

Nonaqueous synthesis of crystalline anatase nanoparticles in simple ketones and aldehydes as oxygen-supplying agents†

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Highly crystalline anatase nanoparticles of 5–20 nm in size were obtained by reacting titanium tetraisopropoxide with common ketones and aldehydes under solvothermal conditions.

There is an increasing demand for crystalline, monodisperse nano-sized titania particles due to the growing market of applications, especially in photocatalysis.¹ Consequently, the development of cheap, straightforward synthesis routes has become one main focus of research. Nonaqueous routes to TiO₂ constitute a very elegant method, as the high reactivity of titania precursors towards hydrolysis can be circumvented.² Research in this field mainly focused on reacting titanium alkoxides and halides with ethers and alcohols and the direct reaction between the two precursors.^{3,4} Even though ketones such as acetone represent an interesting class of reaction media, as they are cheap, almost nontoxic and provide a slow and controllable reaction with metal alkoxides, only few examples have been reported including the formation of ZnO gels⁵ and BaTiO₃ powders.⁶ Aldehydes, on the other hand, have not been shown so far to react with metal alkoxides to form oxides. However, there are reports about the formation of gels upon reaction of benzaldehyde with silicon halides⁷ and TiCl₄.⁸ The scope of this work is to show that also ketones and aldehydes are suitable solvents with high potential within the framework of novel nonaqueous sol–gel reactions.

Simple ketones such as acetone, 2-butanone, 3-pentanone, cyclohexanone and benzophenone as well as the aldehydes butyraldehyde and benzaldehyde were mixed with titanium tetraisopropoxide in a glove box under Ar (for details see ESI†). The samples were prepared in a rather concentrated fashion using a molar solvent to Ti ratio of 10. The reaction mixtures were transferred into a steel autoclave equipped with a Teflon liner, which was sealed, removed from the glove-box and heated in an oven. For all solvents, yellow to amber suspensions were obtained, which were separated by centrifugation. The precipitate became white to slightly yellow upon washing with chloroform and dichloromethane, and was dried *in vacuo*. Fig. 1(a) shows the XRD pattern acquired for the system acetone–Ti(O*i*Pr)₄ (using a Bruker D8 diffractometer in reflection mode, Cu–K α radiation). All reflections correspond to anatase with a particle size of about 15.2 nm (calculated from the (101) reflection using Scherrer's equation). The crystallinity is excellent, considering the low synthesis temperature of 130 °C. For all the other ketone and aldehyde solvents, similar reflections corresponding to pure

anatase were found in the XRD. The synthesis details as well as the properties of the obtained nanoparticles are summarised in Table 1. The yields are in the range of 80–100% for all tested solvents except benzophenone. It is noteworthy that significantly larger particle sizes are found with aliphatic ketones and aldehydes than for aromatic systems. The purity of the samples was evaluated by thermogravimetric analysis (TGA). It can be observed that the content of organic/volatile species is higher for aromatic solvents and for acetone compared to higher aliphatic ketones. FT-IR measurements revealed the presence of unsaturated ligands, probably in the form of enolates or aldolates, on the surface of the particles prepared in acetone (found: $\nu_{C=C}$ 1636 cm⁻¹). Therefore, we propose that acetone and aromatic species ligate more strongly to the titania surface. Accordingly, the particle growth is restricted, resulting in a smaller particle size. We hence infer that the solvents (respectively their reaction products) strongly influence the particle morphology.

Transmission electron microscopy was performed on a Zeiss EM 912 Ω instrument at an acceleration voltage of 120 kV (Fig. 1(b)). Although the particles are agglomerated to some extent, their average diameter can be determined as about 15 nm, which is in good consistency with the data calculated from XRD.

In order to evaluate the formation mechanism, the obtained reaction solutions were filtered to remove any remaining particles and then subjected to ¹H and ¹³C{¹H} liquid-state NMR to investigate the side products of the reactions. It turned out that the composition was generally rather complex. Below, the acetone system is discussed as a model. Aside from acetone and isopropyl alcohol, several aldol condensation products of acetone are found, mainly mesityl oxide (4-methyl-3-penten-2-one) and mesitylene (1,3,5-trimethylbenzene), which lead to the yellow colour of the solution. From ¹H NMR, the molar ratio was calculated to 3.0 isopropyl alcohol:1.0 mesityl oxide:0.07 mesitylene. Based on these side products, we propose the formation mechanism depicted in Scheme 1, which is related to the mechanism for ZnO gel formation described by Goel *et al.*:⁵ first, acetone is coordinated to the titanium centre, and deprotonation leads to the enolate complex under concurrent release of isopropyl alcohol (1). The enol ligand nucleophilically attacks a second acetone molecule to form a C–C bond (2). Analogously to the elimination of water, the ligand reacts with another titanium centre (3) to form a Ti–O–Ti bond, which represents the starting point of nanoparticle formation and crystallisation. Isopropyl alcohol and mesityl oxide are released (4). Further condensation of mesityl oxide leads to phorone and mesitylene which are, however, only found in small quantities. The higher *i*PrOH to mesityl oxide ratio found (3:1

† Electronic supplementary information (ESI) available: Experimental details, TEM images, NMR and TGA data. See <http://www.rsc.org/suppdata/cc/b4/b414510k/>

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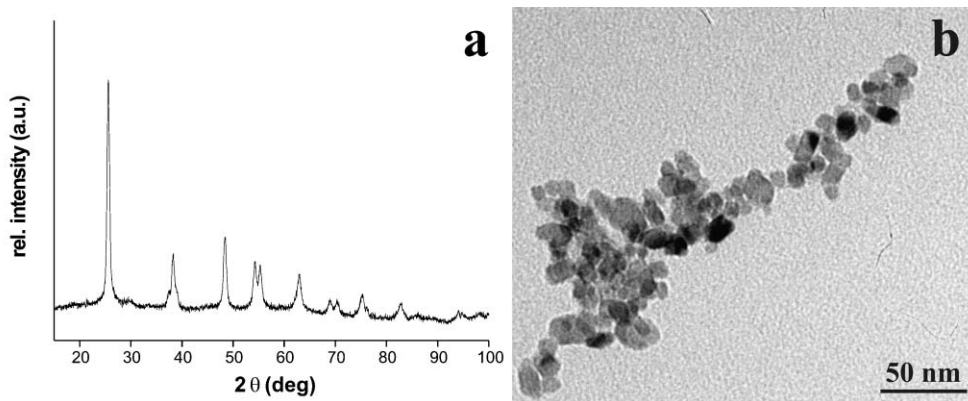
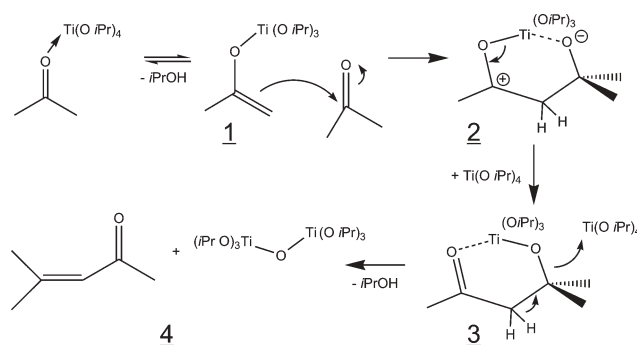


Fig. 1 Analysis of the as-prepared powder obtained from the acetone-Ti(O*i*Pr)₄ system: (a) XRD diffraction pattern, (b) TEM image.

Table 1 Features and results of the investigated systems

Solvent	Reaction conditions	Yield (%)	Size ^a /nm	Oxide cont. (%)
Acetone	1 d, 130 °C	90	15.2	91.4
2-Butanone	1 d, 180 °C	80	20.3	97.2
3-Pentanone	1 d, 180 °C	79	20.3	97.6
Cyclohexanone	3 d, 200 °C	84	15.1	96.2
Acetophenone	3 d, 200 °C	85	10.8	92.9
Benzophenone	3 d, 200 °C	48	7.0	92.3
Butyraldehyde	3 d, 200 °C	90	10.5	94.6
Benzaldehyde	1 d, 200 °C	100	6.9	88.9

^a As calculated from the (101) reflections using Scherrer's equation.



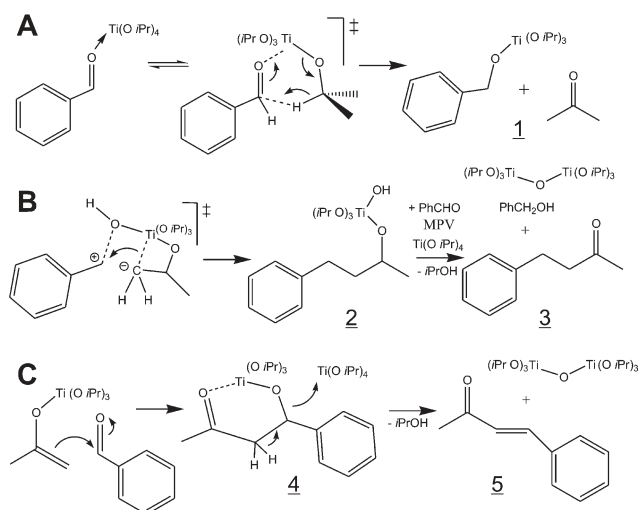
Scheme 1 Proposed formation mechanism of TiO₂ in acetone.

instead of 2:1) is explained by adsorption of acetone condensation products on the titania surface.

For higher ketones, to a great extent a Meerwein-Ponndorf-Verley (MPV) reaction takes place, similar to a side reaction observed in the formation of BaTiO₃ in benzyl alcohol⁹ and in cyclohexanone.⁶ This reaction does not contribute to the formation of the oxide itself, but constitutes a redox reaction between the solvent and the ligand. For the systems discussed here, the ketone is reduced by the isopropoxide to form the corresponding alkoxide ligand and acetone. Now both acetone and the higher ketone are present and can undergo condensation, resulting in a complex mixture of ketone condensation products. In all cases, the alcohol formed by reduction of the ketone was found in quite high amounts, confirming the occurrence of an MPV reaction. For the 2-butanone and 3-pentanone systems, we

found a complex mixture of condensation products, whereas for cyclohexanone, 2-(1-cyclohexenyl)cyclohexanone was identified among condensation products with acetone. This side-path even allows the synthesis within benzophenone, which does not possess any α -H atoms, necessary for direct condensation between two ketone molecules. The obtained NMR spectra suggest the presence of 4,4-diphenyl-3-buten-2-one, which is the condensation product of acetone with benzophenone. The presence of both benzhydrol (diphenylmethanol) and acetone supports our assumption that first benzophenone undergoes MPV reduction to benzhydrol. This leads to the release of acetone, which next condensates with another benzophenone and thus provides the formal oxygen needed for titania formation. Due to the steric hindrance of benzophenone, the system shows a lower reactivity, which is expressed in the low yield (*ca.* 50%).

The benzaldehyde system is discussed in detail to illustrate the reaction path when using aldehydes as solvents. ¹³C NMR analysis of the reaction solution showed the presence of benzyl alcohol in addition to the aldehyde. Benzyl benzoate (a disproportionation product of benzaldehyde) was detected in substantial quantities. Interestingly, a significant amount of 4-phenyl-2-butanone was found, but no 4-phenyl-2-butanol, which we have reported to form *via* a C–C coupling reaction from Ti(O*i*Pr)₄ and benzyl alcohol under basic conditions during BaTiO₃ formation.⁹ Therefore, we assume intermediate formation of 4-phenyl-2-butanol which is then oxidised by the aldehyde to form the ketone. The aldol addition product of acetone to benzaldehyde, 4-phenyl-3-buten-2-one, could also be identified. A number of smaller peaks in the NMR spectrum are attributed to higher condensation products of the aldehyde. Therefore, a more complicated reaction sequence leading to the formation of TiO₂ is proposed as illustrated in Scheme 2: First (A), an MPV-like reaction of benzaldehyde with Ti(O*i*Pr)₄ leads to acetone and benzyl alcohol (1). Then, there are two possible routes: the alcohol can react (B) with another isopropoxy ligand *via* the aforementioned C–C coupling reaction (2). Due to the surplus of benzaldehyde as oxidising agent, the resulting 4-phenyl-2-butanol is readily oxidised to 4-phenyl-2-butanone (3). For the second pathway (C), aldol addition of acetone to the aldehyde (4, 5) is proposed. In the case of benzaldehyde, route B is favoured as the intermediate carbocation is stabilised (product ratio of route B to C found is 2.2), whilst it does not take place in butyraldehyde. Thus, aldol coupling



Scheme 2 Proposed pathways leading to the formation of anatase in benzaldehyde.

reactions (route C) are the probable pathway to TiO_2 formation in aliphatic aldehydes.

These results clearly prove that the nonaqueous sol–gel synthesis of nanoparticles can be extended to oxygen-containing organic solvents other than alcohols or ethers, and proceeds *via* a variety of reactions providing the oxygen to form Ti–O–Ti bridges. The resulting materials show high crystallinity even though the

synthesis is performed at low temperatures. The high concentration of the TiO_2 precursor in the reaction system and the excellent yields are promising aspects with respect to practical applications. Moreover, the approach described here is understood as a potential model system for the synthesis of other binary and ternary metal oxides.

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