

# Ceramic Powder Processing Science

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# FORMATION AND PROPERTIES OF CHELATED ALUMI-NUMALKOXIDES

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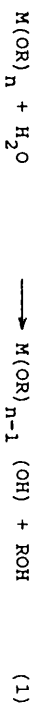
## ABSTRACT

Chelated aluminumalkoxides have been prepared from the reaction of aluminum-secbutoxide with acetylacetone (AcAc) or ethylacetacetate (EAA) in different alkoxide/chelating agent molar ratios. These compounds have been used to study the possibility of controlling the rate of hydrolysis of aluminumalkoxides and/or the polycondensation of the related hydroxides. Hydrolysis was followed by NIR-spectroscopy and showed no differences for chelated aluminum-secbutoxide and the pure alkoxide. In contrast the polycondensation of aluminumhydroxides chelated with ethyl-acetoacetate decreased remarkably and depends on the alkoxide/chelating agent molar ratio. The properties of these aluminum hydroxides have been studied by different methods and a structural model for  $Al(OH)_2EAA$  has been evaluated.

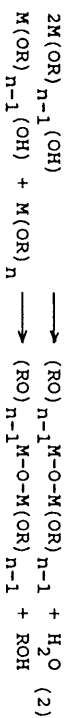
## INTRODUCTION

Sol-gel processing for the preparation of glass, glass ceramics, and ceramics has been studied intensively during the last few years. A survey over the literature shows that most of the elaborated synthesis for these different materials involve the use of molecular precursors, mainly metal alkoxides, as the starting material. The macromolecular, inorganic network is then obtained by hydrolysis and polycondensation, which may be written as follows (eqs. 1 and 2):

### Hydrolysis



### Polycondensation



To a great deal, the properties of the final product depend on the competitive/complementary rates of these two reactions, as it has already been shown for the preparation of silica from alkoxysilanes [1]. For tailoring the properties of the final product a good knowledge of the kinetic of these reactions is necessary as well as the de-

velopment of methods for reaction control. In the present paper we report first results about reaction control for the preparation of alumina by chemical modification of aluminum-secbutoxide with  $\beta$ -dicarbonyl compounds.

#### EXPERIMENTAL

A solution of aluminum-secbutoxide,  $\text{Al}(\text{O}i\text{Bu}^s)_3$  in iso-pro-panol (2 mol/l) has been reacted with acetylacetone (AcAc) or ethylacetoacetate (EAA) in different molar ratios, giving clear solutions. The modified precursor was hydrolysed with stoichiometric quantities of water in relation to the number of hydrolysable  $\text{O}i\text{Bu}^s$ -groups. The experimental procedure is shown in detail in figure 1 and the reaction conditions along with the experimental observations during hydrolysis are summarized in table 1. Clear solutions or sols were studied by FTIR spectroscopy using a circle cell with a ZnSe-crystal and gel-powders were measured using KBr pellets.

Dynamic light scattering experiments were performed with freshly prepared sols (E1, E2) using a Malvern 4700. The chemical composition of the sample E1 was determined by C, H analysis and the aluminum content was determined as  $\alpha\text{-Al}_2\text{O}_3$ .

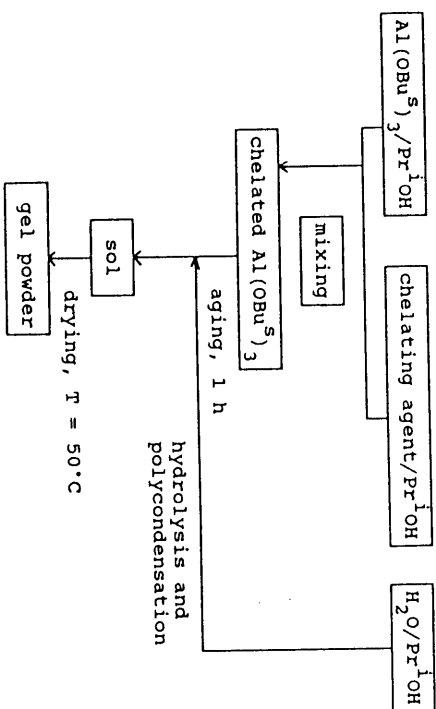


Figure 1: Flow chart for the preparation of chelated aluminumhydroxides

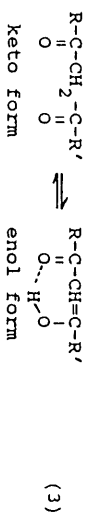
Table 1. Reaction conditions and experimental observations for the preparation of chelated aluminumhydroxides

Sample no.	chelating agent (Fig)	$\text{Al}(\text{O}i\text{Bu}^s)_3/\text{Fig}(\text{O}i\text{Bu}^s)_3/\text{Fig}$	molar ratio $\text{Fig}(\text{O}i\text{Bu}^s)_3/\text{Fig}$	product after hydrolysis
A1	AcAc	1	2	precipitate
A2	AcAc	2	2	precipitate
A3	AcAc	3	2.75	precipitate
E1	EAA	1	2	clear sol.
E2	EAA	2	2.5	clear sol.
E3	EAA	3	2.75	precipitate

#### RESULTS AND DISCUSSION

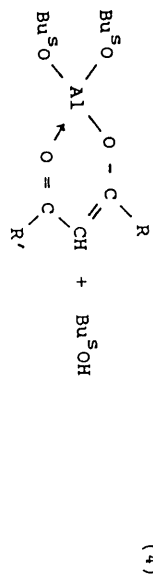
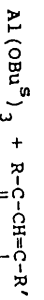
##### Chelation

Acetylacetone and ethylacetoacetate are both  $\beta$ -dicarbonyl compounds and therefore exhibit keto-enol-tautomerism (eq. 3).



R, R':  $\text{CH}_3$  (AcAc)  
 R:  $\text{CH}_3$ , R':  $\text{OC}_2\text{H}_5$  (EAA)

The chelating properties of these compounds are due to the presence of a reactive hydroxyl group in the enol form which reacts like an acid. The amount of present enol strongly depends on the nature of the groups R and R'. In the case of AcAc (R, R':  $\text{CH}_3$ ) according to [2] the enolic content is about 76.4 % whereas the enolic content of EAA (R:  $\text{CH}_3$ , R':  $\text{OC}_2\text{H}_5$ ) is only about 8 %. These differences have to be taken into account for the reaction of  $\text{Al}(\text{O}i\text{Bu}^s)_3$  with one of these chelating agents, because the time required to complete chelation may be rather different for different R and R'. For this reason the solutions were aged for 1 hour after mixing to be sure that chelation was complete to the greatest possible extent. However, the reaction of AcAc and EAA, respectively, with  $\text{Al}(\text{O}i\text{Bu}^s)_3$  can be written as follows (eq. 4):



(4)

The reactive enol form of the  $\beta$ -dicarbonyl compound substitutes a  $\text{OBu}^S$ -group of  $\text{Al}(\text{OBu}^S)_3$  giving a structure where the anion of the chelating agent is stabilized by chelating the aluminum atom. The formation of chelated species has been confirmed by FTIR-spectroscopy of the solution. Both  $\beta$ -dicarbonyl compounds exhibit strong carbonyl stretching vibrations between 1710  $\text{cm}^{-1}$  and 1610  $\text{cm}^{-1}$  in a solution of iso-propanol. These vibrations are shifted to lower wavenumbers (1620  $\text{cm}^{-1}$ , 1520  $\text{cm}^{-1}$ ) after the reaction, typical for complexes of AcAc and EAA, respectively [3].

It is quite important to note that  $\beta$ -dicarbonyl compound substitutes alkoxygroups in  $\text{Al}(\text{OBu}^S)_3$  and therefore changes the functionality of the precursor. This provides a possibility to fix the type of network formed later on through hydrolysis and polycondensation on a molecular level depending only on the molar ratio is equal to one (Al, E1) a two dimensional structure can be formed only, whereas molar ratios greater than one should lead to a well defined mixture of two- and three-dimensional crosslinking. This principle has already been applied successfully to the preparation of alumina fibres from  $\text{Al}(\text{OBu}^S)_3$ , EAA and  $\text{H}_2\text{O}$  [4].

#### Hydrolysis

Hydrolysis was performed with stoichiometric quantities of water with regard to the different molar  $\text{Al}(\text{OBu}^S)_3$ /chelating agent ratios. The behaviour of the precursors depends on the nature of the chelating agent and the molar ratios of the reactants (table 1). Immediately after the addition of the water/iso-propanol solution precipitates were formed, except the samples E1 and E2.

The appearance of precipitates makes it impossible to study the hydrolysis behaviour of the different precursors (Al - A3, E3) in solution by FTIR and NIR spectroscopy. However, the formation of precipitates is very similar to the hydrolysis of pure  $\text{Al}(\text{OBu}^S)_3$ . In this case the addition of water to an alcoholic solution of  $\text{Al}(\text{OBu}^S)_3$  yields to a gelatinous precipitate at once and this behaviour can be interpreted as a fast hydrolysis and condensation. For

E1 and E2 which form clear sols after hydrolysis, NIR spectroscopy was chosen for the  $\text{H}_2\text{O}$  analysis because water exhibits a distinct absorption around 1940 nm which is not influenced by vibrations of the other compounds in the solution.

The results of these experiments are shown in fig. 2 for the systems E1.

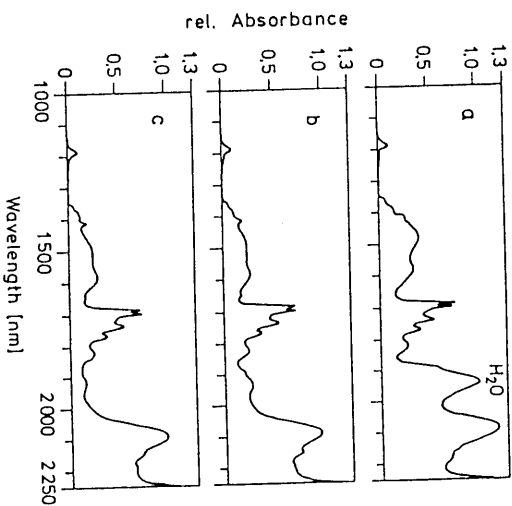


Figure 2. NIR-spectra of the system E1 and the  $\text{H}_2\text{O}/\text{PrOH}$  solution

- $\text{H}_2\text{O}/\text{PrOH}$  solution
- sample after hydrolysis (reaction time 1 minute)
- unhydrolyzed sample

Water exhibits a distinct, intensive absorption around 1940 nm in the  $\text{H}_2\text{O}/\text{PrOH}$  solution (fig. 2a) which was used to perform the hydrolysis of the chelated alkoxide (fig. 2c). The absorption at 1940 nm should decrease slowly after mixing the reactants, if the rate of hydrolysis is significantly influenced by the chelating agent. Fig. 2b shows a NIR spectrum after a reaction time of 1 minute. It is obvious that no water can be detected in this spectrum. This result must be explained in a way that hydrolysis is complete even after a reaction time of one minute and therefore the rate of hydrolysis of the chelated alkoxide (E1) cannot be very different from that of the pure  $\text{Al}(\text{OBu}^S)_3$ . The same results were obtained for the system E2 and therefore one must assume that the hydrolysis of  $\text{Al}(\text{OBu}^S)_3$  is not influenced by chelation with  $\beta$ -dicarbonyl compounds.

The nature of the aluminumhydroxides formed during hydrolysis of the chelated  $\text{Al}(\text{OBU})_3$  was studied by FTIR spectroscopy and the formation of chelated aluminumhydroxides would be proved by this method. In all cases the presence of the chelating agents (AcAc, EAA) was indicated by the strong  $\text{C}=\text{O}$  stretching vibrations around  $1620 \text{ cm}^{-1}$  and  $1520 \text{ cm}^{-1}$ , whereas the hydroxyl groups bonded to alumina gave intensive absorptions around  $3600 \text{ cm}^{-1}$ . Furthermore, no hint of advice could be found for the hydrolysis of the chelating agent. These results agree with the partial charge model developed by Livage and Sanchez [5]. Following this model alkoxy groups are preferentially hydrolysed in comparison to chelating agents like AcAc and EAA, respectively.

#### Polycondensation

The extent of polycondensation was determined indirectly by dynamic light scattering experiments on freshly prepared sols and solubility tests with gel-powders for the samples E1 and E2, respectively. The results are summarized in table 2.

Table 2. Properties of chelated aluminumhydroxides

Sample no.	size of sol particles [nm]	solubility of gel powder in toluene [g·cm <sup>-3</sup> ]
E1	1.2 - 2.5	≈1 clear solution
E2	2.3 - 4.7	≈0.8 translucent

The size of the sol particles depends on the molar  $\text{Al}(\text{OBU})_3/\text{EAA}$  ratio and with a decreasing quantity of EAA the particle size increases. However, the particles are smaller than  $5 \text{ nm}$  and for this reason polycondensation has taken place only to a very limited extent. Furthermore, the rate of condensation seems to be rather slow at room temperature because the sols do not gel after aging for more than 3 months. Similar results have recently been reported for the preparation of titania from titanium tetraethoxide and AcAc [6]. In this system the particle diameter is around  $50 \text{ nm}$  and this fact has been explained in terms of a low degree of condensation. In the case of alumina this assumption was proved for the sample E1 because the good solubility of the gel powder in toluene makes it ideal for further studies. The chemical analysis which fit gel powder was determined by chemical analysis which fit the formula  $\text{Al}(\text{OH})_2\text{EAA}$  as expected from the reactant ratios. The molecular weight of the molecules in solution was studied by vapor pressure osmometry. This method gave an average of  $940 \text{ g/mol}$  as molecular weight and in view of the fact that the molecular weight of  $\text{Al}(\text{OH})_2\text{EAA}$  is  $190 \text{ g/mol}$  a pentameric compound  $[\text{Al}(\text{OH})_2\text{EAA}]_5$  can be assumed.

In order to get more information about the structure and the coordination of the  $^{27}\text{Al}$ -aluminum in this oligomer, the solution was studied by  $^{27}\text{Al}$ -NMR-spectroscopy. This method is quite suitable to determine the coordination number of aluminum atoms, because the chemical shift of four-fold coordinated is quite different from that of a six-fold coordinated aluminum [7]. A typical  $^{27}\text{Al}$ -NMR-spectrum of  $\text{Al}(\text{OH})_2\text{EAA}$  is shown in figure 3.

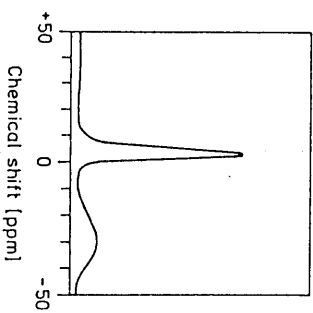


Figure 3:  $^{27}\text{Al}$ -NMR-spectrum of  $\text{Al}(\text{OH})_2\text{EAA}$

The  $^{27}\text{Al}$ -NMR-spectrum shows one sharp intensive peak centered at  $+3,5 \text{ ppm}$  and a second broad peak of lower intensity around  $-26,6 \text{ ppm}$ . The shape and chemical shift of the first peak is typical for a six-fold coordinated aluminum atom whereas the broad peak is due to a coordination number of four. On the basis of these data a model for the structure of  $[\text{Al}(\text{OH})_2\text{EAA}]_5$  can be supposed which is shown in figure 4.

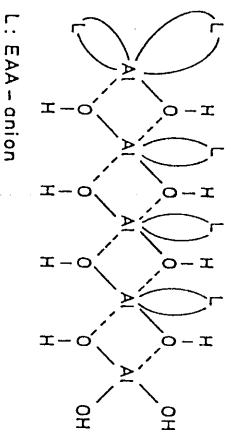


Figure 4: Model for the structure of  $[\text{Al}(\text{OH})_2\text{EAA}]_5$

This model is based on the NMR data and the assumption that a five-fold coordination state is an unfavorable one. Therefore, for the five membered species it becomes necessary that one six-fold coordinated Al atom carries two ligands and another one remains in the four-fold coordinated uncomplexed state (according to fig. 4).

A similar behaviour has been described previously by Williams and Interrante for the reaction of aluminum-isopropoxide and Acac on the basis of a structural analysis [8] which supports our model. Nevertheless, these results show that polycondensation may be controlled by the use of  $\beta$ -dicarbonyl compound.

#### CONCLUSIONS

New precursors for the preparation of alumina via the sol-gel process can be prepared from aluminumalkoxides and  $\beta$ -dicarbonyl compounds. The main advantages of these precursors are:

- The preparation of aluminumhydroxides which are soluble in organic solvents like toluene is possible.
- Polycondensation can be completely suppressed and therefore very small sol particles ( $< 5$  nm) can be prepared.
- Chelating agents with reactive organic groups can be used and give the possibility to prepare completely new inorganic-organic materials.

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