NMR, X-RAY AND MASS SPECTROMETRY CHARACTERIZATION OF SOME HETEROLEPTIC ALUMINUM ALKOXIDE COMPLEXES

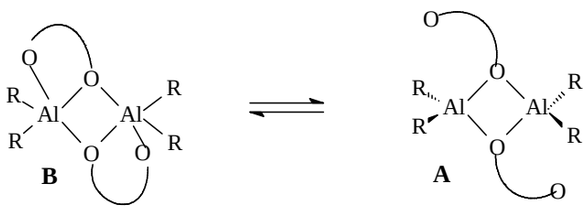
D. Baù [a], G. Carta [a], F. Benetollo [a], G. Rossetto [a], S. Tamburini [a], A. Turgambaeva [b*] and P. Zanella [a]

[a] CNR-ICIS, C.so Stati Uniti, 4- 35127 Padova, Italy
[b] Institute of Inorganic Chemistry SB RAS, Novosibirsk 630090, Russia

Heteroleptic di-alkyl aluminum alkoxide compounds have revealed to be very efficient precursors to deposit alumina thin films by metal organic chemical vapor deposition (MOCVD) technique, even though they are very reactive towards oxygen and moisture. This reactivity strongly depends on the nature of the alkyl group as well as on the alkoxide ligand. While the di-methyl methoxide, ethoxide and isopropoxide compounds are very reactive; the use of alkoxy-alkoxide derivatives with more sterical hindrance increases the chemical stability of the precursors as the aluminum atom is coordinatively saturated by the formation of intra- and inter-molecular oxygen bridges.

In this work some $(CH_3)_2AlOR$ compounds ($R=CH_2CH_2OCH_3$ (**1**), $CH(CH_3)CH_2OCH_3$ (**2**), $CH_2CH_2OCH(CH_3)_2$ (**3**), $CH(CH_3)CH_2OC(CH_3)_3$ (**4**)) were synthesized by an already known method and characterized by ^{1}H and ^{27}Al NMR spectroscopy, X-ray diffraction and mass spectrometry with an instrument equipped with a special designed input system imitating a CVD reactor to obtain data on heterogeneous thermal decomposition.

While in the solid state it is clear that the compounds are present in the form of an oxygen-bridged dimer with a five-coordinated aluminum center (Fig. 1 and 2), in solution an equilibrium exists between two fluxional species containing tetra- (**A**) and penta- (**B**) coordinated Al atoms respectively (Scheme 1). Mass spectra confirm the presence of dimer molecular compounds in the gas phase.



Scheme 1. The probabile equilibrium established between the two dimeric Al fluxional species in solution.

Mass spectrometric experiments have shown that compounds **1**, **2** and **3** compounds exhibit good vaporization stability. Thermal stability of the compounds **2** and **3** is higher than compound **1** due to branched structure of the molecules. Decomposition of the compounds vapor on hot surface proceeds through the loss of methyl groups with the formation of oxygenated species, which can act as good intermediates for the deposition of alumina thin films via MOCVD (Scheme 2). Based on the similarity of gaseous products, it can be concluded that the investigated compounds decomposed on hot surface by common mechanism and that the change of the ligand structure affects only thermal stability of the compounds.

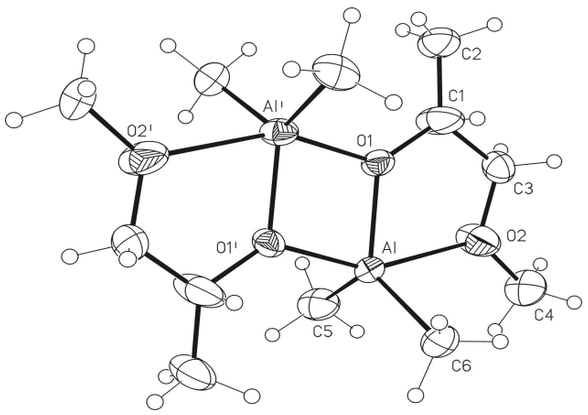


Figure 1. Molecular structure of the compound **2.**

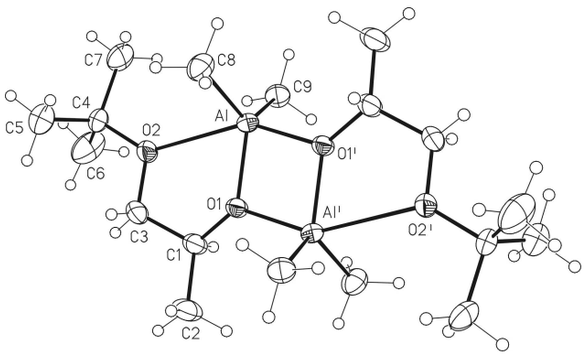
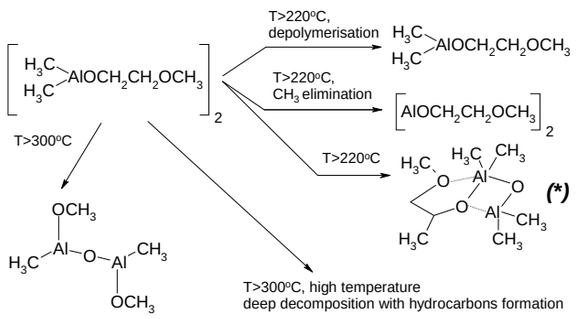


Figure 3. Molecular structure of the compound **4.**



Scheme 2. Decomposition paths of the compound **1** on hot surface.

** Present address: LAMP, Pohang University of Science and Technology, Pohang, 790-784, Korea.*