Transformation of Organosilicon-Loaded Alumina Gel to Homogeneous Alumino-silicates: A Solid-State NMR Study

Dmitry Bravo-Zhivotovskii,‡,§ Semyon Melamed,† Yitzhak Apeloig,†,§ Asher Schmidt,*,†,§

Silicates: A Solid-State NMR Study

Alumina Gel to Homogeneous Alumino-
Transformation of Organosilicon-Loaded

35

The
includes a homogeneously entrapped precursor of a
the heating of a gel matrix of one component that
homogeneous bicomponent oxides. Our method involves
restricts the choice of precursors and limits the prepara-
tion of homogeneous bicomponent gels.2 A
difference in reactivity and is much more efficient for
gel approach, pioneered by Corriu et al., reduces the
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
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 ethelymination of a mixture of
metal chlorides (eq 1), condensation of metal halides
with alkoxides (eq 2),3,4 and transformation of hetero-
metallic 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 prepara-
tion of new multicomponent materials.

\[ MX_m + M'X_n + ROR \rightarrow MOM^* + RX \] (1)

\[ MX + M'OR \rightarrow MOM' + RX \] (2)

\[ (RO)_mMOM'(OR)_n \xrightarrow{\text{H}^+} MOM^* + ROH \] (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 nonhydro-
lytic alumina gel loaded with organosilicon compounds,
which were dispersed and entrapped unreacted at the
gelation stage.23Si and 27Al solid-state NMR study
showed that the silicon was incorporated into the
alumina skeleton during heating, forming a homoge-
neous aluminosilicate structure.

The transformation of gel samples was based on the
nonhydrolytic route to aluminosilicates proposed by
Corriu et al. (eq 4).3 However, instead of SiCl₄ as
the silicon precursor, we used tetrakis(trimethylsilyl)isilane
(1, eq 5)60 or tetrakis(chlorodimethylsilyl)isilane (2, eq
6).60 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 found8 that xerogels A and B, resulting from
reactions 5 and 6, respectively, were transformed into
mullite (Al₂O₃/Fe₂O₃ = 3/2) by being heated in air at \( \approx 980 \)°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 pre-mullite amorphous alumi-
nosilicate network.

\[ \text{SiCl}_4 + \text{AlCl}_3 + \text{Pr}_2\text{O} \xrightarrow{(1) 110 \degree C; CH}_2\text{Cl}_2} \text{aluminosilicate gel} \] (4)

\[ \text{Si(SiMe}_2\text{Cl})_4 + \text{AlCl}_3 + \text{Pr}_2\text{O} \xrightarrow{(1) 110 \degree C; CH}_2\text{Cl}_2} \text{xerogel A} \] (5)

\[ \text{Si(SiMe}_2\text{Cl})_4 + \text{AlCl}_3 + \text{Pr}_2\text{O} \xrightarrow{(1) 110 \degree C; CH}_2\text{Cl}_2} \text{xerogel B} \] (6)

To follow the incorporation of the silicon atoms into
the alumina network and the formation of Si-O-Al
linkages, high-resolution 29Si and 27Al 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 29Si CP/MAS NMR spectra9 of the raw
xerogels heated at specified temperatures are shown in
Figure 1 (A, A₁–A₆) and in Figure 2 (B, B₁–B₆).

9 To whom correspondence should be addressed.
1 Department of Chemistry and the Lise Meitner-Minerva Center for Computational Quantum Chemistry.
2 Department of Chemical Engineering.
3 Institute of Catalysis Science and Technology, Technion-Israel Institute of Technology, Haifa 32 000, Israel.
4 Received May 9, 2000 Revised Manuscript Received November 20, 2000.
The 29Si 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 29Si 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 approximately −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-type peaks within the Q-type peak is taken as evidence for Si incorporation into the alumina matrix.

The 27Al 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

---

(9) 29Si CP/MAS NMR spectra were recorded on a Chemagnetics/Varian CPX-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. Their typical ranges of 29Si 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.


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

**Acknowledgment.** This research was supported in part by the Fund for the Promotion of Research at the Technion, the Israel Ministry of Science and Arts, and the Israel Science Fund administrated by the Israel Academy of Science. We thank Dr. D. Igner and Dr. S. Kababya for help in performing the NMR measurements.