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Preparation of silica–titania xerogels and aerogels by sol–gel processing of new single-source precursors

Wolfgang Rupp, Nicola Hüsing and Ulrich Schubert*

Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria. E-mail: uschuber@mail.zserv.tuwien.ac.at

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Reaction of 3-(propyltrimethoxysilyl)acetylacetone with $Ti(O^iPr)_4$ results in new single-source precursors for dispersed silica–titania mixed-metal oxides with low titania crystallization tendencies.

An inherent problem for the preparation of mixed oxides by sol–gel processing of a mixture of different metal alkoxides is that phase separation may occur because of different hydrolysis and condensation rates. For example, addition of water to a solution of $Si(OR)_4$ and $Ti(OR)_4$ results in the precipitation of titania. Common solutions to this problem which allow the preparation of homogeneous (well mixed on the nanometer scale) silica–titania gels involve pre-hydrolyzing $Si(OR)_4$ as the slower reacting component[1,2] or lowering the reactivity of the faster reacting precursor, $Ti(OR)_4$, by chemical modification, *e.g.* by replacing part of the alkoxide groups by chelating or bridging ligands, such as carboxylates or β-diketonates.[3] A third possibility is to use single-source precursors such as $Ti(O^iPr)_n[OSi(O^tBu)_3]_{4-n}$ (n = 0,[4] 1–2[5]), $[Si(O^tBu)_2OTi(acac)_2O]_2$,[5] or $[Si(OEt)_2OTi(OEt)_2O]_x$ polymers.[6] In these precursors, the titanium and silicon atoms are linked by oxo bridges. Homogeneous silica–titania gels were also obtained by non-hydrolytic sol–gel processes, in which one component is an alkoxide and the other a chloride or acetate.[7] TiO_2–SiO_2 mixed oxides are used as catalysts for epoxidation reactions of olefins.[8]

In this paper, we report a combination of the second and third approach by using 3-(propyltrimethoxysilyl)acetylacetone (**1**),[9] a molecule that combines the features of a complexing β-diketone and a hydrolyzable alkoxysilane. When **1** was reacted with one or half an equivalent of $Ti(O^iPr)_4$, the bi- and trinuclear compounds **2** and **3** were obtained (eqn. 1), in which the β-diketonate group is coordinated to a $Ti(O^iPr)_x$ (x = 2 or 3) group, as evidenced by the IR spectra. In the new single-source precursors the $Si(OR)_3$ and $Ti(OR)_x$ moieties are thus linked by an organic group.

Sol–gel processing of **2** and **3**[10] under basic conditions resulted in yellow, monolithic gels. Gelling occurred after about 30 min. To check whether the covalent linkage of the $Ti(OR)_3$ and $Si(OR)_3$ units has an influence on the gelation behavior, an equimolar mixture of (propyl)$Si(OMe)_3$ and (acac)$Ti(O^iPr)_3$ was reacted under the same conditions, but no gelation occurred over the course of a few days. Therefore, the relatively fast gelation of **2** and, as a consequence, of **3**, is not due to electronic effects (which should be approximately the same for a 1 : 1 mixture of (propyl)$Si(OMe)_3$ and (acac)$Ti(O^iPr)_3$), but instead to the linkage of both moieties.

Drying of the wet gels formed by hydrolytic polycondensation of **2** and **3** in air by evaporation of the pore liquid at ambient temperature gave transparent monolithic xerogels or xerogel powders. Powders were obtained when the gel was dried in a flask (large gel to air interface), while hard, transparent and crack-free monoliths were obtained when the gelation was performed in a plastic tube which was cut open at both ends for drying (small gel to air interface) (Fig. 1). The overall appearance of the dried gels was very similar to what has been described for gels obtained from bis(trialkoxysilyl)-organyl monomers.[11] Mixed-oxide powders with the nominal composition $TiO_2 \cdot SiO_2$ or $TiO_2 \cdot 2SiO_2$ were obtained when the organic groups were removed from the xerogels by calcination at 550 °C.[12] Upon supercritical drying with CO_2 of the gels formed from **2** and **3** (the shrinkage was 14%), monolithic but opaque aerogels were obtained. Preliminary SAXS (small angle X-ray scattering) experiments suggest that larger scattering objects are present than in pure silica aerogels prepared under the same conditions. This may explain the opaque appearance of the aerogels.

The BET surface area of the aerogel obtained from the binuclear precursor **2** (230.7 $m^2\ g^{-1}$) was larger than that obtained from the trinuclear precursor **3** (89.7 $m^2\ g^{-1}$), probably because of the lower number of organic groups in **2**. It

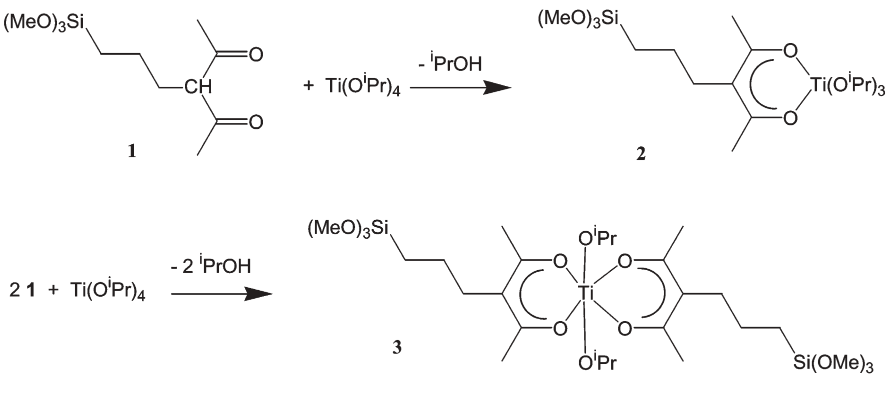

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Fig. 1 Xerogel powder (left), xerogel monolith (center; 2.5 mm diameter), and aerogel monolith (right; 4.1 mm diameter) prepared from **2**. In the wet gel stage, the samples had about the same diameter as that of the aerogel sample, *i.e.* the xerogel monolith shrank to about 60% of its original size during drying.

cannot be excluded at this stage of the investigations that **3** has a different network structure to **2**, which could also affect the surface properties. The BET surface areas of the calcined xerogels followed the opposite trend; the $TiO_2{\cdot}2SiO_2$ sample (361.2 m^2 g^{-1}) had a higher surface area than the $TiO_2{\cdot}SiO_2$ sample (207.7 m^2 g^{-1}), probably because most of the organic groups were lost during calcination.

The UV-Vis spectrum of the $TiO_2{\cdot}SiO_2$ xerogel prepared from **2** showed a broad band between 230 and 370 nm, which is assigned to 6-coordinate titanium.[13] The UV-Vis spectrum of the $TiO_2{\cdot}2SiO_2$ xerogel prepared from **3** showed a second band with lower intensity centered at 220 nm. This band is assigned to 4-coordinate titanium, *i.e.* both 4- and 6-coordinate titanium is present in $TiO_2{\cdot}2SiO_2$.

X-Ray diffraction studies were carried out at different temperatures to determine the crystallization temperature of the TiO_2 phases. As can be seen in Fig. 2 and 3, the onset temperature for the crystallization of anatase was very high (800–850 °C) in both $TiO_2{\cdot}SiO_2$ and $TiO_2{\cdot}2SiO_2$, and cristobalite started to crystallize at about 1050 °C. In $TiO_2{\cdot}SiO_2$, the anatase–rutile transformation took place at about 1000–1200 °C (Fig. 2). The crystallite diameter of anatase in $TiO_2{\cdot}SiO_2$, as calculated by Scherrer's equation,[14] was 6.7 nm at 900 °C and increased to 20.9 nm at 1100 °C.

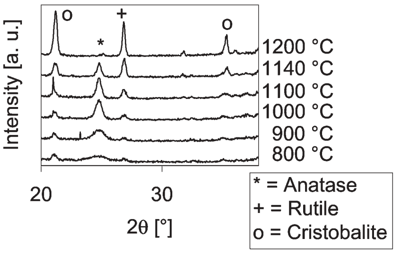

Fig. 2 High-temperature XRD pattern (Cu-Kα radiation) of a gel prepared from **2**.

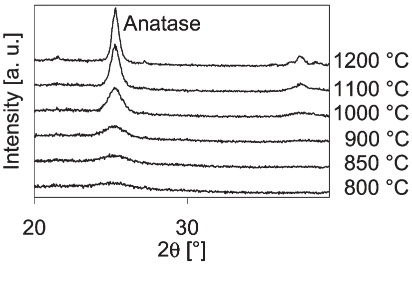

Fig. 3 High-temperature XRD pattern (Cu-Kα radiation) of a gel prepared from **3**.

The crystallite diameter of anatase in $TiO_2{\cdot}2SiO_2$ grew from 3.7 nm at 900 °C to 10.4 nm at 1100 °C, *i.e.* crystal growth of anatase is delayed to higher temperatures compared with the $TiO_2{\cdot}SiO_2$ sample. This higher crystallization temperature is consistent with the observation that some of the titanium atoms are still 4-coordinate after calcination. This may be due to the higher SiO_2 content. In $TiO_2{\cdot}2SiO_2$, no rutile phase was observed up to 1200 °C (Fig. 3). The absence of rutile at such high temperatures was also observed for $TiO_2{\cdot}4SiO_2$ obtained from $Ti[OSi(O^tBu)_3]_4$.[4] It was shown that the crystallization temperature of anatase in TiO_2–SiO_2 mixed oxides increases when the silica content is increased.[15]

It was previously noted that the crystallization temperature and the crystallite size in silica–titania mixed oxides is controlled by the precursor structure.[16] The unusually high crystallization temperature of anatase in the systems discussed in this article indicates a homogeneous distribution of titanium and silicon. For the anatase–rutile transformation, the anatase particles obviously need to exceed a certain size. This could explain why rutile is observed at higher temperatures in $TiO_2{\cdot}2SiO_2$ (smaller anatase particles) than in $TiO_2{\cdot}SiO_2$.

An apparent disadvantage of single-source precursors is their fixed stoichiometry. However, the Si : Ti ratio can be increased when **2** or **3** are reacted with $Si(OR)_4$ as co-monomers. Homogeneous xerogels and aerogels were also obtained when the Si : Ti ratio was increased up to 4 : 1 by adding the corresponding amount of $Si(OEt)_4$ to the solution of **2** or **3**.

In conclusion, we have shown that **1** is a versatile precursor for the preparation of homogeneously dispersed silica–titania. This approach can be easily extended to other silica–metal oxide combinations, because most transition metal oxides form stable complexes with β-diketones. We have obtained silica–zirconia and silica–tungstia systems with related properties by the same approach in preliminary experiments.

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overnight to give 3-iodopropyltrimethoxysilane. After filtration, an equimolar amount of acetylacetone and K_2CO_3 was added. The mixture was refluxed overnight and filtered, the solvent was removed in vacuo and the product distilled. All syntheses were carried out under an argon atmosphere. Only C-alkylation was observed by NMR. IR (CO): **1** 1697; **2** 1718, 1738; **3** 1718, 1744 cm^{-1}.

10 Compound **1** was mixed with a stoichiometric amount (1 : 1 or 2 : 1) of $Ti(O^iPr)_4$, and the same amount (in weight) of methanol was added. A calculated amount of 0.01 M NH_4OH (one molar equivalent of H_2O per alkoxy group) was added to this solution immediately. The mixture was shaken for 5 min and aged for one week. Gelation occurred after 30 min. The gels were air-dried to give xerogels or supercritically dried with CO_2 to give aerogels. Calcination of the xerogels at the given temperatures resulted in powders.

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