

Innovative applications of Nanophase alumina as dehydration catalyst and as humidity sensor

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ABSTRACT

The nanophase alumina δ -Al₂O₃ powder was synthesized by using the novel DC thermal arc-plasma method. The as-synthesized powder was characterized by using physical techniques viz. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray analysis (EDAX), and transmission electron microscopy (TEM). The catalytic behavior and humidity sensing characteristics of nanophase alumina δ -Al₂O₃ pellets were studied. The humidity sensing behaviour of compact nanophase δ -Al₂O₃ pellet was studied by using home-built static gas sensing characterization system. As-synthesized δ -Al₂O₃ particles were found to be spectroscopically phase-pure with δ symmetry, stoichiometric and spherical morphology with sizes in the range of 20-80 nm. Further, humidity sensing behaviour of compact nanophase δ -Al₂O₃ pellets showed the profound effect in capacitance rise with respect to % relative humidity (RH) as compared to the commercial compact and coarse fine grained α -Al₂O₃ pellets. Its catalytic activity was also studied with good results during ethanol dehydration.

Keywords: Catalyst, DC thermal arc plasma route, Nanomaterial, δ -Al₂O₃, Humidity sensor.

INTRODUCTION

There is increased growing interest in synthesis, characterization and applications of innovative nanophase materials [1] due to their vast technological importance.

The nanophase particles [2] which are ultrafine one with high surface energy provides a large surface to volume ratio and large fraction of atoms reside in the grain boundaries. Consequently the grain boundary structure of these materials play a significant role in the novel chemical, electro-mechanical, optical and magnetic properties which are different and improved from their conventional coarser grained counter parts [3] [4].

The humidity sensing is becoming ever more important for agricultural, industrial processes, human comfort and academic interest. We have explored presently the possibility of utilizing the larger surface area and grain boundary structure present in the nanophase powder of aluminum oxide (Al_2O_3 -alumina) for sensing different humidity levels.

Various varieties of ceramic, polymeric and composite sensors are being synthesized, processed and produced to serve these applications. Each of these types of sensors has limitations and new sensor concept continues to emerge. A better efficiency of sensing is expected from these materials compared to their counterpart consisting of coarser grained alumina. Ceramic capacitive air humidity sensors have emerged in increasing numbers [6] [7] [8].

However, a sensor with fine structure alumina has not been studied in detail. A Novel DC Arc plasma method was employed for synthesis of nanocrystalline alumina in the present paper.

METHODOLOGY

In this paper the laboratory made arc plasma reactor consisting of A1-C electrodes system were used in the present experimental setup. The arc was excited across A1-C electrodes by application of 70 V, 50 Amp D.C power supply at an electrode separation of 0.3-0.5 cm in a closed chamber. The fine powder which issued from the arc was deposited onto the inner walls of the reaction process chamber. The powder was gently scrapped after cooling of the interior surface from the roof of the chamber. This powder has shown a white colored appearance. The elemental analysis was carried out by 14 MeV Neutron Activation Analysis (N.A.A.) [5]. D-T reaction was used for

generating 14 MeV neutrons. Aluminum is irradiated with these neutrons to give radioactive Mg^{27} which has the life time of 10 min. and emits γ -rays of energy 0.84 MeV which is detected through detectors to give the amount of aluminum.

The TEM was used to study the topography of the particles using the bright field mode [9]. Through the XPS measurements the purity and stoichiometry were estimated properly.

Catalytic activity of alumina has been utilized in many chemical reactions since a pretty long time. However there are not many reports emphasizing the added advantages of its fine grained nature on the catalytic activity. Here an attempt is made in this direction and the ethanol dehydration reaction in presence of our as synthesized nanophase alumina and vis-a-vis coarse grained alumina was studied. The present work concerned with use of technique involving the capacitance measurement to study this activity with similar studies conducted with the coarse grained alumina catalyst. There are number of ways of making gaseous alkenes like ethane. If ethanol vapors are passed over surface of heated alumina pellet the ethanol is essentially cracked to give ethane and water vapor. This reaction is normally occurs at $\sim 250^\circ\text{C}$ in usual alumina [13]. Alumina enhances typically acid catalyzed reactions which its surface is saturated with water [14]. In another application the same powder was studied and tested for novel application as catalyst in alcohol dehydration process at different conditions. For this, the comparison between as synthesized and commercial grade alumina was carried out. It has been clear that the surfaces of most metal oxides have hydroxyl groups in the atmosphere which play important role in surface phenomenon such as catalytic action, selective adsorbability and hydrophilicity. IR spectroscopic studies have shown that water molecules are get adsorbed on the surface of oxides through hydrogen bonding with surface hydroxyl groups [15]. The oxidizing power and catalytic activities may be due to defects in the structure that is in coordination of metal ions in oxides [16]. The comparative studies for novel application of alumina as catalyst in the ethanol dehydration have shown challenging and remarkable results.

The humidity sensing was experienced and realized by measuring the change in the capacitance of a parallel plate capacitor made. Here the dielectric medium consisted of compacted powder of nanophase alumina pellets. The static controlled humidity chamber was used for obtaining different humidity levels. The capacitance was measured using a Systronics make digital capacitance meter. The steady state capacitance was measured for various solutions viz. distilled water, prepared solutions of CrO_3 , CuSO_4 , NH_4Cl , and LiCl .

RESULTS AND CONCLUSION

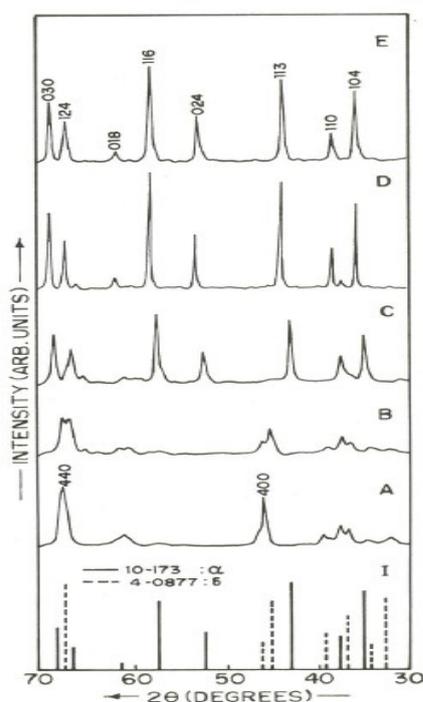


Fig. 2. XRD pattern of: (A) as-deposited; (B) calcined at 1200°C; (C) calcined at 1400°C; (D) calcined at 1600°C; (E) commercial alumina; and (I) pattern adapted from JCPDS 10-173 (α) and 16-394 (δ).

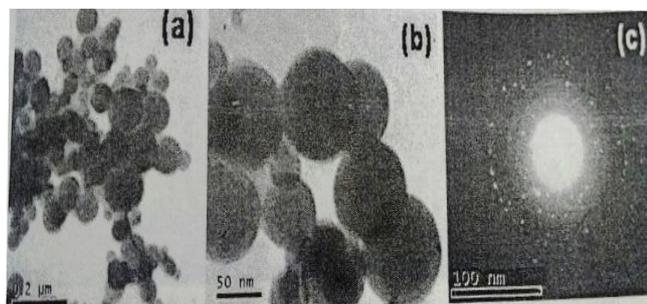
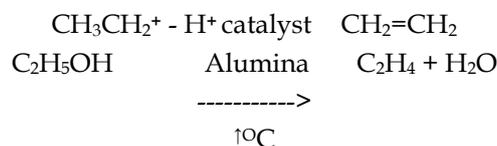


Figure 4: TEM images of nanophase alumina: Selected area diffraction pattern for nanophase δ - Al_2O_3

As revealed from XRD study shown in fig. 2 the as prepared powder of alumina exhibited δ -alumina phase. Using the Debye-Scherrer formula the particle size was estimated and was found to confirm the nanophase nature (20nm.). From the TEM analysis [10] the spherical size of particulate was confirmed as shown in fig.4. The special Neutron activation analysis (N.A.A.) was carried out on powders at 270°C, 300°C, 500°C, 700°C and 900°C. The results indicated that the concentration of aluminum and oxygen in 0.5 gm of Al_2O_3 varied with the calcinations temperature. The oxygen concentration increase indicating a peak for 500°C [5] for a nanophase powder wherein a similar peak was observed for the commercial microphase (Good Fellow UK, 45 mm size spherical particle) Al_2O_3 powder for a temperature of 700°C [5]. The increase in the oxygen concentration is explained on the basis of higher diffusion rates of oxygen into the pores. However, the grain growth prohibits the further diffusion of oxygen. The peak temperature might probable indicate the temperature at which the grain growth has occurred. Nanophase material seems to grow at lower temperature as compared to the micro phase powder. This experiment also clearly indicates that the oxygen adsorption capacity for nanophase powder is higher as compared to the coarser grained powder.

Among the vapors of different chemicals when vapors of ethanol were passed over the heated surface of nanophase alumina and the coarse grained alumina it exhibit dehydration reaction to give ethylene. In case of use of our as synthesized nanophase alumina the ethanol dehydration was observe to be occurred at the temperature $\sim 135^\circ\text{C}$. This reaction is normally occurs at $\sim 250^\circ\text{C}$ in usual alumina [13]. In this case the catalytic activity is not connected with the electron transfer mechanism. It is assumed that that the H^+ ions present in the alumina catalyst is responsible for this dehydration activity. A carbonium ion is formed in this step. It is destroyed on the surface of the catalyst to liberate the molecule of an unsaturated hydrocarbon and the proton is returned to the catalyst.



An H^+ ion in alumina obstructs the conductivity so the capacitance increases. Thus the mechanism of proton catalysis consists of continuous transition of proton from the catalyst to the reacting molecule. This mechanism was studied by the measurement of capacitance and graphically results are shown. When the protons are removed from the catalyst surface then there is change in the capacitance we observed and noted precisely.

The results show that the dehydration process occurs at quiet lower temperature using as synthesized alumina than commercial grade alumina as shown in fig.3. This has important and novel applications in industry. The reduction in temperature for certain chemical process has importance in view of cost also.

A comparative measure of the sensing capability of the fine grained Al_2O_3 as compared to the coarser grained powder is studied for various humidity levels fig.5

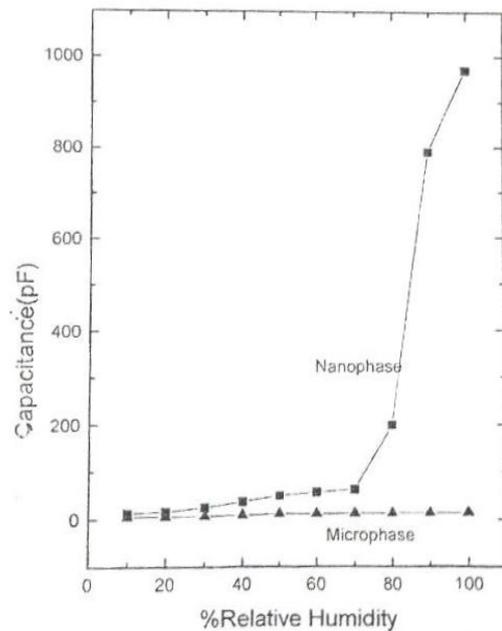


Fig: 5: Humidity sensing: Capacitance measurement

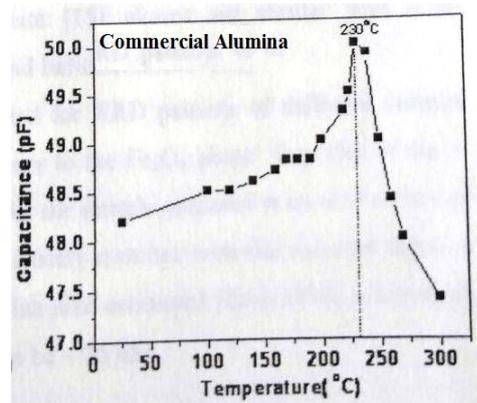
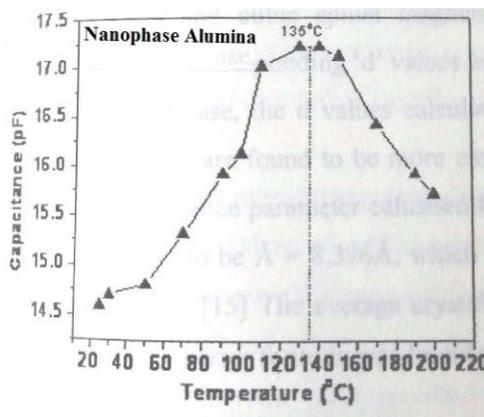


Figure 3: Catalytic activity: Role of Nanophase and Commercial alumina during dehydration

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