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# Efficient and Alternative Characterization of transition aluminas (η, γ, Θ, δ-$Al_2O_3$) Derived from Aeroxide: Application of FT-IR and SEM

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ABSTRACT

Heat treatment of Aeroxide (Alu C) at 500 °C in high vacuumproduced reactive phase onaluminum oxide surface. While Aeroxide from Degussa shows a mixture of transition aluminas (γ, δ, and Θ) phases, precise understanding on the development, surface morphology and microstructure of this catalytically active $Al_2O_3$ are not readily available. Combination of scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDS) and Fourier transform infra-red (FTIR) spectroscopy were used in this study to probe the transition alumina phase induced at the high temperature calcination. Assignment of IR bands on the pretreated sample at 500 °C unambiguously distinguished Θ-$Al_2O_3$ phase which is a mixture of tetrahedral and octahedral $Al^{3+}$ sites on the face centered cubic (fcc) Oxygen sub lattice.

## 1. Introduction

Alumina heated above 1200 °C generates alpha-alumina (α-$Al_2O_3$) regarded as the most stable crystalline alumina resulting from rearrangement ofthe face-centered cubic (fcc) oxygen sub lattice associated with transition alumina into an hexagonal-close- packed (hcp) structure with the $Al^{3+}$ ions in octahedralsites.[1] Whilst these metastable aluminas (η, γ, Θ, δ-$Al_2O_3$) are catalytically active, the alpha alumina (α-$Al_2O_3$)is catalytically inactive.[1-2] Before reaching the most stable α-$Al_2O_3$, various transition phases are formed. Precise characterization of each transition phase involves tedious classical X-ray diffraction (XRD) which provides similar pattern for different transition structures. This is often due to the fact that the various transition aluminas, especially γ, Θ, δ phases can be simultaneously present at any particular temperature.[2] Transmission electron microscopy (TEM) has been used to study the oxidation of intermettalic $Fe_3Al$ and FeCrAl.[3-5]The structures and polymorphs of transition alumina can be investigated using complimentary Fourier transform infra-red (FTIR) spectroscopy, imaging and computer simulation techniques.[5] The aim of this work is to present efficient and less tedious characterization of the particle shapes, microstructures and infra-red absorption bands of these polymorphous aluminas as an alternative to classical X-ray diffraction.

However, alumina pretreated at temperature between 300 °C and 600 °C produces a set of catalytically active alumina capable of activating reaction involving C-H bonds, carbonyl groups and also adsorption of $N_2$ on the most Lewis acidic $Al^{3+}$ "defect" sites in ambient condition.[6] This set of alumina is referred to as transition aluminas, namely gamma-alumina, rho-alumina delta alumina, and theta-alumina. The rho-alumina produced at about 575 °C is highly active but also quite unstable due to its high free energy.[2] It is often stored under high vacuum. The unique properties of transition aluminas in catalysis is attributed to the Lewis acidic surface of Aluminum.[7-9] Infrared spectroscopy is often employed in probing the Lewis sites of $Al_2O_3$ by their characteristic absorption of either carbon monoxide (CO), dinitrogen ($N_2$) or pyridine. The transition alumina adsorption of these probe molecules induces a pronounced additional peak on the IR spectrum: a blue-shift in the case of the N-N vibration.[10-11] This band is not detected for pre-treatment temperature below 400 °C.

Similarly, $N_2$ has been used to probe Bronsted acidic sites of zeolites which upon adsorption produces higher frequency band around 2355 $cm^{-1}$ on the IR spectrum.[12-13] Aeroxide is a highly dispersed fumed aluminum oxide ($Al_2O_3$) with high surface area and low water content. It has high thermal and chemical stability. It finds applications in ceramic material as a bonding agent, filler in thermoplastic polymers, catalysis and control of electric charging.

Here, we investigated and characterized the transition aluminum induced at 500 °C in a tubular furnace under vacuum. A combination of scanning electron microscopy(SEM), FTIR and energy dispersive x-ray (EDS) analysis were used to characterize the transition aluminum induced at the calcination temperature. This approach was necessitated due to difficulty associated with X-ray diffraction (XRD) which provides similar patterns for various transition aluminas and thus, unable to unambiguously distinguish the phases.[1]

Scanning electron microscopy study provides surface microstructure with respect to shapes and sizes of the various polymorph structures whilst the energy dispersive x-ray technique provides support information on the elemental composition.

Each transition alumina exhibits characteristic bending and stretching modes of $AlO_4$ and $AlO_6$ units. The lowest energy in the FTIR band of 350 $cm^{-1}$ is assigned to the bending mode of $AlO_6$. The IR spectrum of γ-$Al_2O_3$ presents pattern from 350$cm^{-1}$ to 850 $cm^{-1}$ with specific peaks around 380, 600 and 800 $cm^{-1}$. The structure of δ-alumina is similar to γ-alumina leading to

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similar bands. But θ-alumina has characteristics IR doublets[14-16]: 330 and 370 $cm^{-1}$ followed by 560 and 620 $cm^{-1}$ and the final and third doublet around 760 and 820 $cm^{-1}$.

At high calcination temperature, δ-$Al_2O_3$often transforms to θ-alumina which is isomorphous to β-$Ga_2O_3$ with some minor differences due to partial occupancies in their lattice structures.[17-18] In general, the polymorphic transformations of transition aluminas proceed gradually due to gradual reordering Al on its structural unit.

## 2. Result and Discussion

The IR spectrum obtained on the sample is presented on Fig. 1-2 on appendix of figures with band extending from 722 to 1302 $cm^{-1}$. The band at 722$cm^{-1}$ and 842$cm^{-1}$ result from both octahedron $ALO_6$ and tetrahedron $AlO_4$ stretching vibrations equivalent with the theta phase (Θ-$Al_2O_3$) of transition alumina. The bands at 1151$cm^{-1}$ and 1302$cm^{-1}$ are attributed to the asymmetric bending and stretching vibration respectively of Al-O-H groups. The O-H stretching modes are also observed at 3176$cm^{-1}$. When alumina samples are heated, γ-alumina develops first as the OH groups from physically and chemically absorbed moistures are eliminated. It follows the sequence of γ⋯→δ⋯→Θ⋯→α-alumin.[1] The presence of theses characteristic bands at 722$cm^{-1}$ and 842$cm^{-1}$ on the heat treated sample at 500 °C are indicative of Θ-alumina.

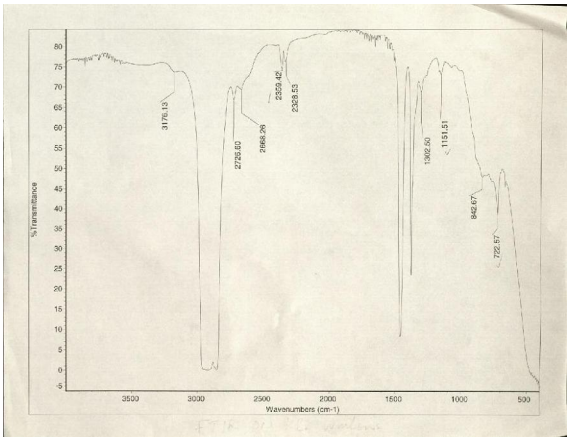


**Fig .1** FT-IR of calcined alumina at 500 °C

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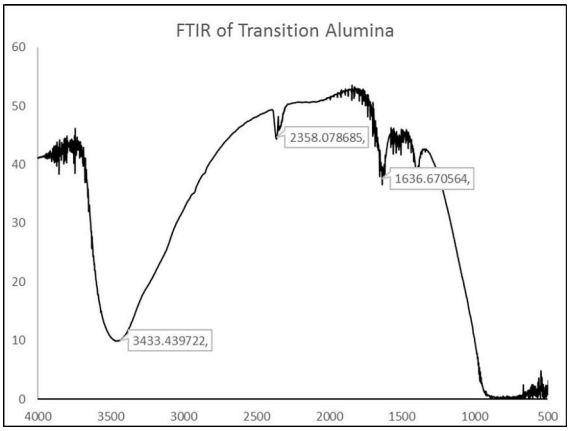


**Fig .1** FT-IR of uncalcined alumina at 500 °C.

The X-ray dispersive analysis provides both qualitative and quantitative information for desired samples. This indicates that Aluminium (Al) and Oxygen (O) are the main components in the EDS elemental analysis (Fig. 3-4) (Table 1-2). Other useful information from EDS analysis were the quantitative information such as At. % and Weight %. The validity of this piece of information depends on proper calibration of instruments. This is expected to reveal the proportion of Al:O arrangement of transition aluminas. The EDS wt% analysis indicated 41.94% Oxygen and 58.06 % Aluminium corresponding to a ratio of 2.6: 2.1 of O: Al respectively. This may constitute a basis for further investigation.

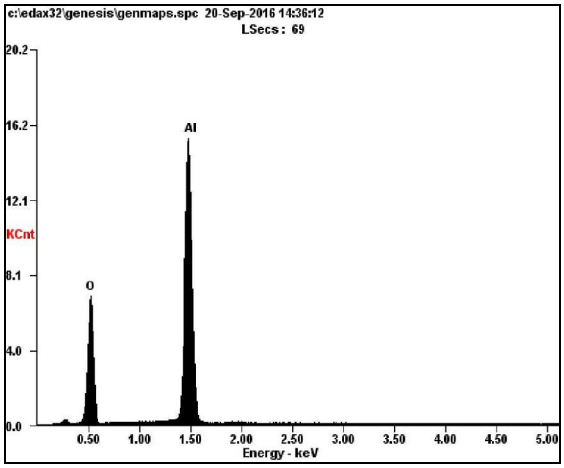


**Fig. 3** EDS elemental analysis calcined sample at 500 °C.

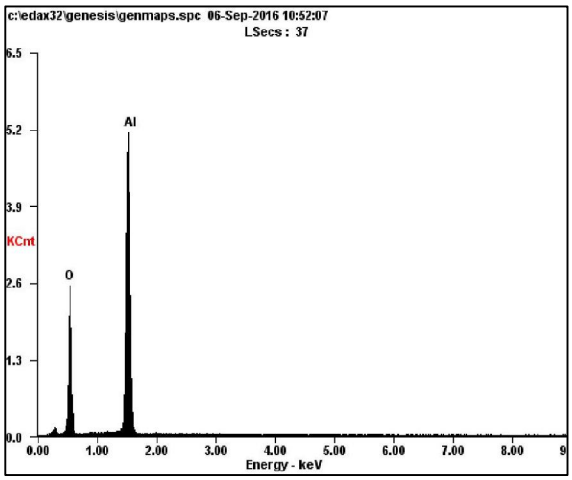


**Fig. 4** EDS elemental analysis uncalcined sample at 500 °C.

| Element | Wt% | At% |
|---|---|---|
| OK | 41.94 | 54.91 |
| AlK | 58.06 | 45.09 |
| Matrix | Correction | ZAF |

**Table 1**. Percent weight distribution of uncalcined sample at room temperature

| Element | Wt% | At% |
|---|---|---|
| OK | 40.77 | 53.72 |
| AlK | 59.23 | 46.28 |
| Matrix | Correction | ZAF |

**Table 2**. Percent weight distribution of calcined sample at room temperature

The SEM (Fig. 5-6) shows that the powder at different calcination temperatures are spherical aggregates with diameter ranging from 5 to 50µm. The heated sample at 500 °C shows greater portion of white pattern than the dark region on the surface morphology indication rearrangement of the $Al^{+3}$ cations as it migrate from octahedron to tetrahedral holes in the face centered (fcc) oxygen sub lattice structure.

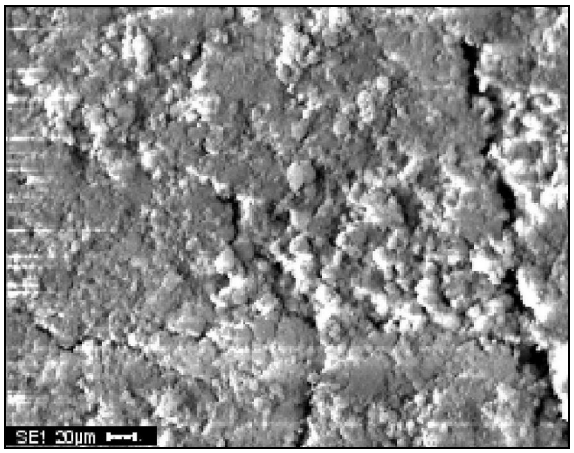


**Fig. 5** Scanning electron microscopy (SEM) of transition alumina sample (uncalcined sample) at 500 °C

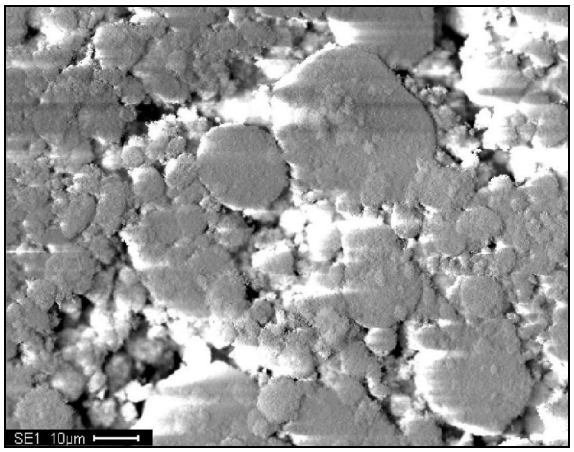


**Fig. 6** Scanning electron microscopy (SEM) of transition alumina sample (calcined sample) at 500 °C

## 3. Conclusion

Transition alumina especially γ, δ, and Θ are catalytically active phases capable of carbonyl reduction. They are potential candidate for $CO_2$ reduction in the environment. Combination of FT-IR spectroscopy and scanning electron microscopy (SEM) provide efficient technique to characterize and different microstructures of these transition aluminas.

## 4. Experimental

Heat treatment of Aeroxide (Alu C) at 400 °C, 500 °C and 700 °C was carried out in a tubular furnace in accordance with the procedure described below. The alumina was placedon a ceramic boat inside a stainless steel tube and heated under vacuum line for 18 hours. The pretreated Alumina was maintained under inert atmosphere for 24 hours before characterization. The SEM was performed on both the un-calcined and pretreated powder with a JEOL JSM-6380LV at 15 Kv for surface morphology. Imaging was taken at 1500 magnification. The EDS was performed using the energy dispersive X-ray analysis attached to the SEM above (fig.1 and 2 on appendix) for elemental analysis. Percent weight composition was computed automatically. FT-IR spectra of Aeroxde (Alu C) and calcined samples at hig-her temperatures (500 °C) were obtained using Thermo-scientific Nicolet 6700 in the transmission mode in the 300-4000 $cm^{-1}$ range. The sample powder was prepared under milling in mineral oil and compressed in a KBr window.

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