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# Transformation of Organosilicon-Loaded Alumina Gel to Homogeneous Aluminosilicates: A Solid-State NMR Study

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Sol−gel processes have been applied extensively to the preparation of single- and multicomponent oxide gels.[1] In bicomponent systems containing the metals M and M′, homogeneous condensation of MOM′ bridges occur only if the homocondensation reactions for M and M′ (i.e., formation of MOM and M′OM′ bridges) have comparable reaction rates. Therefore, a high degree of homogeneity of bicomponent gels is difficult to achieve by the hydrolytic sol−gel route.[2] The nonhydrolytic sol−gel approach, pioneered by Corriu et al., reduces the difference in reactivity and is much more efficient for the preparation of homogeneous bicomponent gels.[2] A number of mixed oxide gels with a high level of homogeneity have been recently prepared by using several routes; among them are etherolysis of a mixture of metal chlorides (eq 1), condensation of metal halides with alkoxides (eq 2),[3,4] and transformation of heterometallic alkoxides with pre-existing MOM′ linkages (eq 3).[5] However, in these routes the formation of a MOM′ joint network is still based on a series of complex condensation processes during the gelation stage. This restricts the choice of precursors and limits the preparation of new multicomponent materials.

$$\mathrm{MX}_m + \mathrm{M'X}n + \mathrm{ROR} \rightarrow \mathrm{MOM'} + \mathrm{RX} \qquad (1)$$

$$\mathrm{MX} + \mathrm{M'OR} \rightarrow \mathrm{MOM'} + \mathrm{RX} \qquad (2)$$

$$(\mathrm{RO})_m\mathrm{MOM'}(\mathrm{OR})_n \xrightarrow{\Delta\text{ or }\mathrm{H}^+} \mathrm{MOM'} + \mathrm{ROH} \qquad (3)$$

In this paper we report on a novel approach to prepare homogeneous bicomponent oxides. Our method involves the heating of a gel matrix of one component that includes a homogeneously entrapped precursor of a second component. Using this method, Si/Al bicomponent oxides were prepared by heating in air nonhydrolytic alumina gel loaded with organosilicon compounds, which were dispersed and entrapped unreacted at the gelation stage. $^{29}$Si and $^{27}$Al solid-state NMR study showed that the silicon was incorporated into the alumina skeleton during heating, forming a homogeneous aluminosilicate structure.

The preparation of gel samples was based on the nonhydrolytic route to aluminosilicates proposed by Corriu et al. (eq 4).[3] However, instead of $SiCl_4$ as the silicon precursor, we used tetrakis(trimethylsilyl)silane (**1**, eq 5)[6a] or tetrakis(chlorodimethylsilyl)silane (**2**, eq 6).[6b] While the details of gel preparations are given elsewhere,[7,8] we note that in the starting solutions an initial ratio of Si/Al = 2.5 was employed for both **1** and **2**. It was found[8] that xerogels **A** and **B**, resulting from reactions 5 and 6, respectively, were transformed into mullite ($Al_2O_3/SiO_2 = 3/2$) by being heated in air at ≈980 °C. The formation of mullite at such a low temperature, as was stressed by Corriu et al.,[3] indicates an atomic level homogeneity of the premullite amorphous aluminosilicate network.

$$\mathrm{SiCl_4} + \mathrm{AlCl_3} + {}^{\mathrm{i}}\mathrm{Pr_2O} \xrightarrow[\text{(2) vacuum drying}]{\text{(1) 110 °C; CH}_2\text{Cl}_2} \text{aluminosilicate gel} \qquad (4)$$

$$\underset{\mathbf{1}}{\mathrm{Si(SiMe_2Cl)_4}} + \mathrm{AlCl_3} + {}^{\mathrm{i}}\mathrm{Pr_2O} \xrightarrow[\substack{\text{(2) vacuum drying}\\ \text{at room temp.}}]{\text{(1) 110 °C; CH}_2\text{Cl}_2} \text{xerogel }\mathbf{A} \qquad (5)$$

$$\underset{\mathbf{2}}{\mathrm{Si(SiMe_2Cl)_4}} + \mathrm{AlCl_3} + {}^{\mathrm{i}}\mathrm{Pr_2O} \xrightarrow[\substack{\text{(2) vacuum drying}\\ \text{at room temp.}}]{\text{(1) 110 °C; CH}_2\text{Cl}_2} \text{xerogel }\mathbf{B} \qquad (6)$$

To follow the incorporation of the silicon atoms into the alumina network and the formation of Si−O−Al linkages, high-resolution $^{29}$Si and $^{27}$Al solid-state NMR spectroscopy was employed. For this purpose xerogels **A** and **B**, obtained after the gelation stage, were heated in air for 5 h at different temperatures in the range of 100−900 °C. The $^{29}$Si CP/MAS NMR spectra[9] of the raw xerogels heated at specified temperatures are shown in Figure 1 (**A**, **A1**−**A6**) and in Figure 2 (**B**, **B1**−**B6**).

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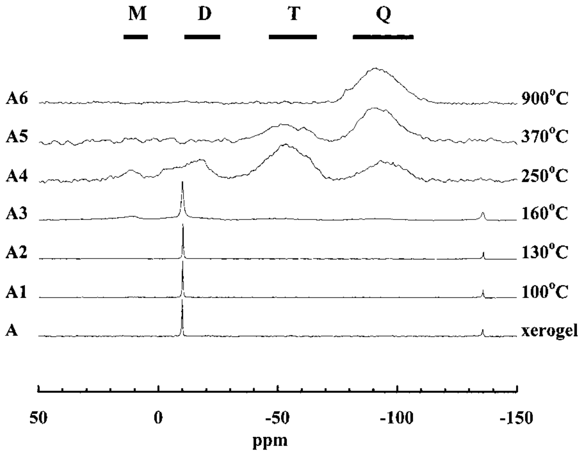

**Figure 1.** $^{29}$Si CP/MAS NMR spectra of xerogel with $(Me_3Si)_4Si$ (**1**): **A**, raw xerogel; **A1**−**A6**, xerogel **A** heated for 5 h in air at specified temperatures in the 100−900 °C range.

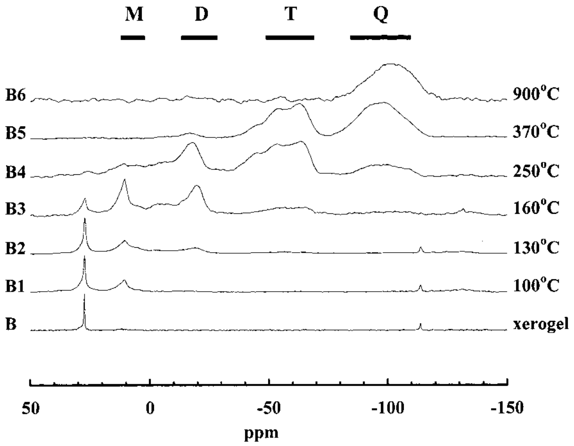

**Figure 2.** $^{29}$Si CP/MAS NMR spectra of xerogel with $(ClMe_2Si)_4Si$ (**2**): **B**, raw xerogel; **B1**−**B6**, xerogel **B** heated for 5 h in air at specified temperatures in the 100−900 °C range.

The spectrum of raw xerogel **A** shows the characteristic signals of unreacted **1** at −9.8 and −135.5 ppm, indicating that **1** is not involved in the condensation reactions leading to gelation and formation of the alumina matrix. At 160 °C (**A3**) these peaks broaden and the formation of new peaks is observed in the NMR spectra, indicating that **1** starts to react. The NMR peaks of **1** completely disappear at 250 °C (**A4**), indicating its absence in the sample. The $^{29}$Si NMR spectra of samples **A3**−**A5** clearly show the gradual progression of the condensation reactions accompanied by the formation of new condensation products with characteristic silicon species of types M, D, T, and Q.[10−13] The broad peaks, besides reflecting typical site heterogeneity, indicate the presence of Si−OR or Si−OH sites in addition to Si−O−Si linkages. As the temperature is elevated, there is a gradual decrease in the M, D, and T peaks and a buildup of a Q-type peak, indicating the formation of a three-dimensional Si network and the removal of organic ligands from the silicon units. At 900 °C the spectrum consists of a broad peak with a maximum at about −90 ppm (**A6**), indicating that only Q-type Si species are present. This spectrum is very similar to that of homogeneous premullite aluminosilicates.[3] The fact that the Q-type peak does not exhibit resolved $Q^n$ peaks (**A3**−**A6**), as is observed for amorphous silica,[14]is attributed to the downfiled shifts caused by Si−O−Al bonds and is taken as evidence for the gradual formation of a Si−O−Al network.[10,13]

The $^{29}$Si NMR spectra of xerogel **B** with precursor **2** when heated to 900 °C are shown in Figure 2. The spectrum of xerogel **B** shows the characteristic signals of unreacted **2** at 27.4 and −113.6 ppm. Thus, although **2** has reactive Si−Cl bonds, it is not involved in the reactions at the gelation stage (similarly to **1**). However, in contrast to **1**, at 100 °C (**B1**) a new, relatively narrow M-type peak appears (at ≈10 ppm), and at 130−160 °C (**B2** and **B3**) it is accompanied by a D-type peak (at approximately −20 ppm). The M peak is attributed to the formation of dimeric siloxane products as a result of condensation processes through the Si−Cl bonds, while the D peak is typical to linear siloxane polymers, indicating further condensation of the dimeric products and reflecting the higher reactivity of **2** compared to that of **1**.

The $^{29}$Si NMR spectra of samples **B4**−**B6**, obtained at 250, 370, and 900 °C, respectively, are similar to those of **A4**−**A6**, pointing to analogous processes of the gradual formation of a three-dimensional aluminosilicate network. The broad Q-type signal of sample **B6** is centered at appoximately −100 ppm, 10 ppm upfield compared to this signal in **A6**. The high-field shift, also observed by Corriu et al.,[2] is attributed to a higher Si/Al ratio in **B6** relative to **A6** and is consistent with the final measured Si/Al ratios of approximately 1.0 and 0.4, respectively.[15] The formation of condensation products from **2** at relatively low temperatures (100 °C) probably decreases the loss of **2** upon heating (compared to **1**), therefore leading to the higher Si/Al ratio in **B6** relative to that in **A6**. Also here, the absence of resolved $Q^n$ peaks within the Q-type peak is taken as evidence for Si incorporation into the alumina matrix.

The $^{27}$Al NMR spectra of samples **A**−**A6** and **B**−**B6** (not shown), although they provide only indirect evidence on the incorporation of Si into the alumina matrix, are consistent with the above conclusions based on the

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[9] $^{29}$Si CP/MAS NMR spectra were recorded on a Chemagnetics/Varian CMX-*Infinity* 300 spectrometer at 59.62 MHz with a MAS frequency of 5 kHz (double-resonance probe with a 7.5-mm spinning module), using cross-polarization with 4-ms contact time, Hartmann−Hahn match at 50 kHz, 75-kHz proton decoupling, and 3-s relaxation delay. The resonance at −9.8 ppm in tetrakis(trimethylsilyl)silane (**1**) was used as an external reference. Between 2000 and 10 000 transients were acquired for samples weighing between 70 and 150 mg.

[10] M, D, T, and Q denote Si atoms with one, two, three, and four Si−O bonds in the respective silicon unit.[11,12] Their typical ranges of $^{29}$Si resonances are (in ppm) +15 to +5 for M, −9 to −23 for D, −48 to −66 for T, and −82 to −110 for Q. Typical downfield shifts induced by substitution of each Si−O−Si bond by Si−OH or Si−OR groups are ≈9 ppm. A Si−O−Al linkage leads to a downfield shift of ≈5 ppm compared to a Si−O−Si moiety.[13]

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[15] The final Si/Al ratios were determined from thermogravimetric/differential thermal analysis (TGA/DTA) data.[8] The formation of amorphous silica after mullite crystallization, due to excess of Si over stoichiometric mullite composition (Si/Al = 0.33), was observed by $^{29}$Si solid-state NMR in both samples heated to 1300 °C.[8]

$^{29}$Si NMR spectra.[16] Thus, **A6** and **B6** exhibit $^{27}$Al MAS NMR spectra with four-, five-, and six-coordinated aluminum sites, which are very similar to those reported for homogeneous premullite gels heated at 900 °C,[3] suggesting that both routes lead to similar aluminosilicate networks. In particular, the presence of five-coordinated Al sites, regarded as intermediate environments, was shown to indicate high homogeneity.[3] The details of the stepwise chemical transformations as a function of temperature, leading to the incorporation of the silicon into the alumina matrix, are the subject of further studies.

In conclusion, we have shown that homogeneous Si/Al oxides can be prepared using a novel approach, which involves the physical entrapment of unreacted silicon precursors into a nonhydrolytic alumina gel matrix in the gelation stage, followed by thermal treatment of the so-formed composite gels. The formation of Si−O−Al linkages during heating and the homogeneity of the Si/Al mixed oxides were evidenced by $^{29}$Si and $^{27}$Al solid-state NMR. The entrapment/decomposition approach presented here is advantageous over previously reported routes since it does not require a cogelation process and therefore does not suffer from the problems associated with different gelation rates of the precursors. Hence, our approach opens new possibilities for the preparation of new multicomponent oxides.

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(16) Full detailes of the $^{27}$Al NMR spectra and their evolution as the temperature is raised will be described elsewhere.