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Communications

Mesostructured Silica–Titania Mixed Oxide Thin Films

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The synthesis of porous silica–titania mixed metal oxides is still a challenging task, despite the many industrial applications of the material, for example, in the oxidation of various organic molecules.¹ Not only good accessibility, high dispersion, and homogeneous distribution combined with a high loading of titanium species is required, but also for many applications a deliberate design of porosity is necessary. Moreover, the processing in a controlled morphology is a prerequisite because not only powders but also porous silica–titania *thin films* are of special interest, for example, for sensor applications. Synthetic procedures that have been applied in the synthesis of mesoporous silica–titania mixed metal oxide powders, such as hydrothermal Si/Ti coprecipitation or postsynthetic grafting, are not viable for the preparation of thin films.^{2–8}

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There are several publications on porous but non ordered silica–titania mixed metal oxide films,^{9–13} several on mesostructured porous silica films,^{14–16} and a few on mesostructured porous titania films.^{17–19} However, only very recently the preparation of a *mesostructured porous silica–titania mixed metal oxide film* with a Si/Ti ratio of 50:1 has been reported by Ogawa et al.²⁰ This study extends the publication by Ogawa et

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al.²⁰ by using a novel approach which allows the preparation of well-ordered mesostructured silica–titania mixed metal oxide films with a high titanium loading of up to a Si:Ti ratio of 5:1 and a good dispersion of the titanium atoms in the silica pore wall.

The underlying principle is based on an evaporation-induced self-assembly of a modified amphiphile in combination with simultaneous sol–gel processing of the inorganic species. Typically, the sol–gel process allows precise control of the chemical composition, the crystallinity, and the texture of the final material. However, an important problem associated with it is the unequal hydrolysis rate of the metal alkoxide precursors. For example, titanium tetraisopropoxide ($Ti(O^{\prime}Pr)_4$) is well-known to hydrolyze faster than silicon alkoxides.²¹ Previous experiments in our laboratory have shown that the addition of titanium alkoxides to a sol which is designed for the formation of well-structured silica films¹⁴ resulted in an instantaneous precipitation of titanium oxide.

For good control over the morphology of the resulting materials, it is necessary to slow the hydrolysis rate of the transition metal alkoxide. A typical method is the coordination of the reactive titanium species by a bidentate ligand, which occupies potential reaction sites. In the present study, we used the hydrophilic headgroup of a surfactant molecule for coordination to the titanium alkoxide. The thus-modified surfactant serves two essential functions: it acts both (a) as a structure-directing agent and (b) as a coordinating ligand to lower the reactivity of the titanium alkoxide. A related approach has been reported in the literature as ligand-assisted templating (LAT) for the preparation of purely non-silicate mesostructured materials by using amine- or phosphate-based surfactants.²² However, so far this procedure was not applied toward the synthesis of mixed metal oxide systems.

In this work, oligo(ethylene oxide) alkyl ether surfactants (Brij56 [$C_{16}H_{33}(OCH_2CH_2)_{10}OH$]/Brij92 [$C_{18}H_{35}(OCH_2CH_2)_2OH$]) were employed, which contain ethylene oxide moieties as hydrophilic headgroups. Scheme 1 gives an example of how the titanium alkoxide could be coordinated to these groups.²³

Two types of interactions can be envisioned: trans-alkoholysis of the OH unit of the surfactant and the alkoxides in $Ti(O^{\prime}Pr)_4$ and possibly also a chelating coordination of the titanium by the poly(ethylene oxide) units.²⁴ The structure of the product complex could not be elucidated; however, the addition of this modified template molecule (Ti–Brij56 complex) resulted in a stable sol in which no precipitation of titanium oxide species was observed.²⁵

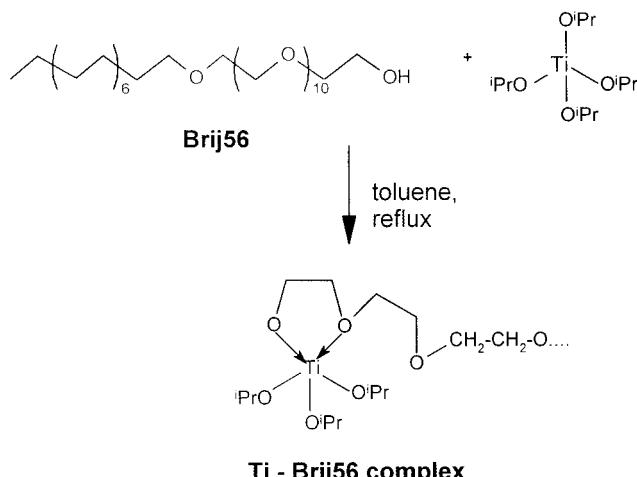
From this stable sol, thin films were deposited by dip coating²⁵ and after calcination at 450 °C for 3 h,

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(23) Synthesis: Brij56 [$C_{16}H_{33}(OCH_2CH_2)_{10}OH$] was dried by azeotropic distillation with toluene. $Ti(O^{\prime}Pr)_4$ and Brij56 were mixed in a molar ratio of 1:1 in toluene and refluxed overnight. Distillation to remove 2-propanol and toluene yielded the titanium isopropoxide modified Brij56 surfactant (Ti–Brij56 complex) as an orange paste. All syntheses were carried out under an argon atmosphere.

Scheme 1



transparent, crack-free, and optically uniform silica–titania films with a thickness of 200–250 nm were obtained.

Variation of the amount of the structure-directing molecule (Ti–Brij56) in the sol solution had two consequences for the final film: (a) the liquid-crystalline phases formed from the Ti–Brij56 surfactant were concentration-dependent and (b) the Si/Ti ratio in the film was determined by the amount of the Ti–Brij complex in the starting solution. For example, the addition of 5 wt % of Ti–Brij56 to the prehydrolyzed silica sol led to a Si/Ti ratio of 15. In the described experiments the Si/Ti ratio was varied from 74 to 5.

With respect to later applications, the nature and coordination of the Ti species in the silica–titania film is very important. UV spectroscopic investigations of calcined films showed only one single intense band at 205 nm, characteristic for titanium atoms in a tetrahedral coordination. No band at 330 nm of octahedral extraframework titanium was observed.²⁶ The absence of these species suggests that the titanium phase is well-dispersed within the silica pore wall of the material and no aggregation of the titanium species to larger clusters occurred. This result was supported by FT-IR investigations in which an absorption band at 950 cm^{-1} was observed, which can be attributed to $\nu(\text{Si}—\text{O}—\text{Ti})$ or $\nu(\text{Si}—[\text{OH}])$ vibrations. This absorption band was retained even after heating to 800 °C, which is a clear indication for Si–O–Ti bonds.

Thus, the coordination of the metal to the surfactant headgroup is obviously favorable for several reasons. The mobility and reactivity of the titanium alkoxides is strongly hindered and aggregation of the hydrolyzed species to titanium oxide particles does not occur. In

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(25) Precursor solutions were prepared by mixing tetraethoxysilane (TEOS), ethanol, H_2O , and hydrochloric acid in a molar ratio of 1:20:4:0.004. To 5 g of this sol solution the Ti–Brij complex was added (1–20 wt %) and the mixture was stirred until a homogeneous solution was obtained. Silicon wafers were cleaned with toluene and ethanol prior to dip coating, which was performed in a controlled atmosphere at a withdrawal speed of 4 mm s^{-1} . The coatings were calcined at different temperatures in air, typically for 3 h.

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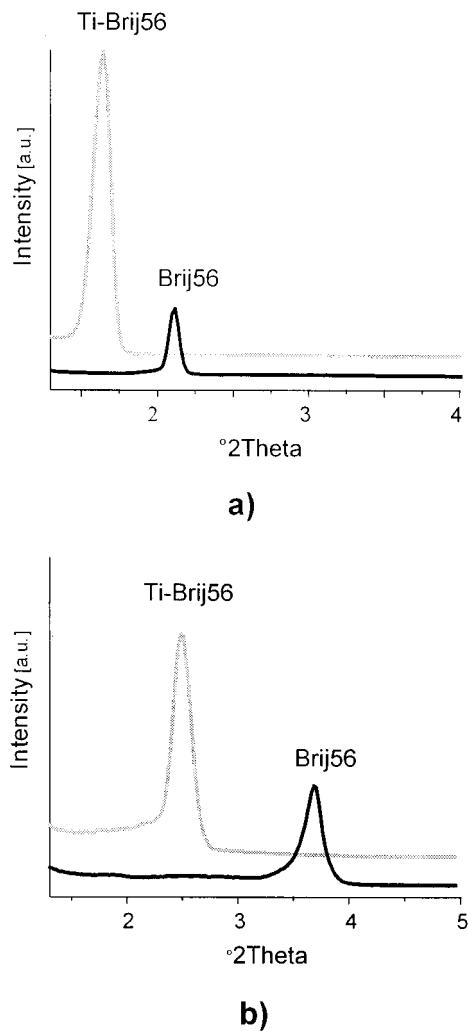


Figure 1. Low-angle XRD (LAXRD) pattern of (a) as-synthesized films from Brij56 and Ti-Brij56 (5 wt %) and (b) calcined films from Brij56 and Ti-Brij56 (5 wt %).

addition, the titanium is efficiently positioned at the surfactant–silica interface at which the final inorganic network formation occurs, leading to well-dispersed titanium oxide in the silica pore wall.

The lyotropic liquid-crystalline (LLC) properties and the resulting phase diagrams of the oligo(ethylene oxide) surfactants are crucial for the formation of the inorganic mesostructures. An important question was whether these properties are strongly influenced by the coordination of the titanium alkoxide to the amphiphile and whether self-assembly is thus hindered to some extent. This was determined indirectly by X-ray diffraction and transmission electron microscopy of the final film. The Ti-Brij templated material was compared to films templated with the pure Brij surfactant. The low-angle X-ray diffraction (LAXRD) patterns for samples modified with 5 wt % of either template are shown in Figure 1. Both as-synthesized samples exhibit one strong low-angle reflection at $d = 41.7$ and 53.1 \AA , indicating a high degree of ordering. The larger repeating unit distance for the titanium-modified sample can be explained by (a) the different amounts of surfactant (the titanium-modified surfactant has a higher molar mass; therefore, a lower molar concentration is present in the coating mixture) and (b) the different polarity of the modified surfactant headgroup, resulting in a different interac-

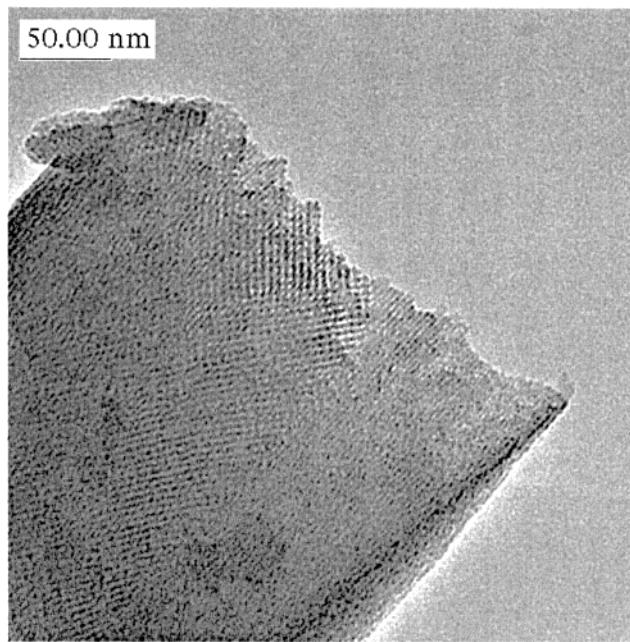


Figure 2. TEM image of a Ti-Brij56 (5 wt %) film deposited on a silicon substrate, calcined at 450°C for 3 h.

tion with the aqueous environment. After calcination at 450°C for 3 h, porous thin films were obtained, which still showed reflections in the LAXRD at $d = 23.84$ and 35.18 \AA for Brij56 and Ti-Brij56 templated films, respectively, still indicating long-range ordering. The decrease in d spacing, that is, from 53.13 to 35.18 \AA , is due to a contraction of the structure often observed after removal of the surfactant and further condensation of the network.

Figure 2 shows the transmission electron micrograph of a calcined Ti-Brij56 film. The image confirms the well-defined mesoporous character of the film. The mesopore center-to-center distance was estimated to be 3.5 nm , which is consistent with the long-range order parameter obtained from the LAXRD pattern.

Knowledge of the stability of the materials at higher temperature is important with respect to later applications. X-ray diffraction studies were carried out at different temperatures to determine the crystallization temperature of the TiO_2 phases. The X-ray diffraction patterns of thin films of Ti-Brij56 (Figure 3) showed no reflections at temperatures below 450°C , indicating a homogeneous distribution of the titanium species in an amorphous structure. After 3 h at 450°C two small reflections at $2\theta = 25.1^\circ$ and 47.1° appeared in the pattern which were assigned to anatase (d_{101} and d_{200}). With increasing temperature the anatase reflections became more prominent, and above 800°C a transformation from anatase to rutile was visible by the appearance of a new reflection assigned to the (d_{110}) reflection of rutile at $2\theta = 27.4^\circ$. Above 900°C only the rutile phase was observed.

In conclusion, we have demonstrated a novel, rapid, and continuous process for the formation of mesoporous silica–titania mixed metal oxide thin films utilizing the self-assembly behavior of new metal-coordinated surfactant molecules and simultaneous sol–gel processing. This novel combination of well-known processes such as (a) the complexation of transition metal alkoxides by multidentate ligands to slow their reactivity and (b)

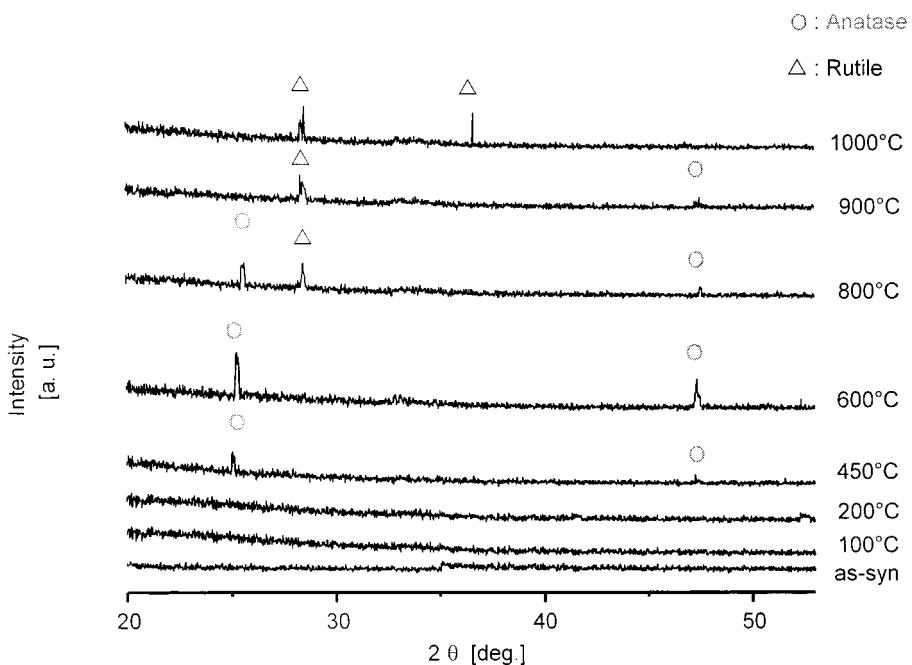


Figure 3. X-ray diffraction patterns of thin Ti-Brij56 (5 wt %) films after heat treatment at different temperatures.

the use of surfactants to tailor the porosity of mesostructured materials is a universal approach and opens the way to a variety of mesostructured mixed metal oxides.

The tailored design of the titanium-coordinated surfactant and its application in an evaporation-induced self-assembly process enabled the preparation of mesostructured films with a high loading and good dispersion of tetrahedral titanium atoms within the silica matrix. Only upon heat treatment to temperatures above 450 °C

the amorphous titania phase converts to anatase and later on (800 °C) to rutile.

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