XANES measurements on Sol-Gel TiO_2-SiO_2 Epoxidation Catalysts

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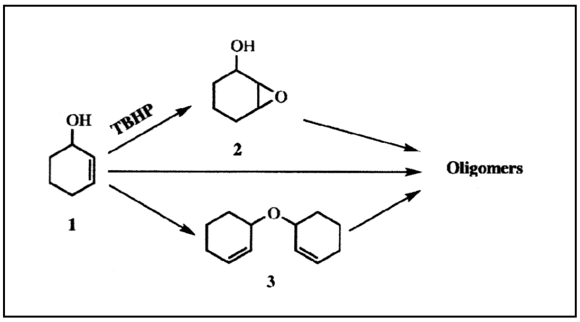
Heterogeneous catalytic epoxidation of functionalized olefines in the liquid phase can be catalyzed by supported and mixed oxides, framework-substituted molecular sieves/zeolites, layered-type materials, and heterogenized homogeneous catalysts [1,2]. One of the applications is the epoxidation of allylic alcohols by tert-butylhydroperoxide on Ti-based catalysts [3]. Recently, we have studied the epoxidation of 2-cyclohexene-1-ol over TiO_2-SiO_2 based aerogels (cf. scheme, [3]). The activity of aerogels, characterized by the epoxide formation (2) in the first 60 min, was highest at low Ti contents (Table 1, [3]). One of the approaches to correlate catalytic activity and the structure is the characterization of the titanium species present on the surface. Apart from UV-vis, DRIFTS, NMR, and XPS, X-ray absorption near edge structure at the Ti K-edge is a useful technique to identify the structure (symmetry, coordination number, oxidation state) of Ti in the solid matrix. Several XANES studies have been reported on Ti based materials and catalysts (e.g. TS-1 [4,5], xerogels [6], and minerals [7,8]) and in the present study we have used this technique to gain additional information to the previous characterization with UV-vis, DRIFTS, and XPS.



Experimental:

The XANES measurements were performed at station E4 (HASYLAB, DESY). The synchrotron radiation was monochromatized by two Si(111) crystals. Ca. 40 mg of the samples were pressed to self-supporting wafers and placed in a vacuum cell (~10^{-4} Pa). An overview on the samples is given in Table 1 and the 20% TiO_2-SiO_2 sample was diluted 1:4 with polyethylene. The spectra were recorded in transmission mode around the Ti K-edge (4920 – 5200 eV). Since the Ti K-edge spectra were interpreted based on the accurate calibration in energy scale, a Ti foil was placed after the transmission chamber as reference and measured simultaneously with a third ionization chamber. The obtained raw data were energy-calibrated (Ti K-edge energy of Ti foil: 4966 eV, first inflection point), background corrected (Victoreen fit), and normalized. X-ray photoelectron spectra (XPS) were obtained using a Leybold LHS 11 instrument (cf. [3,9]) and diffuse reflectance infrared Fourier transform spectra (DRIFTS) on a Perkin-Elmer series 2000 instrument (cf. [3]). Epoxidation reactions were carried in a batch reactor at 363 K.

Table 1: Investigated catalysts, turnover frequencies (TOF) in the epoxidation reaction, binding energies from XPS (Ti $3p_{3/2}$), pre-edge intensity and edge energy from XANES at the Ti K-edge

Catalyst	Ti/Si bulk ratio (wt%/wt%)	TOF (s^{-1})	BE (Δ BE)[a] by XPS [eV]	Pre-edge intensity [a.u.]	Edge-Energy [eV]
TS-1	1:41.6	-	460.3 (1.8)	0.84	4969.9
Ae-1	1:132	0.40	459.9 (1.4)	0.58	4970.0
Ae-2.5	1:54	0.16	460.0 (1.5)	0.62	4970.0
Ae-20	1:5.3	0.02	459.1 (0.6)	0.38	4970.1

[a] Δ BE (in parentheses) corresponds to the increase of the binding energy with respect to TiO_2

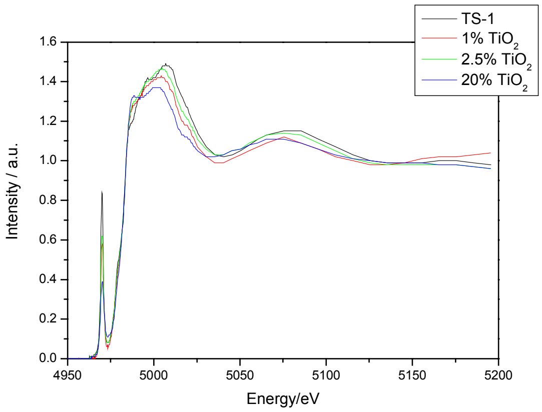


Figure 1: Overview on the XANES spectra at the Ti K-edge

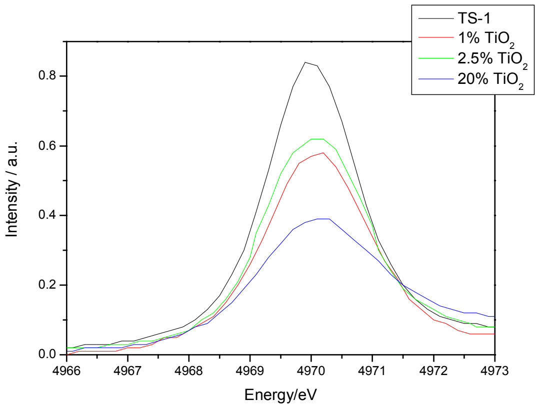


Figure 2: Pre-edge peaks at the Ti K-edge showing that the intensity is TS1>Ae-2.5 ≈Ae-1>Ae-20

Results:

The results from the XANES measurements on 1.0wt%, 2.5wt%, and 20wt% TiO_2-SiO_2 aerogels as well as a TS-1 sample are shown in Table 1 and Figs. 1 and 2. The turnover frequency (TOF, Table 1) decreases according to Ae-1 > Ae-2.5 > Ae-20. The highest intensity for the pre-edge was measured for the reference sample TS-1. The high pre-edge intensity of about 0.84 indicates that Ti^{4+} has tetrahedral coordination and is in accordance with literature [4]. Previous work (e.g. [7, 8] has demonstrated that the pre-edge peak which occurs at the Ti K-edge gives information about Ti coordination. The pre-edge peak occurs due to p-d mixing and the dominant pre-edge peak is assigned to T_{2g} states. Its intensity decreases, and energy raises as the degree of centrosymmetry increases. The pre-edge peak intensities of the Ti-aerogels develop according to Ae-1 ≤ Ae-2.5 >> Ae-20. Hence, a high amount of tetrahedral species is present in the low loaded samples, but a significant amount of octahedral species in the 20% TiO_2 sample. For Ti in octahedral coordination the pre-edge peak intensity is principally very small but can increase to 0.2 – 0.3 if the octahedra are distorted [6]. The results are in agreement with those from XPS which also indicate that the number of octahedrally coordinated species is much higher in the 20 wt% TiO_2-SiO_2 aerogel. The intensity of the pre-edge peak in the low loaded Ti-aerogels is, however, significantly lower than for the TS-1 reference. Though the loading is relatively low and one would expect Ti in tetrahedral coordination, adsorption of water can partly lead to octahedral Ti species on the surface and thus lead to smaller pre-edge intensities than in TS-1, which has a relatively hydrophobic surface. The difference in hydrophilicity can also explain the slightly lower pre-edge peak intensity in Ae-1 compared to Ae-2.5. Recent DRIFTS measurements have, indeed, shown that the prepared aerogels are hydrophilic, which can be circumvented by silylation [3]. Thus *in situ* dehydration studies combined with XANES can give more information both on the hydrophilicity of the samples and the number of species in tetrahedral coordination after drying. In addition, these studies can reveal, if and to which extent nanodomains of octahedrally coordinated Ti species are also present on Ae-1 and Ae-2.5.

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