

Structural investigation of the formation of organically surface-modified metal oxo clusters by EXAFS spectroscopy

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In recent years the formation of inorganic-organic hybrid materials, in particular nanocomposites, attracted much interest. For the formation of these materials the sol-gel process is often used due to its solvent-based mild conditions. Contrary to the well controllable conditions of the silicon-based sol-gel process, transition metal alkoxides require a reduction of their reactivity to avoid immediate precipitation of the metal oxide after water addition. For this purpose, carboxylic acids that coordinate to the metal as bidentate ligands and thus reduce the reactivity of the precursor are added. Furthermore, the addition of carboxylic acids to metal alkoxides may also produce in situ well-defined surface-modified crystalline metal oxo clusters of the general formula $M_wO_x(OR)_y(OOC-FG)_z$ (FG = functional group). A three step mechanism was proposed for the formation of the clusters: (i) the partial substitution of alkoxide groups at the metal by carboxylic acids; (ii) the formation of an ester by the reaction of free carboxylic acid and the released alcohol and hence the controlled production of water; and (iii) the condensation of partially substituted building blocks in solution. The confirmation of this proposed reaction scheme by a single analytical technique is difficult because conventional spectroscopic methods do not allow a reliable insight into the reactions that take place in the solution. Hence, to prove the reaction mechanism and to get information on the rate of the cluster formation in solution a variety of different analytical methods has to be applied simultaneously. In this report we present the data obtained by EXAFS-spectroscopy.

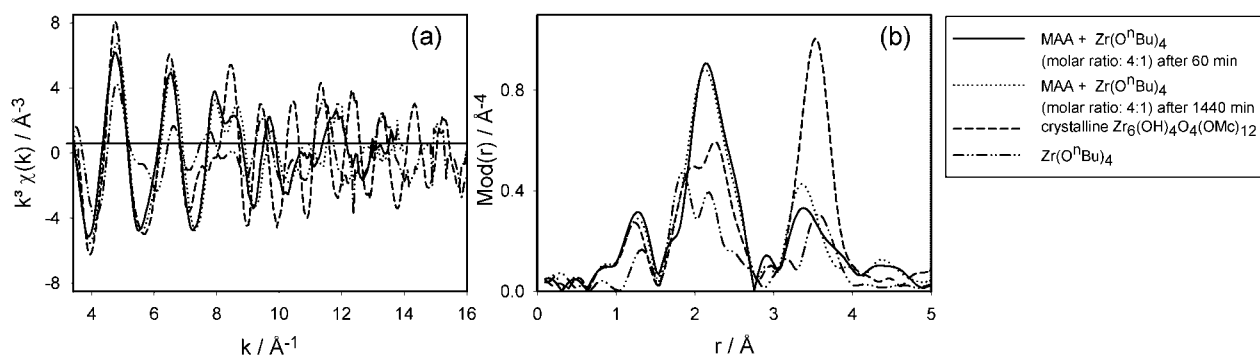


Figure 1: Experimental $k^3\chi(k)$ functions (a) and their Fourier transforms (b) of a mixture of MAA and 80 wt% $Zr(O^iBu)_4$ in n-butanol (molar ratio: 4:1) from the start of the reaction to 1440 min reaction time at the Zr K-edge.

The $Zr_6(OH)_4O_4(OMc)_{12}$ cluster crystallizes quantitatively from a mixture of 80 wt% $Zr(O^iBu)_4$ in n-butanol and 4 molar equivalents of methacrylic acid (MAA) after a few days. In the EXAFS investigation, a 80 wt% n-butanol solution of $Zr(O^iBu)_4$ was first measured as a standard, and then MAA was added. The data for the precursor $Zr(O^iBu)_4$ in n-butanol were in agreement with the results of a previous EXAFS analysis on metal alkoxides in solution.[2] The zirconium atoms have three clearly distinguishable oxygen shells with mean Zr-O distances of 1.97 Å (coordination number $N = 2$), 2.16 Å ($N = 2$), and 2.27 Å ($N = 2$). Two of these oxygen atoms can be assigned to coordinated n-butanol. The Zr backscatterer ($N = 1$) at 3.49 Å proves that $Zr(O^iBu)_4$ has a dimeric structure in solution. 60 minutes after the addition of four equivalents of methacrylic acid, the coordination number of the Zr backscatterer is increased to 1.5, and the mean Zr-Zr distance is shortened to 3.42 Å (Table 1, Figure 1). The three oxygen shells collapsed to one shell with a coordination number of 6.7 and a mean Zr-O distance of 2.22 Å. Additional measurements were carried out

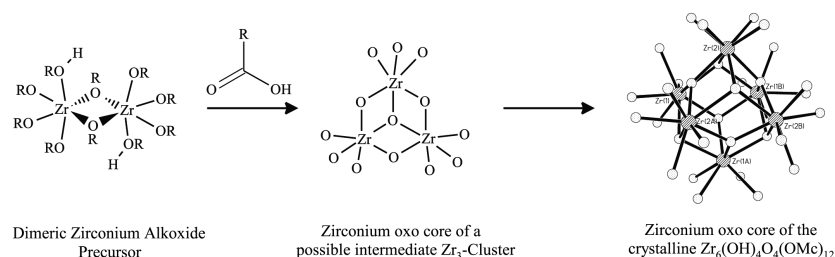
after several time intervals up to 1440 min. The data obtained by these measurements confirm the fast reaction rates between $\text{Zr}(\text{O}^n\text{Bu})_4$ and MAA. During the reaction the average Zr-O distances remained at 2.20 Å and the coordination number of the oxygen atoms continuously increased up to a value of 7.4 ± 0.7 . Both values are, within the standard deviations, similar to those of the crystalline $\text{Zr}_6(\text{OH})_4\text{O}_4(\text{OMc})_{12}$ cluster. This cluster, however, shows two distinguishable oxygen shells whereas the reaction solution has only one shell with a mean Zr-O distance. The Zr-Zr distance of about 3.40 Å is shorter compared to the corresponding value in the crystalline cluster and the Zr coordination number, which is 4 in the resulting cluster, is also much lower, viz. 1.7 ± 0.3 . A possible explanation is the formation of smaller fragments that already have the oxygen coordination of the resulting cluster around the zirconium, but are not condensed to the final octahedral Zr core of the cluster. Bridged trinuclear Zr species, which contain $\mu_3\text{-O}$ or $\mu_3\text{-OR}$ groups capping the face of a Zr_3 triangle (Zr coordination number = 2) are potential intermediates in the cluster formation (Scheme 1). Oxoalkoxides with this structural motif were already characterized by single crystal X-ray crystallography and show Zr-Zr distances of 3.22 Å. In addition also a partly carboxylate-substituted trinuclear Zr compound is known in which longer (3.86 Å) and shorter Zr-Zr distances (3.37 Å, 3.41 Å) were observed depending of the bridging ligands.[1] Condensation of two such trinuclear units could lead to the octahedral cluster.

Table 1: Structural parameters of crystalline $\text{Zr}_6(\text{OH})_4\text{O}_4(\text{OMc})_{12}$ cluster, crystalline $\text{Zr}_7\text{O}_2(\text{OMc})_{12}$ and pure zirconium n-butoxide, determined from the Zr K-edge EXAFS spectrum (Beamline X1, HASYLAB at DESY). Underground correction was performed with AUTOBK 2.61. EXAFS Simulation was done with the EXCURV92 modul of CERIUS².

[a]	A-Bs	r [Å]	N	σ [Å]	ΔE_0 [eV]	k-range [Å ⁻¹] Fit-Index
$\text{Zr}(\text{O}^n\text{Bu})_4$	Zr-O	1.97 ± 0.02	2	0.053 ± 0.010	16.6	3.40 – 17.00 37.2
	Zr-O	2.16 ± 0.02	2	0.050 ± 0.010		
	Zr-O	2.27 ± 0.02	2	0.072 ± 0.010		
	Zr-C	3.07 ± 0.03	2	0.084 ± 0.010		
	Zr-Zr	3.49 ± 0.04	1	0.076 ± 0.010		
MAA + $\text{Zr}(\text{O}^n\text{Bu})_4$ (4:1, t = 60 min)	Zr-O	2.22 ± 0.02	6.7 ± 0.7	0.098 ± 0.010	17.4	3.21 – 13.79 25.6
	Zr-Zr	3.42 ± 0.03	1.5 ± 0.3	0.088 ± 0.017		
MAA + $\text{Zr}(\text{O}^n\text{Bu})_4$ (4:1, t = 1440 min)	Zr-O	2.20 ± 0.02	7.4 ± 0.7	0.102 ± 0.010	18.8	3.27 – 14.00 25.4
	Zr-Zr	3.40 ± 0.03	1.6 ± 0.3	0.082 ± 0.016		
$\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_{12}$ crystalline	Zr-O	2.10 ± 0.02	2	0.065 ± 0.007	20.6	3.51 – 16.00 27.5
	Zr-O	2.24 ± 0.03	6	0.084 ± 0.013		
	Zr-Zr	3.51 ± 0.04	4	0.075 ± 0.022		

[a] absorber (A) – backscatterer (Bs) distance r, coordination number N, Debye-Waller factor σ with its calculated deviation, shift of the energy threshold energy ΔE_0 and the fit-index.

Scheme 1:



References

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