Articles

Development of a New Combinatorial Approach to Multifunctional Catalysts: Metal Silsesquioxanes as Precursors to Microporous Metallosilicates[†]

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Microporous, silica-supported metal oxides with a very narrow pore size distribution around 0.6 nm diameter, typical surface areas ranging from 350 to 700 m^2/g, and loadings of well-dispersed metal oxide (up to $w = 10\%$ of metal) result from the controlled calcination of silsesquioxane metal complexes. A versatile new methodology is envisioned that, in a combinatorial fashion, enables catalyst preparation with control over metal content and dispersity, together with adjustable Lewis and Brönsted acidity. In addition, the method is suitable for the preparation of bi- and multifunctional catalysts containing different metals.

Keywords   Metal silsesquioxanes, microporous catalysts, combinatorial approach

Introduction

The emergence of combinatorial approaches for high-volume materials research promises to revolutionize materials discovery. In order for heterogeneous catalysis research to benefit fully from the use of automated parallel synthesis and high throughput screening systems, routes to microporous materials should be developed that preferably use air-stable, soluble and well defined precursors. Silsesquioxanes and metal complexes thereof seem to ideally meet with these criteria.

The use of silsesquioxane metal complexes in a molecular route to amorphous metallosilicates has been recently demonstrated.[1] This development is clearly driven by the fact that over the last decade, a large number of these complexes has become available. Interestingly, their synthesis is generally straightforward starting from incompletely condensed silsesquioxanes, which in turn, have become readily accessibile.[2] In order to illustrate the versatility of this new area of coordination chemistry, it suffices to list metals that have already been successfully incorporated into Si/O skeletons of silsesquioxanes. These include main group, early and late transition metals, as well as chalcogens:[1,3] Li, Na, Mg, Y, La, Ti, Zr, Hf, V, Cr, Mo, W, Fe, Os, Pt, Zn, B, Al, Ga, Tl, Ge, Sn, P, Sb, Te.

Prior to this paper, calcination of some silsesquioxane metal complexes was undertaken and shown to result in microporous metallosilicates. During the calcination, the organic groups attached to the silicon atoms are replaced by Si—O—Si linkages that seem to connect the initially isolated Si/O-cage structures. Known literature involves the calcination of vanadium and titanium as well as chromium compounds.[4] The structures **1—3** of these silsesquioxane metal complexes that have been used re-

cently as precursors for synthesis of microporous metal-losilicates as well as a schematic image of the chromosili-cate 4 resulting from calcination of chromium silsesquiox-ane complex 3 are presented in Fig. 1. An interesting

finding is that the resulting amorphous materials have a very narrow pore size distribution around 0.6 nm.[5] A relatively high loading (up to $w = 10\%$ of metal) of monodispersed metal oxide could be realized as well.

1 R = c-C$_6$H$_{11}$ or c-C$_5$H$_9$, M = V, Y = O
2 R = c-C$_6$H$_{11}$ or c-C$_5$H$_9$, M = Ti, Y = Cp
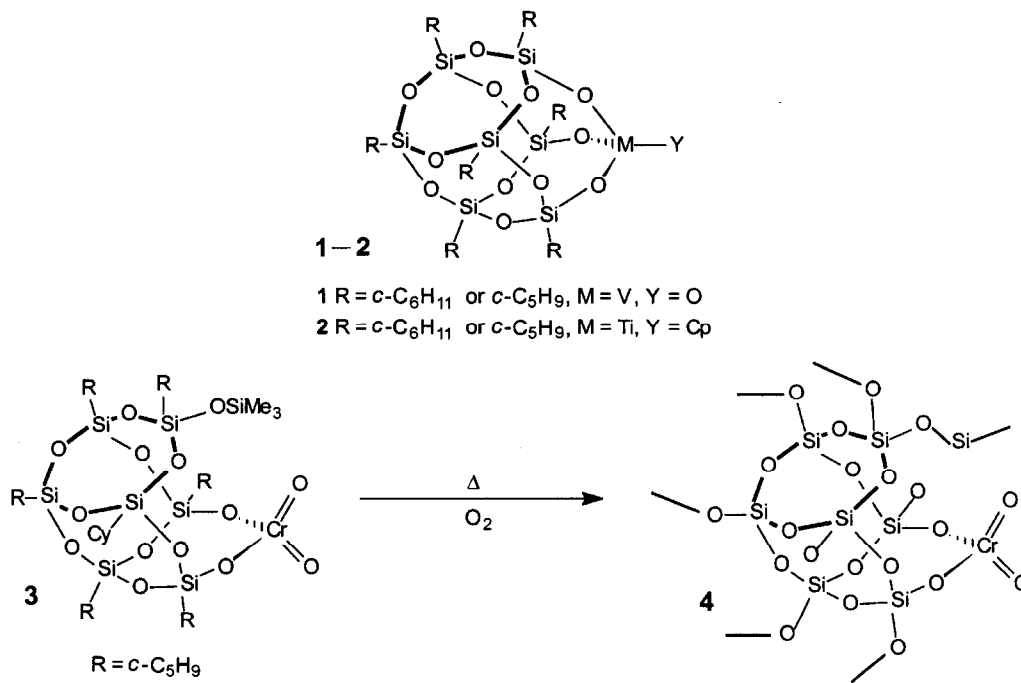

R = c-C$_5$H$_9$

Fig. 1 Examples of metal silsesquioxane complexes used as precursors for synthesis of metallosilicates and a tentative image of the chromosilicate resulting from calcination of the chromium silsesquioxane complex.

We have now embarked on a large investigation on the use of silsesquioxane metal complexes as precursors for porous metallosilicates. In this communication, we access aspects of this new methodology that are relevant for the area of catalysis. These involve: optimization and scope of the method of calcination, the possibility to adjust the texture of metallosilicates and the dispersion of metal oxide by changing the calcination conditions, the extent to which the structure of the Si—O—M skeleton in the precursor complex is retained in the resulting metallosilicate and whether the Si—O—M skeleton determines the pore size and its size distribution. Other important issues that will be addressed should determine whether it is possible to prepare metallosilicates that are exclusively Lewis or Brönsted acids or to get well dispersed supported metal particles when the precursor complex contains no direct Si—O—M bonds. Finally we propose to investigate if this methodology is suitable for a combinatorial fashion of catalyst synthesis of more complex oxidic catalysts, especially mixed metal

systems.

In order to develop and assess this methodology, at this stage one magnesium and two different aluminium silsesquioxane complexes were synthesized as shown in Fig. 2.

Experimental

Synthesis of the M—Si—O *materials*

The incompletely condensed silsesquioxane 5, was prepared by the hydrolytic condensation of cyclopentyl-trichlorosilane. The disilanol 6 was prepared by silylation of 5 with Me$_3$SiCl using a procedure reported elsewhere.[6]

The magnesium silsesquioxane complex 7 was prepared by reacting the trisilanol silsesquioxane 5 with the Grignard reagent CH$_3$MgCl in THF solvent using a recipe reported earlier.[7]

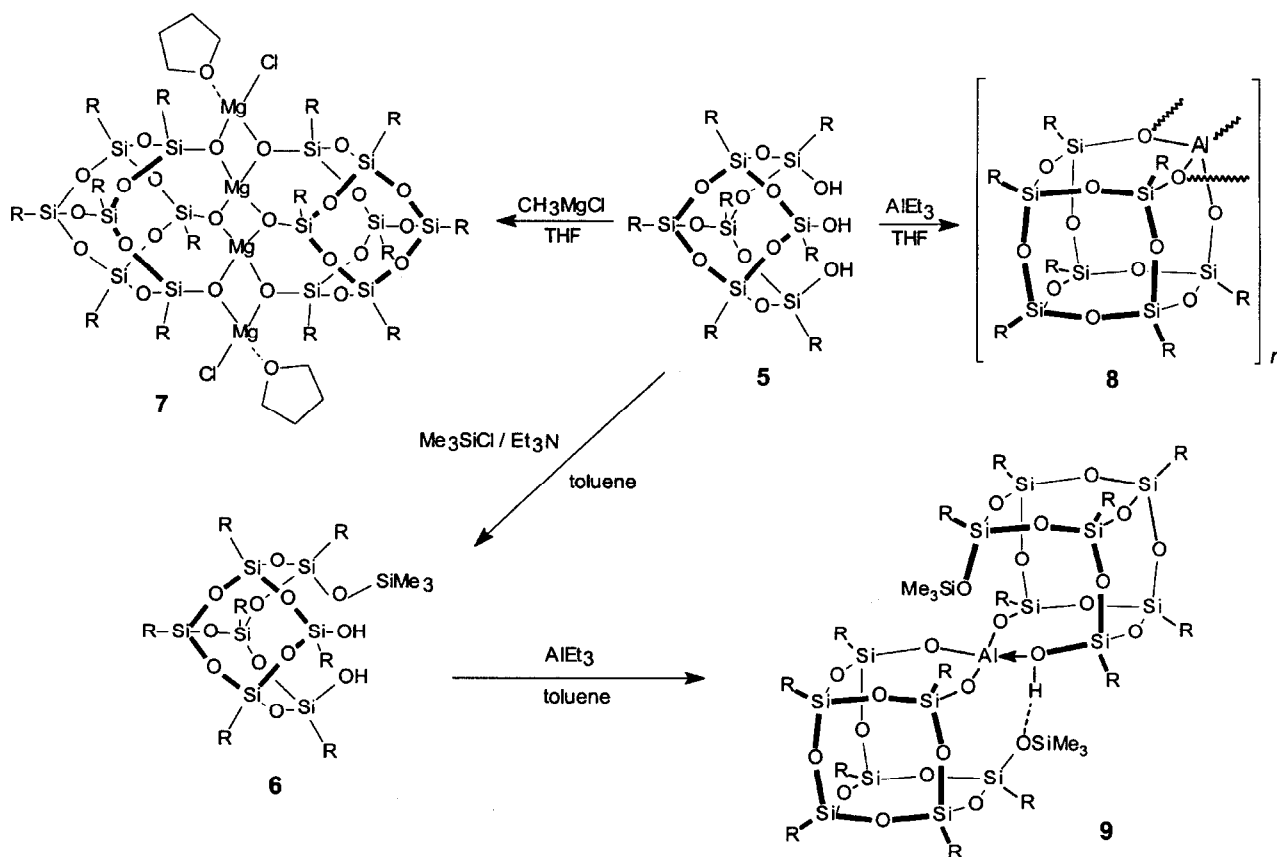Aluminium silsesquioxane complexes 8 and 9 were

Fig. 2 Synthesis of magnesium and aluminium silsesquioxane complexes $(R = C_5H_9)$.

prepared by reacting $AlEt_3$ with trisilanol silsesquioxane **5** in THF and disilanol silsesquioxane **6** in toluene, respectively, using well known procedures.[8] Structures of magnesium and aluminium silsesquioxane complexes were checked out using ^1H and ^{13}C NMR as well as solid state MAS ^{29}Si NMR.

Small portions of 0.5 g of metal containing oligosilsesquioxane **7**, **8** and **9** as well as metal free silsesquioxane **5** were heated by 5 ℃ min^{-1} to 500 ℃ for 4 h in a continuous plug flow reactor of 27 mm internal diameter flushed by an $Ar-O_2$ gas mixture flow of 30 mL/min containing 20 mol% of O_2. The resultant oxides were further designated as MgSiO, AlSiO(I), Al-SiO-(II) and SiO_2. For other calcination conditions than the standard ones mentioned above additional suffixes were used for designations.

Analysis

The carbon content of MSiO materials was measured by heating the samples at 925 ℃ on a Perkin

Elmer automated analyzer Series II CHNS/O Analyzer 2400.

For the nitrogen physisorption analysis all the samples were pretreated just before the measurement in vacuum at 200 ℃ for 2 h. The measurements were performed on an ASAP 2000 Micromeritics apparatus using an equilibriation interval of 5 seconds and a low pressure dose of 3.00 cm^3/g STP. Information about surface area, pore volume and pore size distribution was derived from Horvath-Kawazoe and Dubinin-Radushkevich methods.[9]

X-ray powder diffraction data were collected on a Rigaku diffractometer in the range $5.0° < 2\theta < 80°$ using Cu K_α radiation and the step scan method at 0.1 deg/min scanning speed and 5 s dwelling time.

X-ray Photoelectron Spectroscopy measurements were obtained with a VG CLAM 2 spectrometer equipped with a Mg K_α source and a hemispherical analyzer. Measurements were carried out at 20 eV pass energy. Charging was corrected by using the Si 2p peak of SiO_2 at 103.3 eV. The samples were ground and pressed in in-

dium foil which was placed on a stainless-steel stub. The XPs spectra have been fitted with a VGS program fit routine, with a Shirley background subtraction and Gauss-Lorentz curves. The error in the binding energy was 0.2 eV. Elemental ratios were calculated from the peak areas with correction for the cross-sections.[10]

Solid state MAS ^{29}Si NMR experiments were carried out on a Bruker MSL400 spectrometer operating at ^{29}Si resonance frequency of 79.46 MHz. The peak of Q8M8 at δ 11.8 was used as an external reference for the chemical shift. Magic-angle spinning (MAS) at a sample rotation rate of 4 kHz was employed to eliminate the line broadening caused by the chemical-shift anisotropy. Chemical shift values were estimated from MAS ^{29}Si NMR spectra recorded with direct ^{29}Si excitation combined with high-power proton decoupling and relaxation delays of 30 sec between subsequent scans. (Longer relaxation delays up to 300 sec did not yield lineshape changes.) Typically 64 to 128 scans were recorded.

For Transmission Electron Microscopy a STEM JE-OL 2000 FX transmission electron microscope coupled with an EDX system NORAN 5500 with high angle detector was used. The accelerating voltage was 120 kV.

Results and discussion

Scope of the methodology

Since the calcined magnesium and aluminium silsesquioxane complexes were brownish in colour indicating the presence of residual carbon in the MSiO materials we measured first the carbon content. The effect of O_2 flow, calcination time and calcination temperature on residual carbon content in MgSiO materials is shown in Fig. 3. Obviously the residual carbon removal can be improved by changing calcination conditions. At low calcination temperature (425℃) the higher the O_2 flow the lower the residual C content. An increase in calcination time from 4 h to 16 h significantly diminishes the residual percent of C but O_2 flow effect becomes negligible. However the most effective factor seems to be the calcination temperature, high temperatures being necessary for complete carbon removal. Thus, a calcination temperature of 500℃ led to a MgSiO material with only $w = 0.6\%$ of C. Of course calcination temperatures as high as 550℃ can be used but higher temperatures may

significantly decrease the surface area and pore volume of the samples since it was noted that for an oligomeric silsesquioxane - siloxane copolymer the use of calcination temperatures above 600℃ led to materials with a reduced surface area.[11] Therefore an appropriate calcination temperature in the range 500—550℃ should be used.
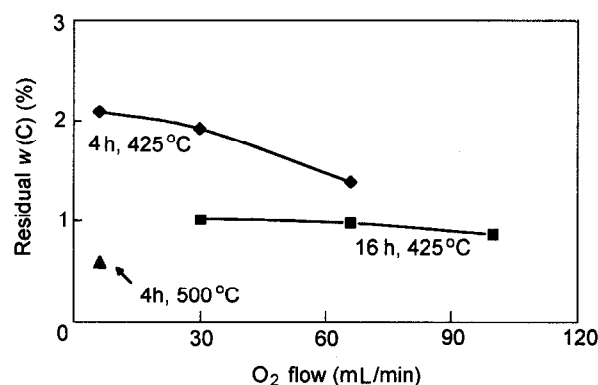

Fig. 3 Effect of calcination conditions on the residual carbon content of MSiO materials (exemplified for MgSiO).

Typical values for surface area, pore volume and average pore diameter for MgSiO and AlSiO as well as for CrSiO-450 and SiO$_2$-450 materials that were derived from N$_2$ physisorption isotherms are presented in Table 1.

Table 1   Nitrogen sorption data for calcined metal silsesquioxane complexes and for a calcined metal free silsesquioxane ligand.

Sample	Surface area[a] $(m^2 \cdot g^{-1})$	Pore volume[b] $(mL \cdot g^{-1})$		Average pore diameter[c] (nm)
MgSiO	347	0.12	0.12	0.60
AlSiO(I)	583	0.20	0.19	0.64
AlSiO(II)	641	0.22	0.21	0.63
CrSiO-450	614	0.21	0.21	0.68
SiO$_2$-450	499	0.17	0.17	0.61

[a] estimated from Dubinin-Radushkevich equation;

[b] estimated from Dubinin-Radushkevich (1st column) and Horvath-Kawazoe equations (2nd column);

[c] estimated from Horvath-Kawazoe equation.

These results indicate the formation of truly microporous materials characterized by high surface areas, rather large pore volumes and a very narrow pore size distribution with an average pore size diameter around

0.6—0.7 nm.

As we found in our previous work on chromium silsesquioxane complex the surface area and pore volume of the CrSiO material depended on calcination temperature.[4] Therefore for optimization of the proposed methodology here we have tried different calcination conditions in order to determine if it is possible to adjust the texture of metallosilicates and their metal oxide dispersion. Calcination conditions which have been tested included: temperature, which was varied in the range 425—550°C, pure O_2 flows of 6-100 mL/min and a 30 mL/min Ar diluted O_2 flow of 20 mol% O_2 as well as a calcination time of 4/16 h.

Thus, the surface area of MSiO materials can be greatly changed, by altering the O_2 flow, as we showed in Fig. 4 for MgSiO, AlSiO(I) and AlSiO(II) materials. However the effect is complex, since an increase in
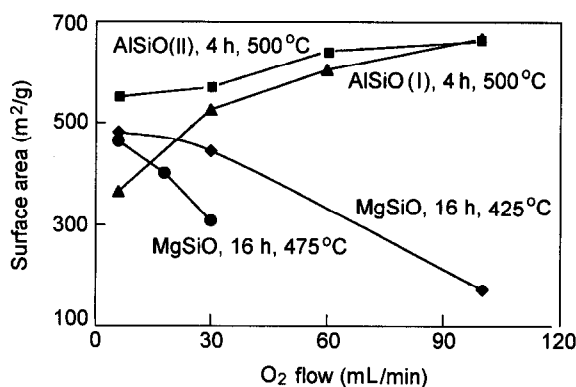

Fig. 4 Effect of calcination conditions on the surface area of MgSiO, AlSiO(I) and AlSiO(II) materials.

O_2 flow is decreasing the surface area of MgSiO while increasing those ones of AlSiO(I) and AlSiO(II). This effect might be attributed to the different kind of metal oxides that are formed in these materials, which present different resistance against sintering. Thus increasing the O_2 flow we increase the amount of water that is formed on the nascent surface of MSiO materials. This could greatly accelerate the sintering processes in the case of MgSiO and therefore result in lower surface areas since it was reported that the surface area of active magnesia prepared by calcination procedures is significantly diminished due to sintering in the presence of water vapors. The greater effect of water on the sintering rate of magnesia compared with alumina and silica was attributed to the low charge and correspondingly high mobility of

the magnesium ions.[12] The reproducibility of the data presented in Fig. 4 is rather good since the difference found between the surface area of two batches of MSiO calcined in the same conditions was below 8%.

There is also a significant temperature effect, since an increase in temperature of 50°C is diminishing the MgSiO surface area with *ca*. 150 m²/g. From this point of view appropriate calcination temperatures are required to obtain high surface areas.

A longer calcination time can be effective for reducing the residual carbon content, especially at low temperatures like 425°C, and it does not affect significantly the surface area. However, at higher calcination temperatures of at least 500°C, a 4 h calcination time seems to be reasonably enough for all the MSiO materials.

Pure O_2 flows can remove more efficiently the residual carbon than diluted O_2 flows. They have usually little effect on textural properties of MSiO materials in comparison with Ar diluted O_2 flows but sometimes they can prevent mesopore formation. When an Ar diluted O_2 flow was used all the MSiOs, excepting the AlSiO(I), yielded type Ib isotherms characteristic to microporous materials. AlSiO(I) afforded a type IIb curve associated with a steep increase in the adsorption amount at low p/p₀, indicative for the presence of both micro- and mesopores. When we used pure O_2 the isotherm became type Ib as well. Attribution of MSiO material isotherms was made according to extended IUPAC classification.[13]

Whereas the surface area and pore volume can be adjusted rather well by changing calcination conditions, the pore size distribution does not change significantly. However, since textural properties like surface area are very sensitive to calcination conditions the later ones must be well controlled in order to achieve a good reproducibility of the samples. Also for comparison reasons we chose a calcination temperature of 500°C, a calcination time of 4 hours and an Ar diluted O_2 flow of 30 mL/min 20 % O_2 as standard conditions.

The metal dispersion for MgSiO and AlSiO materials was investigated by XPS, MAS ²⁹Si NMR, TEM and XRD techniques. Since the photoelectrons excited by the X-ray radiation can only travel a few nanometers through a solid oxide material, the XPS data contain surface sensitive information. If we assume that all the metal species are homogeneously distributed into the MSiO materials then the surface and the bulk ratios

should be similar. M/Si atomic ratios calculated from the composition of silsesquioxane complexes **7**, **8** and **9** are 0.285, 0.142 and 0.062 respectively. These bulk M/Si ratios are compared in Fig. 5 with the surface M/Si ratios determined by XPS analysis.
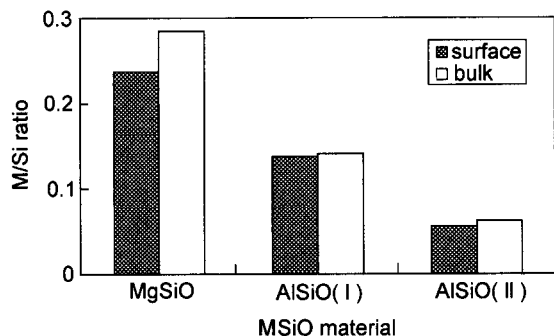

Fig. 5　Comparison of bulk and surface (XPS data) M/Si atomic ratios for MgSiO, AlSiO(I) and AlSiO(II) materials.

The surface and bulk M/Si ratios are almost the same for MgSiO as well as for AlSiO materials indicating a high dispersion of the metal oxide on the formed silica surface. It should be noted also that XPS Al/Si ratio for AlSiO(I) did not change significantly when different O_2 flows in the range 6—100 mL/min were used indicating a rather stable dispersion of aluminium oxide on silica surface.

Solid state MAS ^{29}Si NMR spectra of calcined magnesium and aluminium silsesquioxane complexes **7**, **8** and **9**, as well as of calcined metal free silsesquioxane ligand **5** were recorded. We measured also the spectrum of a physical mixture of calcined metal free silsesquioxane ligand **5** and MgO with the same content of Mg as in the MgSiO material. All these materials present a single, broad ^{29}Si resonance with a clearly defined maximum having a chemical shift value at δ 105.5 ± 0.5 for MSiO materials and around δ 109.5 ± 0.5 for pure silica, as shown in Table 2.

The lower chemical shift for MSiO materials is assigned to a higher proportion of Q3 than Q4 environment in the second coordination sphere of Si atoms. The physical mixture of pure silica and magnesium oxide presents the same chemical shift as pure silica. Thus, the observed shift for the MgSiO cannot be attributed to some susceptibility effect caused by the formation of a separate MgO phase or if some MgO particles are formed they should be very small.

Table 2　Chemical shift for calcined magnesium and aluminium silsesquioxane complexes and for calcined trisilanol ligand in solid state MAS-^{29}Si NMR spectra.

Material	Chemical shift (δ)
MgSiO^a	105.44
SiO$_2^a$	109.50
SiO$_2^a$ + MgO (physical mixture)	109.50
AlSiO(I)	104.89
AlSiO(II)	105.81
SiO$_2$	108.76

^{a} sample calcined at 425℃/16 h/30 mL·min O_2.

Observing the metal dispersion with transmission electron microscopy requires sufficient contrast between the metal oxide and the support, and it can be difficult to detect small and highly dispersed metal oxide particles on the support surface. Nevertheless, MgSiO and AlSiO materials were examined in the transmission electron microscope, which allowed us to get a rather good image for MgSiO-425℃ sample surface as shown in Fig. 6.

Fig. 6　TEM picture of MgSiO—425℃ sample showing particles of MgO of about 3-5 nm size that are well dispersed on silica surface.

In this picture well dispersed darker spots assigned to magnesium oxide particles can be seen on silica surface. Since MgO particles size, which is around 3—5 nm, is much larger than the silica pore size this suggest that they are located either on the outer surface of silica or they are part of the pore walls. Taking into account the very good fit between the surface and bulk Mg/Si atomic ratios we can assume that MgO is present in sample both as atomically dispersed species and as small particles of a few nanometers that are all well dispersed on silica surface. This implies that during the calcination procedure some of the Mg—O—Si bonds can be hydrolyzed by the water formed from combustion of the organic part of magnesium silsesquioxane complex and thus allows the migrationof Mg species on nascent silica surface with the final formation of MgO particles.

It must be noted that since the XRD spectra of both MgSiO and AlSiO materials present only a broad band around 20—30° 2θ angle usually assigned to amorphous silica[14] we cannot exclude the possible assignment of the particles from silica surface to a magnesium silicate phase. However, for calcined chromium silsesquioxane complex 3 Raman spectrum indicated the presence of crystaline α-Cr₂O₃ particles.

We propose to investigate the extent to which the structure of the Si—O—M skeleton in the precursor complex is retained in the resulting metallosilicate by comparing the outcome of calcination experiments using the cluster compound 7 presented before and the cluster compound 10 shown in Fig. 7.
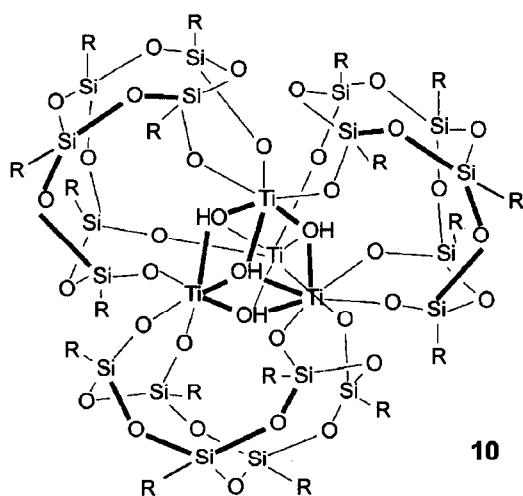

Fig. 7   A titanium silsesquioxane cluster compound with a more complex cage structure (R = C₆H₁₁).

Compound 7 can be considered as a soluble model for a simple clay. If, upon calcination its layered structure is retained, one might expect a real clay to result. However the XRD spectrum of compound 7 calcined under various calcination conditions showed only an amorphous silica band as mentioned before. No peaks that could be assigned to a crystalline clay phase could be detected. This is to be expected because of the high temperature necessary for the calcination procedure. It was actually reported that anionic clays like layered double hydroxides loose their crystalline structure upon calcinationat 450 °C in vacuum. Nevertheless, if the calcination temperature does not exceed 550 °C the crystalline structure of the clay can be partially recovered by rehydration treatment as proved by XRD and solid state NMR techniques.[15,16] Therefore we simply stirred a MgSiO-425 °C sample in water at 50 °C for 48 h and then recorded the XRD spectrum again. The XRD spectrum presented one sharp peak at 18.1 2θ degree angle with a d-spacing of 0.4897 nm, the assignment of which is, however, ambiguous and it is still a topic of investigation. It is to be noted also that the extent of reversibility in the dehydration/rehydration behavior of LDHs is a controversial topic. Moreover if we take into account the Si/Mg ratio in compound 7 which is 3.5 we can conclude that this precursor is too rich in silica to give a common clay composition after calcination.

Interestingly, all silsesquioxane metal complexes that have been subjected to calcination experiments do give rise to microporous materials with the same pore size. This might be attributed to the fact that all these complexes result from the same cube type silsesquioxane ligand. Calcination of 10, which results from a completely different silsesquioxane[17] can therefore give a first indication on whether the Si—O—M skeleton determines the pore size and its size distribution.

The possibility to prepare metallosilicates that are exclusively Lewis or Brönsted acids can be easily investigated using the aluminium complexes 8 and 9. Complex 9 can be considered as a model for a Brönsted acidic zeolite site while complex 8 has aluminium sites that are exclusively Lewis acidic. The aluminosilicates resulting from calcination of 8 and 9 will be investigated with an in situ IR experiment that involves treatment of the sample with acetonitrile. As described previously, this provides a good method to discriminate between Lewis and Brönsted acid sites.[18,19]

The way in which we propose to investigate whether it is possible to prepare MSiO materials with highly dispersed metal oxide particles when the precursor complex contains no direct Si—O—M bonds is outlined below. The chromosilicate 4 shown in Fig. 1 results from the calcination of the precursor 3, which already contains chromium bonded to silicon via Si-O-Cr units.[4] To en-

hance the potential flexibility of the synthetic methods presented here it is worth to investigate the calcination behavior of silsesquioxane derivatives that contain metal bonded via an ancillary ligand system that does not involve direct Si-O-M bonding. This is illustrated in Fig. 8.
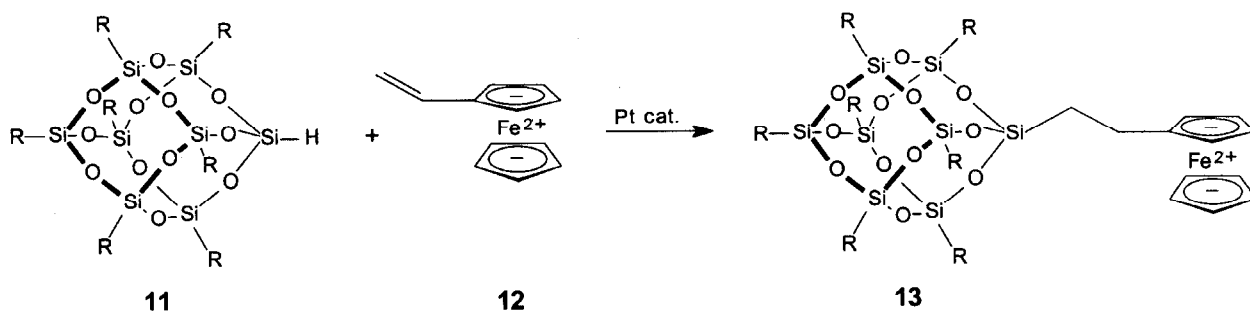

Fig. 8   A silsesquioxane derivative precursor containing metal bonded via an ancilliary ligand system that does not involve direct Si—O—M (compound **13**), (R = C_5H_9). Compound **12** is typical for a large class of vinylmetallocenes that can be linked to a silsesquioxane skeleton (like compound **11**) by hydrosilylation.

Especially in the case of late transitional metals, which are more difficult to bond directly via Si—O—M units, it would be an advantage to use precursors as exemplified by compound **13**.[20] If the calcination behavior of **13** turns out to be of interest, we could easily develop silica precursors for a large number of transition metals by hydrosilylation of vinylmetallocenes (e. g. compound

12) with hydridosilsesquioxanes[21] like compound **11**. In doing so, we shall also investigate the use of silicones as cheap alternatives for silsesquioxanes. This is explained in Fig. 9 where the hydrosilylation employed in the synthesis of **13** is compared with a possible application using a 2-part silicone RTV encapsulant.[22]
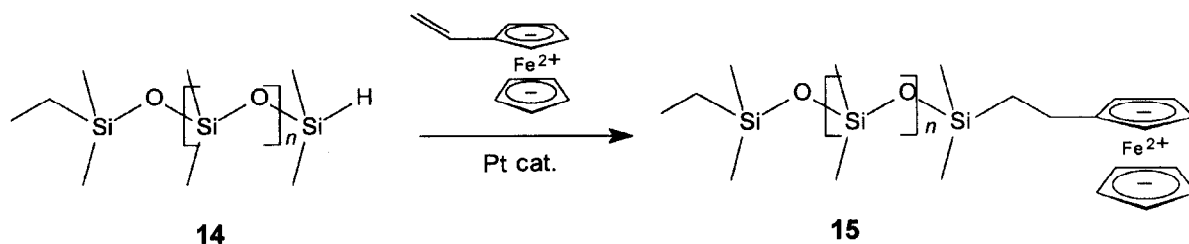

Fig. 9   Preparation of a metal containing silica precursor from a cheap RTV encapsulant.

An additional relevant aspect for the work proposed here is that we and others[1], found that calcination of metal free silsesquioxanes also gave rise to the formation of well defined microporous silica with a similar pore size distribution. Thus, we can use this as a basis for adjusting the metal content in metallosilicate synthesis. This clearly has potential for developing new oxidic catalysts, including mixed metal systems. As showed in

Scheme 1, we envision a potential combinatorial approach that could even be automated.

Conclusion

Controlled calcination of silsesquioxane metal complexes leads to microporous amorphous silica supported metal oxides with a very narrow pore size distribution ,

Scheme 1   Combinatorial approach for synthesis of mixed metal catalytic systems
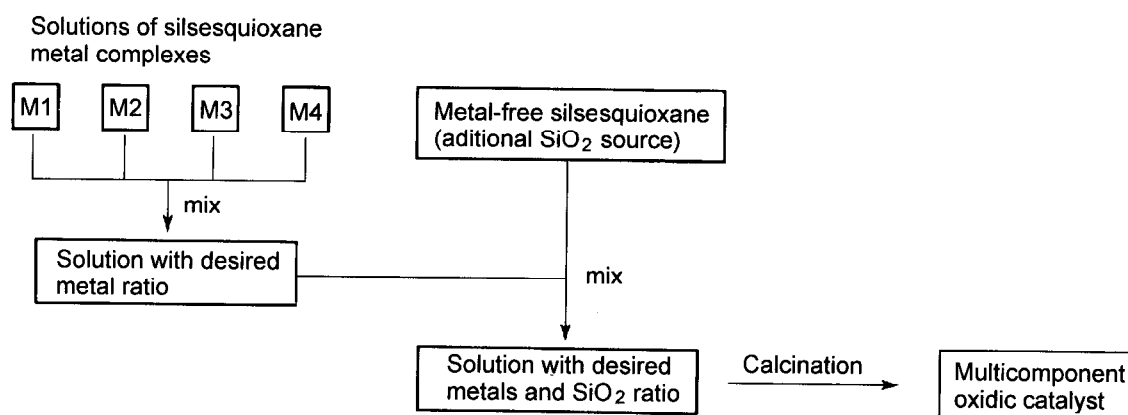
high surface areas and high loadings of well-dispersed metal oxide.

Oxidation of organic matter during calcination of the metal silsesquioxane complex precursor leaves a low amount of residual carbon in the resulting MSiO materials. The amount of residual carbon content can be significantly reduced especially by increasing calcination temperature.

A standard calcination procedure can be generally applied for most of the metal silsesquioxane complex precursors. However, if necessary, calcination conditions like temperature or O_2 flow can be conveniently altered in order to adjust the textural properties of MSiO like surface area while keeping the microporous matrix and the pore size distribution.

A high metal oxide dispersion in the silica matrix is achieved, as indicated by XPS and solid state MAS ^{29}Si NMR spectroscopy, which seems to be rather insensitive to calcination conditions. Taking into accounts both XPS and TEM results we assume the presence of metal oxide in MSiO both as atomically dispersed and as small and well dispersed particles. More investigations are however undertaken to confirm the nature of metal particles.

The textural properties and metal dispersion make MSiO materials promising silica supported metal oxide catalysts. Other issues, like the necessity to have direct Si—O—M bonding, the control of acidity for MSiO and most important the possibility for combinatorial approach on mixed metal catalytic system synthesis are now under investigations. The forthcoming results will allow us to e-valuate and possibly set up a new tool for synthesis of silica supported catalysts.

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22   Such materials like compound **14** are comercially available. For instance the filler free 2-part silicone elastomer Gelest OE™ 41 for which one of the components contains a platinum based hydrosilylation catalyst.

(E200007140   LI, L.T.; DONG, L.J.)