 (49.22)	4.30 (4.56)	8.9 (9.06)	423 (463.7)	–
$[MeSi\{ON{=}C(H)C_5H_4N\text{-}2\}_3]$ (**4**)	Viscous/97.9	6.82 (6.91)	56.02 (56.14)	4.39 (4.46)	20.85 (20.68)	390 (406.5)	–
$[MeSi\{ON{=}C(H)C_4H_3O\text{-}2\}_3]$ (**5**)	Viscous/98.0	7.40 (7.52)	51.30 (51.47)	3.88 (4.05)	11.05 (11.25)	380 (373.4)	–
$[MeSi\{ON{=}C(H)C_4H_3S\text{-}2\}_3]$ (**6**)	Solid/98.5	6.53 (6.66)	45.50 (45.58)	3.39 (3.59)	9.74 (9.97)	–	193 Dec

Table 2. Fragmented molecular ion/m/e values in FAB mass spectra of monomethylsilicon(IV) complexes (**1**) and (**4**)

Complexes	fragmented ions	m/e values
$[MeSi\{ONC(CH_3)C_5H_4N\}_3]$ **(1)**	$[MeSi\{ONC(CH_3)C_5H_4N\}_2\{ONC(CH_3)C_5H_3N\}]^+$	447
	$[MeSi\{ONC(CH_3)C_5H_4N\}_2\{C(CH_3)C_5H_3N\}]^+$	417
	$[MeSi\{ONC(CH_3)C_5H_4N\}_2\{C(CH_3)C_4H\}]^+$	389
	$[MeSi\{ONC(CH_3)C_5H_4N\}_2\{C_5\}]^+$	373
	$[MeSi\{ONC(CH_3)C_5H_4N\}\{ONC(H)C_5H_4N\}\{C_5\}]^+$	359
	$[MeSi\{ONC(CH_3)C_5H_4N\}\{ONC(H)C_4H_2\}\{C_5\}]^+$	331
	$[MeSi\{ONC(CH_3)C_5H_4N\}\{NCC_4(H)N\}\{C_5\}]^+$	327
	$[MeSi\{ONC(CH_3)C_5H_4N\}\{NC(H)C_4\}\{C_5\}]^+$	313
	$[MeSi\{ONC(H)C_5H_4N\}\{NC_5H\}\{C_5\}]^+$	299
	$[MeSi\{ONC(H)C_5H_4N\}\{C_5H\}\{C_5\}]^+$	285
	$[HSi\{ONC(H)C_5H_4N\}\{C_5H\}\{C_5\}]^+$	271
	$[HSi\{C(H)C_5H_4N\}\{C_5H\}\{C_5\}]^+$	241
	$[MeSi\{ONC(H)C_5H_4N\}\{CH\}\{C_5\}^+$	237
	$[HSi\{C(H)C_5H_4N\}\{CH\}\{C_5\}]^+$	193
	$[HSi\{C(H)C_5H_4\}\{CH\}]^+$	119
	$[HSi\{C(H)C_3\}\{CH\}]^+$	91
$[MeSi\{ONC(H)C_5H_4N\}_3]$ **(4)**	$[MeSi\{ONC(H)C_5H_4N\}\{ONC(H)C_5N\}\{ON(H)C_5HN\}]^+$	387
	$[MeSi\{ONC(H)C_5H_4N\}\{ONC(H)C_5N\}\{C_5N\}]^+$	355
	$[MeSi\{ONC(H)C_5H_4N\}\{ONC(H)C_5N\}\{C_5\}]^+$	341
	$[MeSi\{NC(H)C_5H_2N\}\{ONC(H)C_5N\}\{C_5\}]^+$	323
	$[MeSi\{NC(H)C_5H_2N\}\{OC(H)C_5\}\{C_5\}]^+$	295
	$[HSi\{NC(H)C_5H_2N\}\{OC(H)C_5\}\{C_5\}]^+$	281
	$[HSi\{NC(H)C_5\}\{C_6(H)\}\{C_5\}]^+$	249
	$[HSi\{C_5\}\{C_6\}\{C_5\}]^+$	221
	$[HSi\{NCH_3\}\{OC(H)C_5\}\{C_5\}]^+$	207
	$[HSi\{CH\}\{OC(H)C_5\}\{C_5\}]^+$	191
	$[HSi\{OC_5\}\{C_5\}]^+$	165
	$[HSi\{NCH_3\}\{OC(H)C_5\}]^+$	147
	$[HSi\{NH\}\{OC(H)C_5\}]^+$	133
	$[HSi\{NH\}\{OCH\}]^+$	73

Table 3. Selected IR spectral data (in cm^{-1}) of monomethylsilicon(IV) complexes with internally functionalized oximes:-

Complexes	ν (C=N)	ν (Si-O)	ν (N-O)
$[MeSi\{ON{=}C(CH_3)C_5H_4N\text{-}2\}_3]$ (**1**)	1570 (vs)	790 (vs)	928 (vs)
$[MeSi\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_3]$ (**2**)	1562 (m)	828 (vs)	950 (vs)
$[MeSi\{ON{=}C(CH_3)C_4H_3S\text{-}2\}_3]$ (**3**)	1600 (m)	852 (vs)	923 (vs)
$[MeSi\{ON{=}C(H)C_5H_4N\text{-}2\}_3]$ (**4**)	1570 (s)	842 (vs)	963 (vs)
$[MeSi\{ON{=}C(H)C_4H_3O\text{-}2\}_3]$ (**5**)	1620 (vs)	828 (vs)	950 (vs)
$[MeSi\{ON{=}C(H)C_4H_3S\text{-}2\}_3]$ (**6**)	1610 (m)	840 (vs)	960 (vs)

The overall weight loss (*ca* 82–85%; theoretical 84.9%) is in agreement with the formation of a material of definite composition $MeSiO_{3/2}$ (molecular weight 67) from a single molecular precursor (**1**) (molecular weight 448.6).

Hydrolytic studies and material characterization

Hydrolytic study of a single molecular precursor $[MeSi\{ON{=}C(R)Ar\}_3]$ has been carried out by the following method:

$$MeSiL_3 \xrightarrow{\text{hydrolysis}} MeSi(OH)_3 + 3LH \xrightarrow[\text{at} \geq 100\,^\circ C]{\text{condensation}}$$

$$MeSiO_{3/2} + 3LH \xrightarrow{\text{washing}} MeSiO_{3/2}$$

After hydrolysis of a benzene solution of $MeSiL_3$ by moist isopropanol, the mixture was concentrated and then washed several times with acetone–hexane mixture in order to remove the liberated oxime completely. It was then sintered at 100 °C for 3 h to yield $MeSiO_{3/2}$ [%CHN observed (calculated): C, 18.81 (17.89); H, 5.69 (4.50); N, nil]. The same sample ($MeSiO_{3/2}$) was again sintered at 300 °C for 5 h [%CHN observed (calculated): C, 17.92 (17.89); H, 4.24 (4.50); N, nil]. No change was observed in the carbon content of the oxide, indicating retention of the Me–Si moiety even at 300 °C. The stability of the Me–Si bond was also observed in the TGA curve of $MeSiO_{3/2}$ sintered at 100 °C (Fig. 3). The first step in the range 50–400 °C can be attributed to the loss of absorbed water (weight loss 4.7%). Two further weight losses (13.2 and 8.7%) in the range 400–800 °C represent the decompositions of the organic moieties of the hybrid framework and removal of remaining templating groups (oximes). Considering the facts that xerogel had been dried at 100 °C and no further weight loss was observed beyond 800 °C, formation of an oxide material (SiO_2) can

Table 4. ^{1}H, $^{13}C\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR data (in δ ppm) for monomethylsilicon(IV) complexes with internally functionalized oximes;-

Complexes	^{1}H NMR	$^{13}C\{^{1}H\}$ NMR	$^{29}Si\{^{1}H\}$ NMR
$[MeSi\{ON{=}C(CH_3)C_5H_4N\text{-}2\}_3]$ (**1**)	0.78 (s, 3H, Si-Me); 2.48 (s, 9H, oxime-Me); 7.26 (m, 3H, H-4); 7.65 (m, 3H, H-5); 7.97 (d, 3H, $J = 8.0$ Hz, H-3); 8.61 (d, 3H, $J = 4.8$ Hz, H-6).	−6.8 (Si-Me); 11.6 (oxime Me); 121.2 (C-5); 124.0 (C-3); 136.1 (C-4); 148.8 (C-6); 154.2 (C-2); 162.7 (C=N).	−24.9
$[MeSi\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_3]$ (**2**)	0.72 (s, 3H, Si-Me); 2.27 (s, 9H, oxime-Me); 6.41 (m, 3H, H-4); 6.69 (d, 3H, $J = 3.3$ Hz, H-3); 7.46 (d, 3H, $J = 1.6$ Hz, H-5).	−7.1 (Si-Me); 12.2 (oxime Me); 110.0 (C-4); 111.9 (C-3); 143.7 (C-5); 150.0 (C-2); 153.9 (C=N).	−24.5
$[MeSi\{ON{=}C(CH_3)C_4H_3S\text{-}2\}_3]$ (**3**)	0.71 (s, 3H, Si-Me); 2.36 (s, 9H, oxime-Me); 7.02 (m, 3H, H-4); 7.26 (m, 6H, H-3 & H-5).	−6.9 (Si-Me); 12.3 (oxime Me); 126.5 (C-4); 126.8 (C-3); 127.1 (C-5); 140.2 (C-2); 151.8 (C=N).	−25.4
$[MeSi\{ON{=}C(H)C_5H_4N\text{-}2\}_3]$ (**4**)	0.74 (s, 3H, Si-Me); 7.23 (m, 3H, H-4); 7.62 (m, 3H, H-5); 7.88 (d, 3H, $J = 8.0$ Hz, H-3); 8.42 (s, 3H, CH); 8.55 (d, 3H, $J = 4.8$ Hz, H-6).	−7.2 (Si-Me); 121.1 (C-5); 124.4 (C-3); 136.6 (C-4); 149.5 (C-6); 151.3 (C-2); 156.1 (C=N).	−24.3
$[MeSi\{ON{=}C(H)C_4H_3O\text{-}2\}_3]$ (**5**)	0.75 (s, 3H, Si-Me); 6.46 (m, 3H, H-4); 7.40 (m 3H, H-3); 7.49 (m, 3H, H-5); 7.71 (s, 3H, CH).	−7.8 (Si-Me); 112.3 (C-4); 119.3 (C-3); 141.8 (C-5); 143.5 (C-2); 145.2 (C=N).	−24.2
$[MeSi\{ON{=}C(H)C_4H_3S\text{-}2\}_3]$ (**6**)	0.71 (s, 3H, Si-Me); 7.12 (m, 3H, H-4); 7.44 (m, 3H, H-3); 7.58 (m, 3H, H-5); 7.79 (s, 3H, CH).	−7.5 (Si-Me); 124.4 (C-4); 128.9 (C-3); 129.7 (C-5); 138.2 (C-2); 144.2 (C=N).	Poor solubility ^{29}Si NMR signal could not be observed

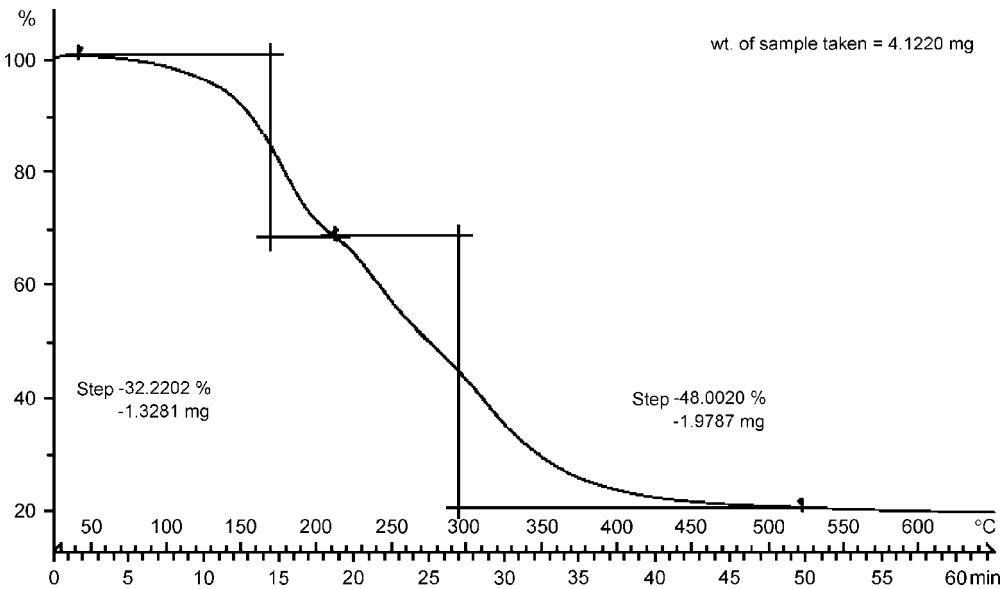

Figure 2. TGA curve (wt% vs temperature) of $[MeSi\{ON{=}C(CH_3)C_5H_4N\text{-}2\}_3]$ (**1**).

be anticipated. This also correlates the TGA pattern of **1** and the expected stability of methylsilica up to 400 °C.

Methyl containing aluminosilicate was also obtained by the hydrolysis of a coordination compound of the type $[MeSi\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_3.Al(OPr^{i})_3]$ (brown viscous liquid), formed by refluxing the solid $[MeSi\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_3]$ (**2**) with the solid $Al(OPr^{i})_3$ in 1 : 1 molar ratio in toluene and characterized by elemental analyses and ^{1}H, ^{13}C, ^{27}Al and ^{29}Si NMR techniques.

Considerable shifting ($\delta = -12.5$ ppm) in tetracoordinated region was observed in the $^{29}Si\{^{1}H\}$ NMR spectra of the above viscous product as compared with the $^{29}Si\{^{1}H\}$ NMR spectrum of **2**. $^{27}Al\{^{1}H\}$ NMR of the viscous product appears a signal at δ 56.1 ppm suggests tetracoordinated environment around

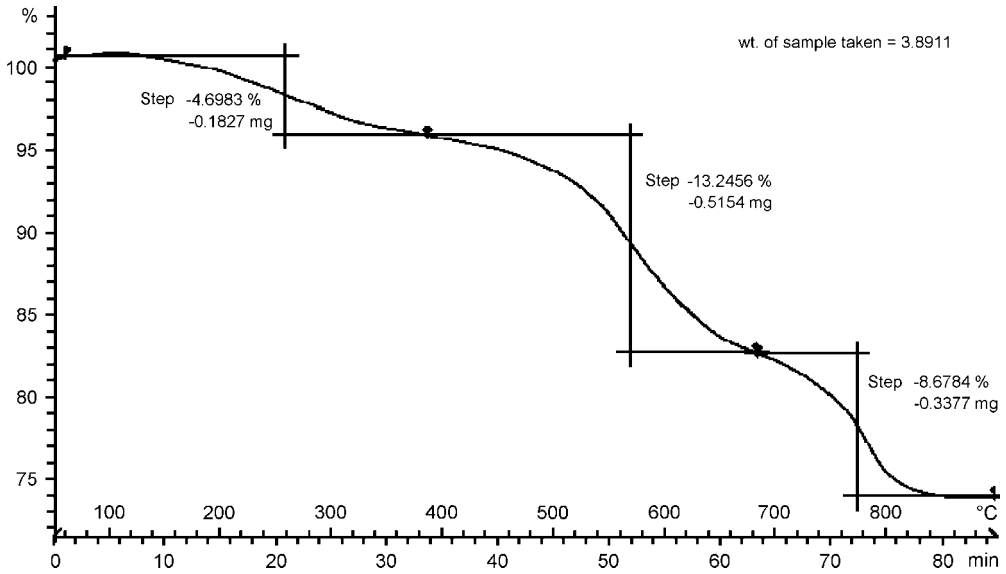

Figure 3. TGA curve (wt% vs temperature) of $MeSiO_{3/2}$ sintered at 100 °C.

the aluminum atom. Therefore, formation of a coordination compound containing tetracoordinated Si and Al environment between [MeSi{ON=C(CH_3)C_4H_3O-2}$_3$] and Al(OPr^i)$_3$ may be inferred. This brown viscous compound was dissolved in dry isopropanol, and hydrolyzed by the sol–gel process. After hydrolysis, the mixture was dried in a preheated oven and then washed with acetone–hexane mixture followed by sintering at 100 °C for 3 h, to yield methylated aluminosilicate material ($MeSiO_{3/2}.{}^1/_2Al_2O_3$) [%CHN observed (calculated): C, 10.93 (10.17); H, 4.04 (2.56); N, nil]. Although the EDX (energy dispersive X-ray analysis) analyses deviate a fair amount from the theoretical values, the analyses do indicate the presence of silicon and aluminum in 1 : 1 molar ratio [% Al Si observed (calculated): Al, 21.78 (22.84); Si, 17.57 (23.78)]. The deviation appears to indicate non-uniform distribution of methylated aluminosilicate.

$$MeSiL_3 + Al(OPr^i)_3 \xrightarrow{\text{reflux}} MeSiL_3.Al(OPr^i)_3 \xrightarrow[\text{condensation}]{\text{hydrolysis}} MeSiO_{3/2}.{}^1/_2Al_2O_3 + 3LH$$

It is interesting to mention here that when the above methylated aluminosilicate material was sintered at 300 °C for 5 h, no appreciable change in the percentage of carbon content was observed [%CHN observed (calculated): C, 9.50 (10.17); H, 3.06 (2.56); N, nil]. However, on sintering at 500 °C for 2 h the carbon content of the methylated aluminosilicate was reduced from 9.50 to 0.09% indicating removal of the methyl group at this temperature.

The presence of the CH_3 group in the silicate and aluminosilicate framework was also confirmed by the appearance of four peaks at 2963, 1260, 863 and 807 cm^{-1} in the IR spectra of $MeSiO_{3/2}$ and methylated aluminosilicate, which can be assigned as CH_3 asymmetric stretching, CH_3 deformation, CH_3 rocking and Si–C stretching mode, respectively.[9]

We were interested in using here the newly prepared methylsilicon oximates as precursors for mesoporous silicas, where the oxime functionalities should act as structure-directing agents offering a precise control over morphology and microstructure. The scanning electron micrographs (SEMs) of calcined xerogels of $MeSiO_{3/2}$ sintered at 100 and 300 °C [Fig. 4(a, b)] showed highly porous materials with a regular structure. As expected from the precursor design, a porous material was left upon the partial removal of the organic framework. Although both mesoporous channels and microporous voids are evident in the SEM analyses, they exhibit less surface area as compared with the surface area reported for the dimethylsiloxane incorporated silicas.

In contrast to $MeSiO_{3/2}$ the methylated aluminosilicate [Fig. 4(c)] exhibited a granular morphology constituted by agglomeration of micro- and nano-sized particles with high specific surface area (464 m^2/g). The dense microstructure and absence of regular voids, as observed in $MeSiO_{3/2}$, are probably due to higher degree of cross-linking among the precursor units, which can be explained on the basis of higher propensity of metal alkoxides towards formation of M–O–M bridges via hydrolysis and condensation reactions. Nevertheless, the presence of metal sites in the material can be interesting for mechanical and catalytic applications.

The powder X-ray diffraction patterns of $MeSiO_{3/2}$ and methylated aluminosilicate are largely amorphous (Fig. 5). The broad peaks observed in the lower 2θ range suggest incipient crystallization in the samples.

Experimental

All manipulations (except hydrolysis) for the synthesis and characterization of the complexes were carried out under strictly anhydrous conditions. The solvents and reagents used were dried and purified by conventional methods.[10] *Appropriate precautions were taken in handling hazardous chemicals and solvents such as benzene*. Trichloromethylsilane was used as supplied (Merck). Oximes were prepared by conventional methods.[7,11] Aluminum isopropoxide was prepared by the reported method and distilled before use.[12] Silicon was estimated gravimetrically as SiO_2 and nitrogen was estimated by the Kjeldahl method.[11] The remaining isopropoxy group was estimated by the oxidimetric method.[13] IR spectra (4000–400 cm^{-1}) were recorded as Nujol mulls on a Shimadzu FTIR 8400 spectrometer. ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H}

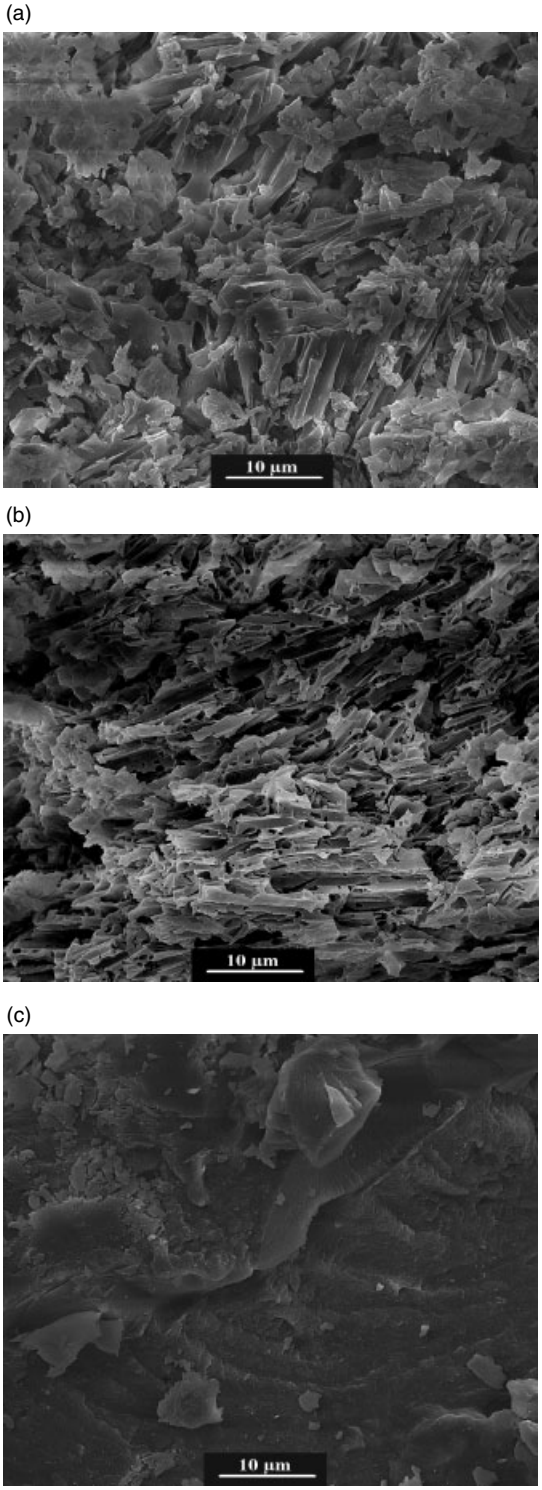

Figure 4. SEM images of (a) $MeSiO_{3/2}$ sintered at 100 °C; (b) $MeSiO_{3/2}$ sintered at 300 °C; (c) methylated aluminosilicate sintered at 100 °C.

NMR data were collected on a Jeol FX 300 FT NMR spectrometer in $CDCl_3$ solutions at 300.4, 75.45 and 59.60 IHz frequencies, respectively, using TMS as an internal standard. $^{27}Al\{^1H\}$ NMR data was collected in $CDCl_3$ solution at 78.18 IHz frequency, using aluminum nitrate as an internal standard. FAB mass spectra were obtained on a Jeol SX 102/DA-6000 mass spectrometer using the *m*-nitrobenzylalcohol matrix described here. Molecular weight measurements were carried out by determining the depressions in freezing point of anhydrous benzene using a Beckmann's thermometer (Einstellthermometer n-Bek) fitted in a glass assembly (supplied by JSGW, India). Microanalyses were carried out on a Heracus Carlo Erba 1108 analyzer. Thermogravimetric analysis was performed on a Mettler Toledo Star SW 701 with the heating rate 25–800/10 °C. XRD diffraction analysis was carried out on a Siemens D500 diffractometer operating with Cu–K_α radiation. SEM and EDX-analysis were performed on an EDX-coupled scanning electron microscope JSM-6400F (Jeol).

Preparation of $[MeSi\{ON{=}C(CH_3)C_5H_4N\text{-}2\}_3]$ (1)

A benzene solution (~30 ml) of a mixture of 2-acetyl pyridyl oxime (2.27 g, 16.67 mmol) and triethyl amine (1.69 g, 16.71 mmol) was added drop-wise to a stirred ice-cooled benzene solution (~25 ml) of trichloromethylsilane (0.83 g, 5.55 mmol). The mixture was stirred for 1 h and then refluxed for 5 h. Triethylaminehydrochloride (2.27 g, 16.50 mmol) formed was filtered off and the filtrate was concentrated *in vacuo* to give a pink liquid (2.46 g, 98.8% yield).

All other methylsilicon(IV) derivatives were prepared by a similar route. Their physical and analytical data are summarized in Table 1.

Hydrolysis of $[MeSi\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_3]$ (2) and $[MeSi\{ON{=}C(H)C_5H_4N\text{-}2\}_3]$ (4)

$[MeSi\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_3]$ (**2**) (2.09 g) was dissolved in benzene (~30 ml) and hydrolyzed with moist isopropanol (1 : 1 water–isopropanol) in small steps with continuous stirring. The mixture was concentrated and then washed thoroughly with acetone–hexane mixture to separate the oxime from the oxide (light brown powder). This powder was sintered at 100 °C for 3 h and 300 °C for 5 h to give a cream-colored powder which was characterized as $MeSiO_{3/2}$ (89% yield).

$[MeSi\{ON{=}C(H)C_5H_4N\text{-}2\}_3]$ (**4**) was hydrolysed by a similar method and yielded a similar oxide, $MeSiO_{3/2}$ (87% yield) [%CHN observed (calculated): C, 18.00 (17.89); H, 4.33 (4.50); N, nil].

When the compound $[MeSi\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_3]$ (**2**) (2.00 g) was dissolved in isopropanol (~30 ml) and was hydrolysed by a similar method, satisfactory results were not obtained [%CHN observed (calculated): C, 14.00 (17.89); H, 3.33 (4.50); N, nil].

Hydrolysis of a coordination compound formed from the reaction of an equimolar mixture of $[MeSi\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_3]$ (2) and $Al(OPr^i)_3$

A toluene solution (~20 ml) of the solid $[MeSi\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_3]$ (**2**) (1.57 g, 3.78 mmol) was added to a toluene solution (~15 ml) of the solid $Al(OPr^i)_3$ (0.77 g, 3.79 mmol) and the mixture was refluxed for about 6 h. The clear solution was dried *in vacuo* to give a brownish viscous liquid in quantitative yield. Elemental analyses [% N observed (calculated): 6.81 (6.78); %OPr^i observed (calculated): 28.41 (28.60)] suggest the formation of $[MeSi\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_3{\cdot}Al(OPr^i)_3]$. ^1H, ^{13}C, ^{27}Al and ^{29}Si NMR [^1H NMR: δ 0.42 (s, 3H, Si–Me); 1.16 (d, 9H, $J = 6.2$ Hz, OPr^i-Me); 2.14 (s, 9H, oxime-Me); 4.23 (m, 3H, OPr^i-CH); 6.34 (m, 3H, H-4); 6.60 (d, 3H, $J = 3.2$ Hz, H-3); 7.37 (d, 3H, $J = 1.4$ Hz, H-5), ^{13}C NMR: δ −6.0 (Si-Me); 11.6 (oxime Me); 25.3 (OPr^i-Me); 65.5 (OPr^i-CH) 109.5 (C-4); 111.0 (C-3); 143.3 (C-5); 150.3 (C-2); 152.3 (C=N), $^{29}Si\{^1H\}$ NMR: δ −37.0, $^{27}Al\{^1H\}$ NMR: δ 56.1]

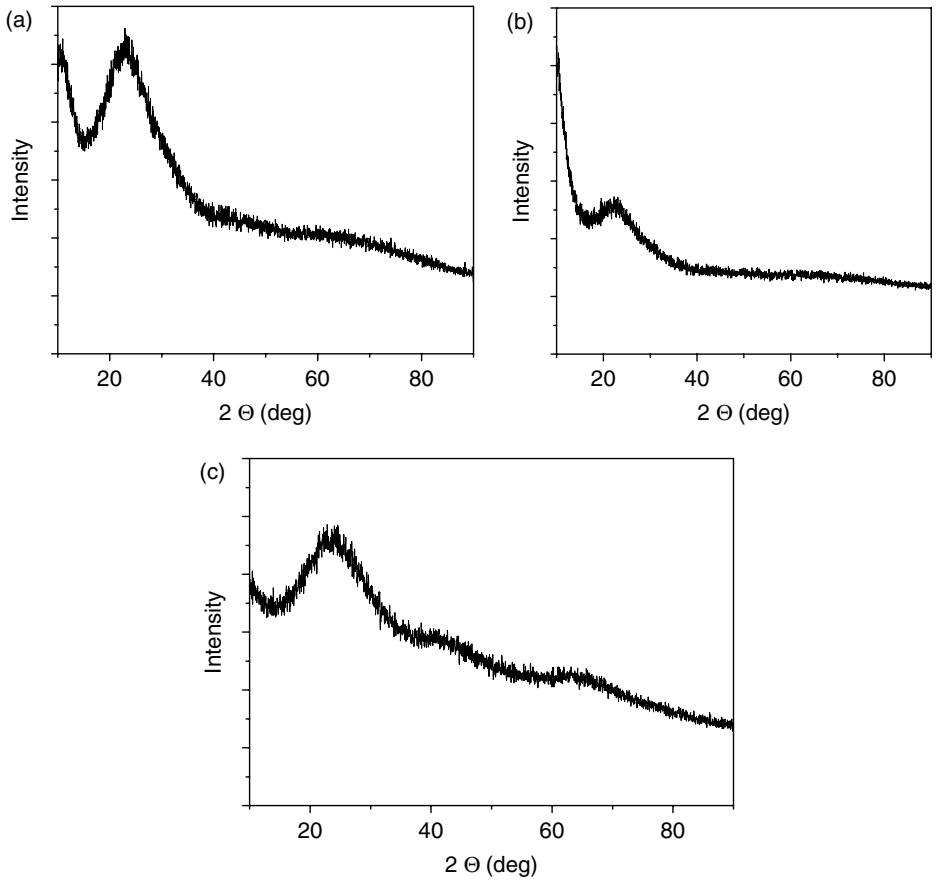

Figure 5. Powder X-ray diffraction patterns of (a) $MeSiO_{3/2}$ sintered at 100 °C; (b) $MeSiO_{3/2}$ sintered at 300 °C; (c) methylated aluminosilicate sintered at 100 °C.

suggest tetra-coordination around both Si as well as Al atoms. The product, $[MeSi\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_3{\cdot}Al(OPr^i)_3]$ was re-dissolved in dry isopropanol and then it was slowly hydrolyzed with 1 : 1 water–isopropanol solution in small steps to yield a homogenous gel (~48 h, no phase segregation). After refluxing it for 8 h the whole mixture was dried in a preheated oven to give a brown powder, which was washed thoroughly with acetone–hexane mixture to remove free oxime from it. On sintering it at 100 °C for 3 h, a light brown powder was obtained (expected to be methyl-bonded aluminosilicate $MeSiO_{3/2}{\cdot}1/2Al_2O_3$). This powder was again heated at 300 °C for 5 h to give a cream-colored powder and at 500 °C for 1 h to give a white powder (expected to be demethylated aluminosilicate) [%CHN observed: C, 0.09; H, 2.60; N, nil].

Conclusion

Sol–gel transformation of molecular precursors $[MeSi\{ON{=}C(R)Ar\}_3]$ under relatively milder conditions offers a facial synthetic route for the preparation of a wide range of well-ordered mesoporous materials. When compared with the surfactant-mediated assembly of periodic mesoporous silica, the chemical functionalization of the precursor framework through covalent coupling of organic or metal-organic moieties is a promising approach to tailor the surface properties of the mesoporous material. The single-molecule-based synthesis allows the organic content and homogenous distribution of heteroelements in the final material to be tuned. As shown in this study, the oxime-functionalized organo-silanes can interact with each other or with other additives [e.g. $Al(OPr^i)_3$] to enhance the framework formation and intimate mixing of different precursors, as evident in the formation of highly ordered aluminosilicate material at low calcination temperatures. Given the surface area, these regularly ordered hybrid structures could be used for catalytic, low *k* dielectrics and optical applications.

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