SYNTHESIS OF FACETTED GAMMA ALUMINA NANOPARTICLES FROM WASTE BEVERAGE ALUMINIUM CANS FOR POTENTIAL CATALYST SUPPORT APPLICATIONS

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Abstract. Green synthesis of gamma alumina (γ-Al_2O_3) nanoparticles (NPs) with facetted and cubeoctahedral morphologies was undertaken from waste (beverage aluminium cans) via precipitation technique and calcination at the temperature of 1000 °C. The structural properties of γ-Al_2O_3 were determined with a combination of techniques including BET surface area, field emission scanning electron microscopy (FESEM) with energy dispersive x-ray spectroscopy (EDX), transmission electron microscopy (TEM) and x-ray powder diffraction (XRD). XRD analysis confirmed the formation of γ-Al_2O_3 NPs by comparing with the standard of γ-Al_2O_3 structure. The BET surface area measured was 129 m^2/g. High-resolution transmission electron microscopy (HRTEM) analysis provided evidence of surface-enhanced contrast in facetted γ-Al_2O_3 NPs structures similar to the commercial γ-Al_2O_3 NPs.

Keywords: Green synthesis, γ-Al_2O_3 nanoparticles, waste aluminium cans, XRD, TEM

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Introduction

The Green Technology Master Plan of Malaysia (2017-2030) outlines the strategic plans for green technology development to create a low-carbon and resource efficient economy [1]. This master plan sets out the immediate course for the country to embark on a green growth journey. Recycling waste beverage aluminium cans is part of a green technology application that provides the solution to realise Malaysian's commitment. In recent years, many efforts have been made on innovative design and packaging to benefit the food and beverage (F&B) industry. As an example, in May 2021 Nestlé invested $220m in a canned beverage plant in Indonesia and the construction of the plant produced canned beverages in order to meet the growing demand for dairy products and ready-to-drink beverages [2]. The F&B industry has gained tremendous benefit from recent advances in packaging technology which mainly serves to maintain the quality of products. Innovation in this area includes the introduction of aluminium as a container which increases the F&B products' shelf life compared with plastic containers. With all the advantages of aluminium containers such as cans, the pollution caused by municipal solid waste and rubbish that occurs around the world today is mainly made up of aluminium beverage cans [2]. According to the U.S. National Park Service, it can take from 80 to 200 years for aluminium to decompose at the landfill [3]. In 2012, approximately 38.2 billion aluminum beverage cans ended up in U.S. landfills, the equivalent of 121 cans for every American man, woman and child [4].

γ-Al_2O_3 NPs is a ceramic material and isostructural with γ-Fe_2O_3 due to similarity in the structural formula. Oxides in NPs form such as γ-Al_2O_3, Fe_3O_4 and γ-Fe_2O_3 are expected to assume an approximate sphere shape in order to minimize the surface energy, however in crystalline NPs, they always take up either octahedral or cubeoctahedral morphologies [5]. Jefferson [5] reported that the structure at the edges of the particles differs greatly from the bulk phase; observed facetted particles on γ-Al_2O_3, Fe_3O_4, and γ-Fe_2O_3 and found surface-enhanced contrast using high-resolution TEM. γ-Al_2O_3 NPs has been deemed as the most important nanomaterial due to their hardness, high melting point and low electrical conductivity have many technological applications in electronics, optics, biomedicine, and mechanical engineering [6]. In catalysis, γ-Al_2O_3 is the most widely used as catalyst or catalyst support; as for example for CO_2 hydrogenation reaction [7], because it has high mechanical strength, distinctive chemical, mechanical and high thermal stability, chemically inert, surface acidity, high surface area and is quite inexpensive to produce [8]. The catalytic activity which is closely related to the structure of exposed crystalline faces has gained huge significance in the synthesis of γ-Al_2O_3 NPs and the study of surface modification such as facetted and surface-enhanced contrast [5]. Also, γ-Al_2O_3 NPs show their wide range of applications in automotive components such as electronic substrates and displays, catalysts in catalytic converters, diesel particulate filters, spark plugs and phase change materials [9,10].

The process of refining bauxite with sodium hydroxide solution in a high-pressure vessel at the temperature of 150–200 ^{o}C, also known as the Bayer process [11], has produced γ-Al_2O_3 commercially. The filtering process leaves behind a toxic sludge, commonly called red mud or red sludge [12]. Mining and mineral processing of bauxite poses risk for human health and generate environmental problems due to dust and greenhouse gas emission [11]. There are many other routes to produce γ-Al_2O_3 NPs. The hydrothermal method is one of the alternative routes to produce pure fine oxide powders such as γ-Al_2O_3, ZrO_2, $BaTiO_3$, Fe_2O_3 and Y_2O_3 [13]. Sol-gel is another possible method for synthesis since it provides low-temperature synthesis with excellent control. This technique originally developed and been widely used for the synthesis of highly porous γ-Al_2O_3 [14]. In this study, γ-Al_2O_3 NPs are prepared using green synthesis which employed recycling of waste beverage aluminium cans and digested with sulphuric acid, later precipitates with ethanol. Extracting aluminium from beverage cans as a precursor for the synthesis of γ-Al_2O_3 NPs is found to be an effective waste management method to reduce the accumulated amount of waste and to transform it into value-added material. Due to γ-Al_2O_3 NPs being widely used in various applications, numerous studies have been focusing on its synthesis using waste beverage aluminium cans [15-17]. From the intensive literature review, the crystallite size, morphology and surface reconstruction of γ-Al_2O_3 NPs produced was not characterised; the crystallite size, morphology and surface termination remain unclear. Therefore, we investigate the synthesis of γ-Al_2O_3 NPs using an aluminium source derived from waste beverage aluminium cans via precipitation technique; this method is a modification work [15]. The γ-Al_2O_3 NPs produced was characterised using BET surface area, XRD, FESEM and TEM for potential catalyst supports applications.

Materials and Methods

Materials. Discarded Nestle's® aluminium beverage cans (Malaysia) as shown in Figure 1were selected as the raw material for this study. The following chemicals were obtained from indicated suppliers; Sulphuric acid (H_2SO_4) solution (chemical purity: 95-98 %, ChemAR, denatured (Systerm) was selected as the reaction reagent and ethanol solution (C_2H_5OH) absolute 99.5%, ChemAR, denatured (Systerm) reacted as the precipitation reagent. The entire solution was used without further purification. As a comparison, commercial γ-Al_2O_3 nanopowders from MKNano (MKN Al_2O_3-015) and labelled as AL5 were used without additional processing. The sample was kept in a desiccator.

Figure 1. Raw material: waste Nestle aluminium beverage cans.

Preparation of γ-Al_2O_3 NPS. The preparation of γ-Al_2O_3 NPS has 7 processes; the details of the processes are as follows. The empty aluminium cans were washed using tap water to remove the stains and dirtiness. The aluminium beverage cans were cut into small pieces as shown in Figure 2 to increase the surface area available to react with the H_2SO_4 acid solution, weighed according to the calculated stoichiometric proportions and were reacted with 8.0 M acid H_2SO_4.

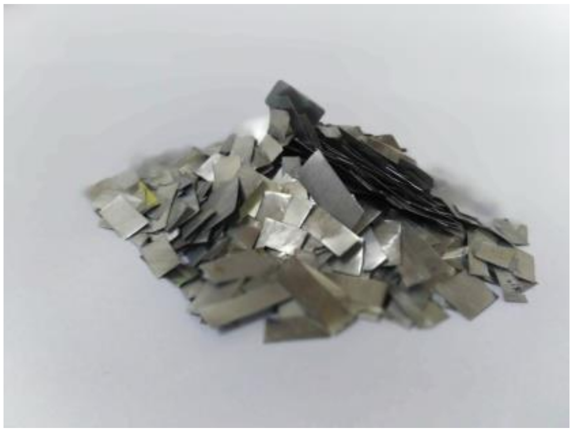

Figure 2. Small pieces of beverage cans

The mixture was stirred constantly at room temperature for 4 hours with a magnetic stirrer (IKA RCT basic) and was left unattended for a week until all pieces of aluminium cans were completely consumed, and the precursor was formed. The acidic aluminium sulfate solution was precipitated using ethanol solution in a ratio of 2:3. The precipitated mixture was cooled, and the cooled mixture was filtered and rinsed with an ethanol solution to remove any excess acid H_2SO_4 on the salt. The filtered aluminium sulfate precipitate was placed in an oven at 50^{o}C for 1 hour for drying. And finally, the dried homogeneous powder was then calcined in an electric furnace for 2 hours at 1000 ^{o}C and labelled as AL1000.

Characterisation of γ-Al_2O_3 NPS. BET-BJH brand Micromeritics was used to study the surface area of γ-Al_2O_3 NPs. About 1.5g sample was degassed at the temperature of 150 ^{o}C. The phase, crystal structure and crystallite size of the bulk sample had been characterised by the X-ray Diffraction (XRD) technique (conventional powder XRD), using a Bruker D8 Advanced model. The diffractometer was set up to measure the 2θ range (10^o-90^o), with a step size of 0.017^o. Field mission scanning electron microscope (FESEM), brand Hitachi model SU 8020, at a beam energy of 30 keV, was used to examine the surface morphology of γ-Al_2O_3 NPs. The sample was ground in a pestle and mortar and ultrasonically dispersed in methanol for 15 minutes. A clean aluminium metal stub was applied with one drop of this suspension using a glass pipette; these stubs were left in the air for 20 minutes. Field emission transmission electron microscope (JEOL JEM 2100F) was used at 200 keV accelerating voltage to determine the morphology and structure of the NPs. For the TEM analysis, one drop of the dispersion was deposited onto a copper grid (400 mesh-Agar Scientific). The sample was dried in the air for about 15-20 minutes.

Results and Discussion

The bulk samples of phase and crystal structure were characterised using XRD analysis. The polycrystalline diffractograms of γ-Al_2O_3 NPs synthesised from waste beverage aluminium cans (AL1000) and commercial γ-Al_2O_3 NPs (AL5) samples (Figure 3) were compared to the XRD standard for γ-Al_2O_3 structure JCPDS reference no. 00-010-0425 in the International Centre for Diffraction Data (ICDD) database. The diffractogram of the AL 1000 sample in Figure 3 displays three distinct reflections at $2\theta = 37.6^{o}$ (311) reflection), 45.8^{o} (400) and 67.0^{o} (440) which agree with the database standard and the powder XRD studies [10]. These also agree with the diffraction peaks observed for AL5 except a distinct reflection at 46.1^{o} (004); it is indicated that AL5 has a more distorted cubic structure compared to AL1000 [18].

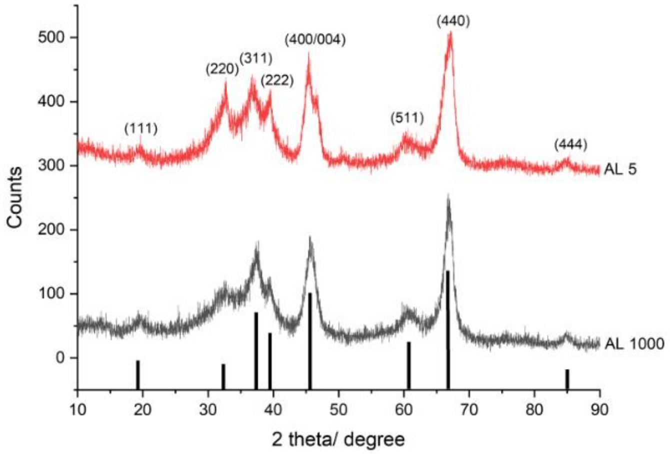

Figure 3. The XRD diffractograms of AL1000 and AL5 and overlapped with the standard XRD pattern of γ-Al_2O_3 (JSPDS no 00-010-0425).

The widths of the XRD peaks allow the calculations of the average crystallite size. The size of crystallite was obtained through the average of (400) and (440) reflections. This analysis has shown the average crystallite size of AL1000 and AL5 to be approximately 6.3 nm and 5.0 nm respectively. However, since different peaks give different crystallite sizes, it suggests that there may be a crystal shape anisotropy (e.g. preferential growth in certain directions). The formation of γ-Al_2O_3 NPs is expected as it has been reported to be the most thermodynamically stable phase when the specific surface area of γ-Al_2O_3 NPs is larger than 125 m^2/g, or when the crystallite size (particle diameter) is less than about 13 nm [19]. The BET surface area analysis for AL1000 and AL5 were 129 m^2/g and 137 m^2/g respectively; the surface area for AL1000 is smaller than AL5. The difference in BET surface area is due to the difference in technique of synthesis; AL1000 was prepared using precipitation technique and heat treatment of aluminium sulphates at 1000 ^{o}C and there is no information on the technique of synthesis of AL5. γ-Al_2O_3 NPs are produced through the calcination of aluminium hydrates, bayerite, gibbsite and boehmite at temperatures ranging between 230-1100^{o}C and yield different values of BET surface area [20]. Porous materials having a surface area value above 100 m^2/g is considered to have a high surface area and is a potential material for catalyst support applications [21]. This value indicated the development of new material with high surface area which was confirmed by the XRD patterns to be γ-Al_2O_3 NPs. Surface area is essential for the contact between the reactants and metal catalyst, larger surface area leads to higher reaction rates. Both the surface area to volume ratio and surface area per unit mass (specific surface area-SSA) of a system as a function of particle size increases drastically for particles < 100 nm in diameter; i.e. for 2 nm particles, the SSA approaches 500 m^2/g [22]. In order to prevent agglomeration and maintain separation, particulate metal catalysts need a supporting material. To increase the rate of chemical reactions, the support should have a large surface area, high porosity, be thermally stable and chemically inert during the desired reaction. Table 1 summarises the BET surface area, crystallite size and morphologies of AL1000 and AL5.

Table 1. Summary Data of AL1000 and AL5.

Name of Samples	**Phase (XRD)**	**XRD Crystallite Size (nm)**	**TEM morphologies and Size (nm)**	**SEM (EDX Analysis) (%)**	**BET Surface Area (m^2/g)**
AL1000	Gamma (γ- Al_2O_3)	D400 =6.87 D440=5.60	Spherical, Cubeoctahedral, and facetted particles	Al=62.36 O= 37.64	129
AL5	Gamma (γ- Al_2O_3)	D400 =5.73 D440=4.33	Elongated (‘long needle-like’) and facetted particles	Al=61.58 O=38.42	1 37

Figure 4 shows SEM images of γ-Al_2O_3 NPs obtained from waste aluminium cans (AL1000) and commercial (AL5) which show similar surface morphology and physical structure. The SEM images for both samples show ‘sponge-look like’. The spongy γ-Al_2O_3 NPs is belief to enhance the diffusion efficiency and mass transfer of reactant molecules due to its improved texture properties [13]. The EDX analysis revealed the weight % of O and Al is 62.36 and 37.64 respectively in AL1000 and 61.58 and 38.42 in AL5. The purity of the samples, with the detection of aluminium and oxygen, has been confirmed through the EDX analysis.

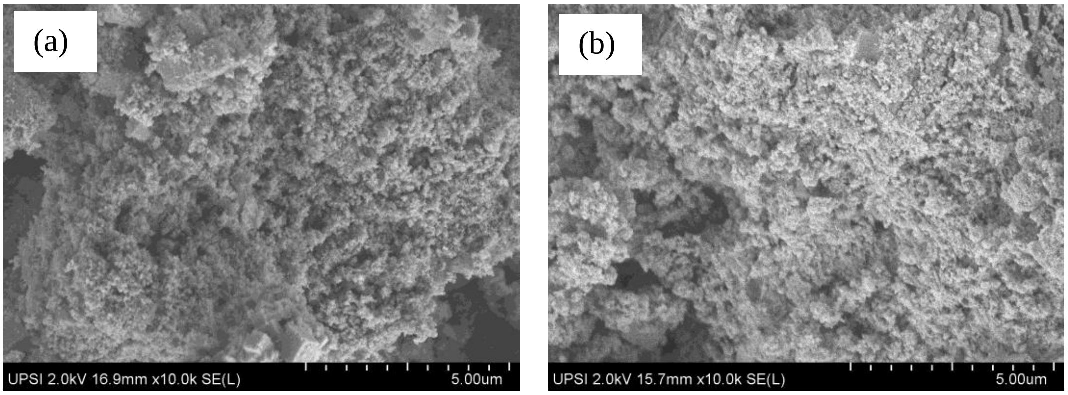

Figure 4. SEM Images of AL1000 (a) and AL5 (b)

Low magnification TEM images shown in Figures 5(a) and 5(b) were used to assess any NPs' agglomeration. AL1000 sample was the least agglomerate compared to AL5. AL1000 unveiled facetted and cubeoctahedral NPs and spherical morphologies (Figure 5(c) while the AL5 sample shows a mixture of elongated ('long needle-like') and facetted NPs (Figure 5(d). In order to minimize the surface energy, γ-Al_2O_3 NPs (AL1000) is found to adapt a cubeoctahedral, facetted and surface-enhanced contrast indicates that AL1000 is more stable and suitable to use as catalyst supports [5]. A more stable surface can be created by using low-index crystallographic planes, such as {111} and {100}, to create a cubeoctahedral particle [5]. Overall results show that AL1000 has nanostructural properties similar to other commercials γ-Al_2O_3 [18].

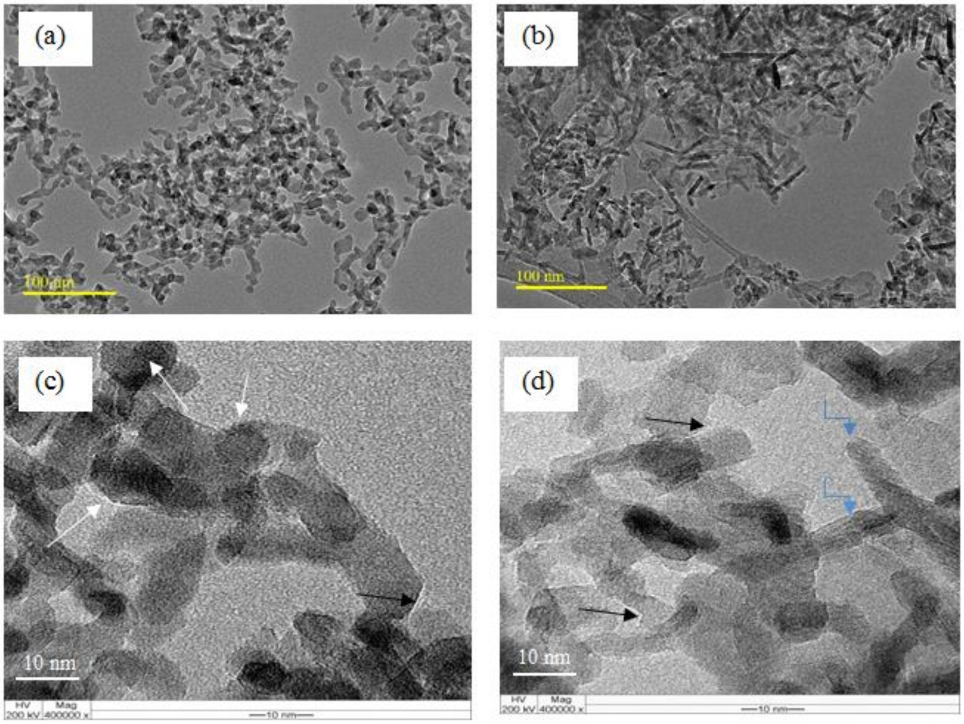

Figure 5. TEM images of AL1000 (a) and AL5 (b) at low magnification and high magnification AL1000 (c) and AL5 (d). The white arrows show cubeoctahedral and spherical NPs, black arrows show facetted NPs while blue arrows show elongated ('long needle-like') NPs.

Figure 6 shows the evidence of surface-enhanced contrast of AL1000 and AL5; these findings are similar to the findings of [5,18]. Through the investigations using high-resolution TEM, additional evidence for the crystallinity of the nanoparticles was gained. The evidence for surface reconstruction on facetted nanoparticles has been found in HRTEM images of both samples.

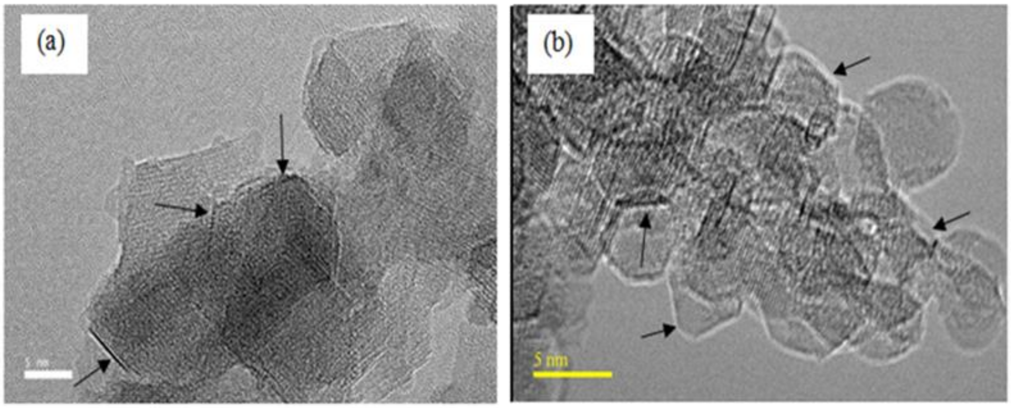

Figure 6. HRTEM Images of AL1000 (a) and AL5 (b), black arrows showing facetted and surface-enhanced contrast.

Conclusion

The feasibility of waste beverage aluminium cans, converted into γ-Al_2O_3 NPs using precipitation technique followed by calcination at $1000^{o}C$ of temperature, has been successfully investigated. XRD analysis has shown the formation of γ-Al_2O_3 NPs phase and the average crystallite size of AL1000 to be approximately 6.3 nm. The BET surface area of AL 1000 is 129 m2/g and it has been reported to be the most thermodynamically stable phase when the specific surface area of γ-Al_2O_3 is larger than 125 m^2/g or when the crystallite size (particle diameter) is less than about 13 nm. TEM analysis shows AL1000 as a cubeoctahedral, spherical, facetted and surface-enhanced contrast morphologies indicated low surface energy and potential to be used as catalyst supports. Overall results indicated that the formation of γ-Al_2O_3 NPs with structural properties similar to the commercial γ-Al_2O_3 NPs was confirmed. In conclusion, AL1000 NPs has the potential to be used as catalyst support for CO_2 hydrogenation reaction.

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Author contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of conflict of interest

The authors have no disclosures to declare.

Compliance with ethical standards

The work is compliant with ethical standards.

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