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NOTE

Homogeneity of Titania-Silica Mixed Oxides: On UV-DRS Studies as a Function of Titania Content

The extraordinary catalytic activity and selectivity of Ti-containing crystalline and amorphous silicates for oxidation reactions with peroxides is attributed to isolated tetrahedral Ti sites in the silica framework (1). Diffuse reflectance UV-VIS spectroscopy (DRS) is commonly used to establish the presence of isolated Ti-sites. The charge transfer (CT) transitions between the oxide ions and the empty d-orbital of Ti^{4+} are strongly shifted from 26,000 cm^{-1} in anatase towards higher wavenumbers with decreasing Ti-content (2). In two recent publications (3, 4) a new class of mesoporous silica-titania aerogels has been described, where the presence of highly dispersed titania in silica matrixes is emphasized. The authors attempted to balance the hydrolysis and condensation tendencies of the precursors and favour the use of the highly reactive tetramethoxysilane, together with acetylacetonate modified, chelated titanium tetraisopropoxide, in order to optimize the molecular mixing of the constituents. The materials were prepared from alkoxides by a sol-gel procedure. A rather monomodal mesoporosity is obtained by semicontinuous extraction with supercritical CO_2. The catalytic potential of these materials in the alkylhydroperoxide mediated epoxidation of olefins is attributed to the high titania dispersion in the silica matrix. These materials are not only important extensions of the available selective oxidation catalysts, but their spectroscopic behaviour is an important contribution to our fundamental understanding of site-isolated Ti-silicates.

DRS UV-VIS spectroscopy has been applied to verify the high chemical homogeneity of the aerogels (3, 4). Materials containing 3.8, 7.7, and 15.8 wt% titania, respectively, show absorption edges between those of anatase (28,000 cm^{-1}) and TS-1 (titanosilicalite with MFI-structure, 34,000 cm^{-1}) (5). This fact is interpreted as the indication for an almost complete titania dispersion with only small concentrations of titania nanodomains in the materials, a confirmation of the other spectroscopic conclusions, and catalytic experiments mentioned (3, 4). A shift of the absorption maximum towards higher wavenumbers on *in situ* drying of the samples is reported but not shown. The authors conclude that an almost perfect elemental homogeneity was achieved in their materials due to the applied preparation.

UV-VIS spectroscopy, a powerful method for the characterization of titania-containing mixed oxides such as titania-silica gels (6) or titanium silicalites (7) is one of the well-accepted means to confirm the homogeneous, isomorphous lattice incorporation of tetrahedral Ti-ions in zeolites and related materials (8, 9). Small amounts of Ti^{4+} in a silicalite network result in UV-absorption maxima in the region of 45,000 to 48,000 cm^{-1}, which had been attributed to the CT-bands of tetrahedral Ti(IV) (8, 10). Following the literature (8, 11), the position of the band can be estimated as

$$\bar{\nu}\ (\mathrm{cm}^{-1}) = 30{,}000\,[\chi_{\mathrm{opt}}(\mathrm{X}) - \chi_{\mathrm{opt}}(\mathrm{Ti})],$$

where $\chi_{\mathrm{opt}}(\mathrm{X})$ is the optical density of a group X (OH^- or O^{2-}) in the coordination sphere of Ti(IV) = 3.45 and $\chi_{\mathrm{opt}}(\mathrm{Ti})$ is the optical density of tetrahedrally coordinated Ti(IV) (1.85). Therefore, the band maximum of the tetrahedral Ti(IV) species is estimated to appear at 48,000 cm^{-1}. In the presence of water, the tetrahedral coordination can be transferred into the octahedral one by the insertion of two additional water ligands, resulting in a shift of $\chi_{\mathrm{opt}}(\mathrm{Ti})$ to a value of 2.05, which alters the position of the corresponding CT-band to 42,000 cm^{-1} (8). This has also been documented Liu and Davis, who recognized a significant shift to higher wavenumbers upon dehydration of a Ti/Si 1 : 8 sample (6). A broad band between 28,000 and 33,000 cm^{-1} has been assigned to extra framework titania (anatase) (12) with a lower detection level of 0.03 wt% including nanoparticles (13).

In our studies of amorphous microporous mixed oxides (14) we have obtained access to amorphous titania–silica mixed oxides (denoted as AMM-Ti_xSi, x = mol% of titania in the mixture), which cover for the first time the UV-VIS DRS to 50,000 cm^{-1} for the full range of composition ($0 < x < 100$) after two different pretreatment procedures. All materials are X-ray amorphous and show a maximum in the pore size distribution at about 0.8 nm and a total surface area of 200–300 m^2/g. No indication of anatase formation is obtained by XRD, HRTEM, and selected area EDX (15), or UV. The results of our UV-VIS-DRS studies indicate various shortcomings in the spectral range used and in the interpretation of the related studies in the past.

UV-VIS-DRS spectroscopy was carried out on a Varian Cary 05 UV-VIS-NIR-spectrometer in diffuse reflectance (DR) technique in the range of 12,500 to 50,000 cm^{-1} (scan

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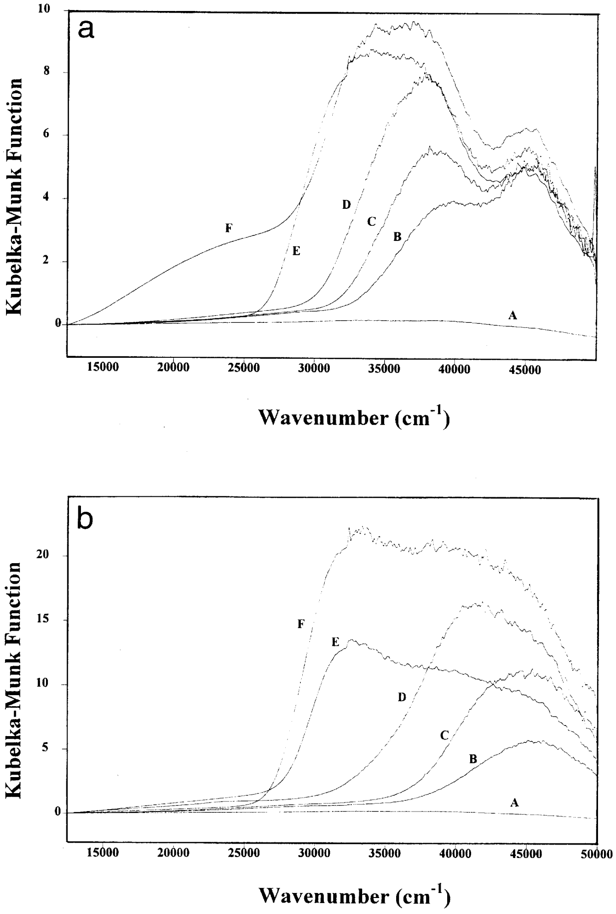

FIG. 1. UV-DRS spectra of amorphous microporous mixed Ti–Si oxides AMM-Ti$_x$Si under (a) ambient and (b) dry conditions: AMM-Si (A), AMM-Ti$_1$Si (B), AMM-Ti$_{4.8}$Si (C), AMM-Ti$_9$Si (D), AMM-Ti$_{50}$Si (E), and AMM-Ti (F).

rate 25,000 cm^{-1}/min) on particles <100 μm. The DR-spectra were recorded using a "Halon"-type white sphere reference standard, which is superior to barium sulfate or magnesium oxide coated spheres and allows measurements at wavelengths down to 210 mm (47,600 cm^{-1}). Previous work by others have used less appropriate cavities and the spectra in the 40,000–50,000 cm^{-1} region are very noisy (7). Our resulting spectra were recorded under ambient as well as under dry conditions using a quartz cell which allows heat treatment (12–15 h at 573 K in a flow of N$_2$) and measurements in a moisture-free atmosphere. The Kubelka–Munk function was used to display the data. The spectra of the AMM-Ti$_x$Si samples (calcined at 523 K subsequent to gelation) under ambient conditions are displayed in Fig. 1a, while Fig. 1b gives the corresponding spectra for the same samples measured *in situ* under moisture-free conditions after removal of water.

The samples measured in the absence of moisture after removal of water show a monomodal DR-spectrum (Fig. 1b, B–D). These samples exhibit mainly the absorption characteristics of isolated, tetrahedral Ti(IV) species in a silica matrix (absorption at 45,000 cm^{-1}). Apparently in the materials with the Ti-contents from 0 to 9 mol%, isolated titania tetrahedra dominate the Ti distribution. In the AMM-Ti$_{50}$ Si and AMM-Ti samples (Fig. 1b, E and F), the main absorption is shifted significantly to lower wavenumbers, consistent with the so-called *quantum size effect* due to the increasing contributions of Ti–O–Ti bonding (15).

In their as-synthesized, partly hydrated state, all AMM-TiSi samples exhibit a bimodal DRS-signal (Fig. 1a, B–E). Due to the coordination of water (or alcohol/residual alkoxide), part of the Ti(IV) is transferred into a coordination higher than tetrahedral (absorption at 35,000 to 40,000 cm^{-1}), while the rest of the Ti(IV) centers are still in tetrahedral coordination (approx. 45,000 cm^{-1}), consistent with the results reported for titanium silicalites. The lower the titania content, the lower the intensity of the low wavenumber component of the spectrum. The as-synthesized hydrated microporous amorphous pure titania (AMM-Ti) reveals an absorption edge around 28,000 cm^{-1} (Fig. 1a, F), similar to anatase (4). The additional band at 23,000 cm^{-1} of the AMM-Ti in Fig. 1a, F, disappears in the waterfree sample (Fig. 1b, F) and is therefore irrelevant for this study. Pure silica prepared and tested under comparable conditions does not show any absorption at all (Figs. 1a and 1b, A).

According to these DRS-results, isolated Ti(IV) sites in the silica matrix are dominant in the overall Ti-population up to ca 9 mol% of Ti. The tendency for the formation of octahedral sites through hydration seems to correlate with Ti-content of the materials, i.e., the increasing presence of Ti–O–Ti bonds. It may be significant that a large portion of the tetrahedral sites associated with the band at 45,000 cm^{-1} does not appear to interact with the moisture. However, no attempt was made to saturate all sites with water; the spectra show the UV-absorption at ambient conditions. Based on the above spectral data, the spectral region from 40,000–50,000 cm^{-1} in UV-VIS-studies of Ti-silicates or silicalites is as important or may be more important than the commonly presented region from 15,000 to 40,000 cm^{-1}. The dependence of the position of the CT-band between 30,000 and 40,000 cm^{-1} on the moisture content of the sample documented in Fig. 1 suggests that assignments about the nature of the Ti-incorporation on this basis alone are not reliable. We propose that characterization of such materials should be based on DR-spectra of moisture-containing and moisture-free samples. Essential is the investigation of the maximum at 45,000 cm^{-1} which, due to the nature of the detector, may not be accessible by most UV-spectrometers.

The high homogeneity of the AMM glasses is consistent with microstructural DRIFT-examinations and high resolution transmisson electron microscopy combined with X-ray microanalysis (HRTEM/EDX). Further results on the material characterization and catalytic performance of

AMM-Ti$_x$Si catalysts are presented along with detailed preparation conditions (16). Our results also show that high homogeneity of titania dispersion can be obtained at highly acidic sol-gel conditions with unmodified tetraethoxysilane and titanium-tetraisopropoxide without the involvement of more complicated sol-gel techniques like chelation, prehydrolysis, or balance of hydrolysis tendency.

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