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Synthesis of Spherical Nanostructured γ-Al_2O_3 Particles using Cetyltrimethylammonium Bromide (CTAB) Reverse Micelle Templating

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ABSTRACT

Gamma alumina (γ-Al_2O_3) is a material that widely used as a catalyst or catalyst support because its abundant Lewis acid sites. However, conventional γ-Al_2O_3 has low surface area and lack of reactant accessibility. Here, we demonstrated synthesis of spherical nanostructured γ-Al_2O_3 using reverse micelle templating to enhance the surface area and reactant accessibility. The essential requirement of material synthesis using reverse micelle templating method is to form a stable emulsion prior any chemical reaction. Three different surfactants were used in this study: benzalkonium chloride (BZK), sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB). BZK surfactant cannot form a stable emulsion, resulting the formation of particles with irregular shape and morphology. Stable emulsions were obtained using SDS and CTAB surfactants. SDS surfactant formed a normal micelle, while CTAB surfactant formed a reverse micelle. SDS normal micelle with aqueous continuous phase cannot limit the growth of particles, thus results particles without regular shape or morphology. We obtained spherical nanostructured particles only using CTAB that form a reverse micelle emulsion. The particles have a wide size distribution with average size of 2.54 μm. The spherical particles consist of nanoplate crystallites with size 20-40 nm randomly arranged forming intercrystallite spaces. The crystalline phase of as-synthesized and calcined particles was boehmite and γ-Al_2O_3 respectively as determined by XRD analysis. Particles morphology did not change during boehmite to γ-Al_2O_3 transformation, thus opening a facile route to synthesize γ-Al_2O_3 particles with complex morphology. Spherical nanostructured γ-Al_2O_3 provides wide potential applications in catalysis due to its high density closed packed structure, large surface area and high accessibility.

Keywords: 3D Open Channel; Boehmite; CTAB; Reverse Micelle; Spherical Nanostructured Particle; γ-Al_2O_3.

1. Introduction

Alumina has been frequently reported as an important material in the field of catalysis, especially its polymorph, gamma alumina (γ-Al_2O_3) [1-5]. This material is very important as catalyst or catalyst support due to its stability at high temperature and abundant Lewis acid sites [6-9]. The commonly used material as catalyst support is the conventional mesoporous γ-Al_2O_3 with closed channel structure formed by the inter-crystalline space [10-13]. Thus, the accessibility of reactants to the catalyst active sites is very limited. To have high catalytic performance, catalyst or catalyst support must have not only high surface area but also high accessibility. Catalyst or catalyst support with high accessibility, provides active sites with high efficiency.

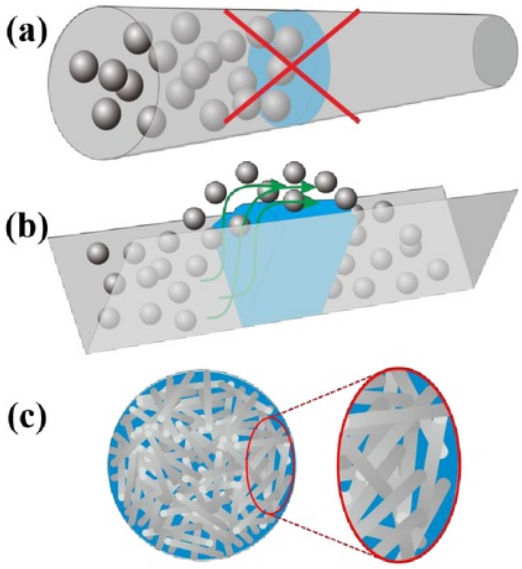

Figure 1. Illustration of reactant accessibility in catalyst support with (a) closed channel structure, (b) open channel structure. (c) Hypothetical representation of a spherical γ-Al_2O_3 microparticle consists of randomly aggregated nanorod crystallites.

A wise strategy that must be considered to increase the accessibility of γ-Al_2O_3 is by modifying its morphology. Aggregated nanocrystallites morphology of the conventional mesoporous γ-Al_2O_3 might only provide pores with closed channel structure [12, 13]. The common strategy to increase the surface area and pore volume in conventional mesoporous γ-Al_2O_3 is by reducing the crystallite size [14]. This strategy mainly affects the number of active sites, but not its accessibility. To

increase the accessibility, we can try to transform the pore structure from closed channel to open channel. **Figure 1a** and **1b** illustrate the comparison on the transport of reactants inside pore between closed channel and open channel structure. The presence of obstacle inside the closed channel pore will completely block the flow of reactants. In open channel pore, the flow of reactants still can reach the active sites through the open channel side. Structural transformation from closed channel to open channel can be interpreted by assembling the crystallites into a conformation with open channel access. In the case of γ-Al_2O_3, we can employ this strategy by growing spherical γ-Al_2O_3 microparticles consist of randomly aggregated nanorod/nanoplate crystallites (**Figure 1c**).

Many research groups reported that γ-AlOOH (boehmite) can easily form γ-Al_2O_3 through calcination at temperature around 500 °C. This phase transformation has been studied theoretically [14] and experimentally [16-19]. The phase transformation occurred through the structural collapse of boehmite framework after hydrogen transfer and internal water dehydration, followed by aluminum migration process [15]. We can synthesize γ-Al_2O_3 with desired morphology only by controlling morphology of boehmite. Thus, any desired morphology of γ-Al_2O_3 can be produced if we have the parent boehmite particles with the same desired morphology. This evidence has been reported by many research groups [20-22]. They successfully obtained nanostructured γ-Al_2O_3 with open channel structure from as-synthesized nanostructured boehmite with the same morphology. However, all reported methods above show lack of controls on particle shape, separation and size. Here, synthesized γ-Al_2O_3 particles tend to form agglomerates.

One reported method that can control shape, separation and size of particles, is the reverse micelle templating method. Febriyanti and coworkers successfully synthesized spherical nanostructured silica with bicontinuous concentric lamellar (*bcl*) morphology using CTAB reverse micelle as a template [23]. In this study, we reported the synthesis of γ-Al_2O_3 using reverse micelle templating method to obtain nanostructured γ-Al_2O_3 with open channel structure.

2. Materials and Methods

2.1 Materials

$NaAlO_2$ and 1-butanol were purchased form Sigma Aldrich; toluene, urea, sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were purchased from Merck; benzalkonium chloride (BZK) solution Sanisol RC-A was purchased from Kao Chemicals. These reagents were used without any further purification.

2.2 Stable emulsion

To make stable emulsion, firstly we made two mother solutions. The first solution is a polar phase (solution A) that contains $NaAlO_2$, BZK surfactant, urea and water, while the second solution is a nonpolar phase (solution B) that contains toluene and 1-butanol. The stable emulsion was made by adding solution A dropwise into solution B with vigorous stirring at 800 rpm for about 1 hour. The stable emulsion is a milky white mixture which did not breakdown if the stirring was stopped. This process also applied to make emulsion using SDS and CTAB surfactant. The stable emulsion was then tested using burn test and dilution test.

2.3 Synthesis of nanostructured γ-Al_2O_3

γ-Al_2O_3 was synthesized by applying solvothermal method. The stable emulsion was transferred into a Teflon-lined stainless-steel autoclave, sealed and heated in oven at 160 ºC for 24 hours. The resulting product was filtered and rinsed with deionized water, ethanol and acetone, respectively. The product was dried in oven at 100 ºC for 4 hours. Finally, the as-synthesized product was calcined at 550 ºC for 4 hours in atmospheric pressure.

2.4 Characterization

The morphology of resulting particles was observed using Scanning Electron Microscope (SEM) Hitachi SU3500 and High-Resolution Transmission Electron Microscope (HR-TEM) Hitachi H9500. From SEM images, we measured diameter of 100 particles using ImageJ software and made a histogram plot to obtain particles size distribution. The TEM images was also analyzed using ImageJ software to obtain gray value profiles of particles. The XRD patterns were recorded on a Bruker Avance diffractometer with Cu Kα (λ = 1.54018 Å) radiation.

3. Results and Discussion

The essential requirement of material synthesis using reverse micelle templating method is to form a stable reverse micelle emulsion prior any chemical reaction. The stable emulsion is an emulsion that will not break after the stirring is stopped. The surfactants used in this research were BZK, SDS and CTAB. The morphology of synthesized particles using these three kinds of surfactant were shown in **Figure 2**.

BZK surfactant did not provide any stable emulsion. The advantages of reverse micelle (w/o) system are lost in this synthesis. This unstable emulsion may due to the formation of ion pairing between BZK cations and sodium aluminate anions (AlO_2^-). Ion pairing causes the micelles lost their ability to repel each other, thus the emulsion becomes unstable and starts to coalesce. Based on the SEM images, synthesized particles using BZK surfactant give no regular shape and morphology. As shown in **Figure 2a**, the particles are aggregates without regularity. **Figure 2b**

details the results with higher magnification, the surface of particles is dense without pores. The irregular shape and morphology are due to the formation of particles occurred in an unstable emulsion system. Thus, the growth of particles take place in water phase providing rapid and uncontrollable hydrolysis/condensation reactions, results particles with irregular morphology. Moreover, coalesced micelles cannot limit the growth of particles providing large particles with irregular shape.

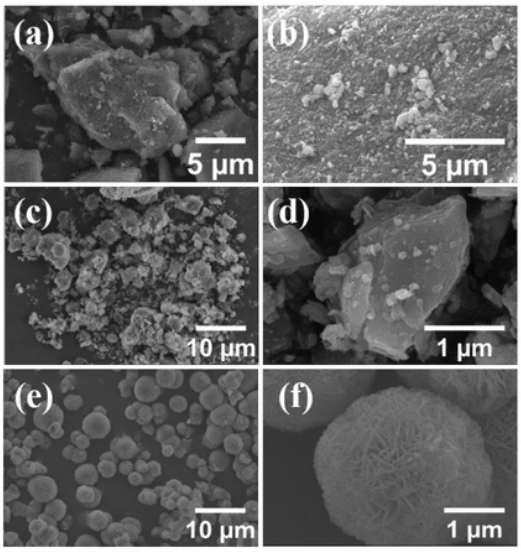

Figure 2. SEM images of synthesized particles using different surfactants; (a,b) BZK, (c,d) SDS, (e,f) CTAB. (b), (d) and (f) showing SEM images at high magnification.

Because the failure of BZK surfactant to form a stable emulsion, then we used anionic surfactant to prevent ion pairing between surfactant and AlO_2^- ion. Using SDS surfactant, we get a stable emulsion. We then tested the emulsion using burn test and dilution test to determine the type of micelle/emulsion. Both burn and dilution tests show that SDS formed a normal micelle (o/w). The hydrophilic lipophilic balance (HLB) value of SDS surfactant is 40 in range of normal micelle [24]. Surfactants with HLB in this range tend to form normal micelle. Although SDS surfactant formed a stable emulsion, the synthesized particles have no regular shape and morphology. **Figure 2c** shows the particles in the form of agglomerates without regularity. At high magnification in **Figure 2d**, particles have dense surfaces without pores or particular features. A normal micelle emulsion (o/w) consists of aqueous continuous phase that will not limit the growth of particles in aqueous phase, such as hydrolysis/condensation reaction, but limit the reaction in organic phase. Therefore, we cannot control the growth of boehmite particles in a normal micelle system.

A surfactant can form either reverse micelle or normal micelle based on its HLB value. Reverse micelle can be formed when HLB = 4-8. CTAB with HLB = 7.375 tends to form reverse micelle based on HLB theory [24]. We can get a stable reverse micelle emulsion using CTAB surfactant. **Figure 2e** shows that CTAB reverse micelle results spherical particles with a wide size distribution. **Figure 2f** details the morphology of particle, showing aggregated nanoplates randomly arranged in a spherical cage forming a 3D open channel structure. **Figure 3** shows the typical characteristics of synthesized particles using CTAB reverse micelle templating. In high magnification, we can see that the particles were composed of nanoplates with size 20-40 nm (**Figure 3a**). The particles have a size distribution in range 0.5-6 μm and average size 2.54 μm (**Figure 3b**). This particular shape and morphology of particles were formed by nucleation and growth of crystallites in the water-pool of reverse micelle. The reverse micelle limits the growth of crystallites and directs their aggregation to form a spherical particle. The possible formation of nanoplate is initiated by nucleation of seeds in the water-pool followed then by growth of crystallites. The spherical shape of reverse micelle facilitates the self-assembly of the nanoplate crystallites to form a spherical particle consists of randomly arranged aggregated nanoplates. Spherical particles provide additional mechanical strength with respect to irregular shape particles due to their high density when they are arranged in a closed packed structure.

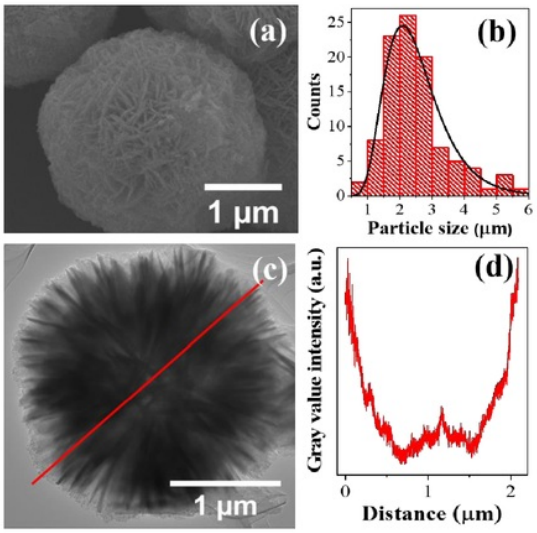

Figure 3. (a) SEM image; (b) particle size distribution; (c) TEM image; (d) TEM profile of synthesized particle using CTAB surfactant forming reverse micelle.

We also observed the internal morphology of synthesized particles using HR-TEM and analyzed the TEM profile using ImageJ software. **Figure 3c** reveals their internal morphology,

where the nanoplates arranged randomly forming abundant open passages as depicted by bright areas. The bright areas represent the intercrystallite spaces between nanoplates. These open passages have interconnected each other deep into the center of particle. This is confirmed by the presence of gray value intensity peaks in the center of particle as shown in **Figure 3d** These passages represent a 3D open channel structure.

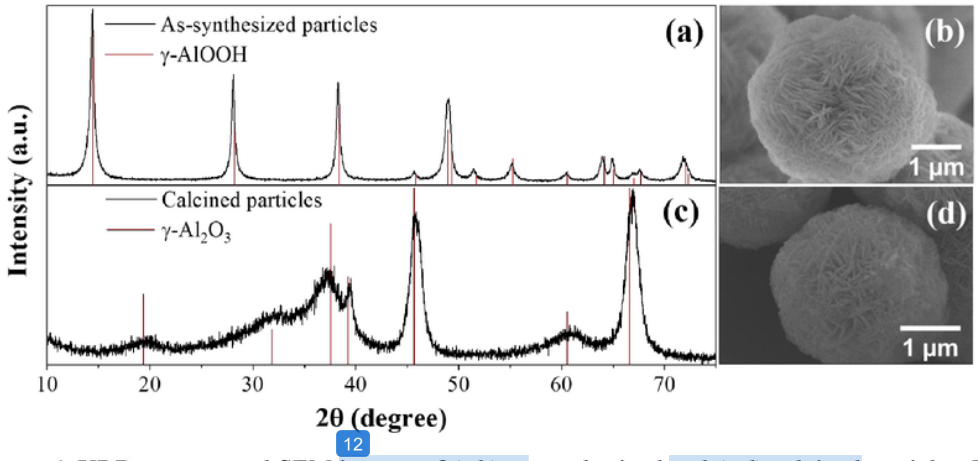

Figure 4. XRD patterns and SEM images of (a,b) as-synthesized and (c,d) calcined particles. The reference γ-AlOOH and γ-Al_2O are JCPDS card 021-1307 and JCPDS card 10-1245, respectively as published by Tang and coworkers [21].

We also investigated the structure of as-synthesized and calcined particles using XRD. XRD patterns in **Figure 4a** and **4c**, show that diffraction peaks of both as-synthesized and calcined particles are matched with their references the orthorhombic γ-AlOOH (JCPDS card 021-1307) and cubic γ-Al_2O_3 (JCPDS card 10-1245), respectively. No peaks from other phases are observed in both diffractograms indicating that the as-synthesized particles are boehmite and the calcined particles are γ-Al_2O_3, respectively. We cannot see any significant changes on particle morphology after calcination at 550 °C (**Figure 4b** and **4d)**. It indicates that there is no massive structural deformation during boehmite to γ-Al_2O_3 transformation deteriorating particle morphology. Thus, we can synthesize nanostructured γ-Al_2O_3 only by controlling the shape and morphology of γ-AlOOH.

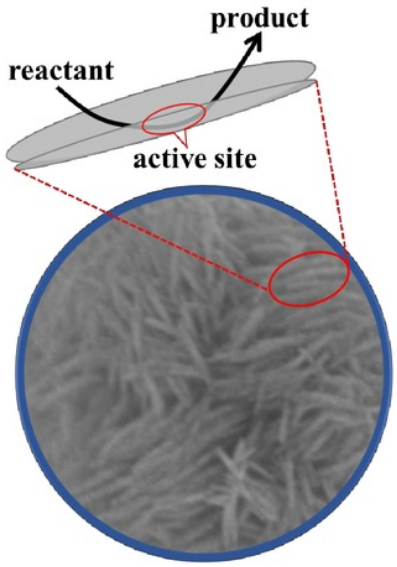

Figure 5. Illustration of reactant accessibility in γ-Al_2O_3 spherical nanostructured particles.

Open channel structures of γ-Al_2O_3 provide wide potential applications, such as catalyst or catalyst support due to its high accessibility. **Figure 5** illustrates reactants/products accessibility in γ-Al_2O_3 particles. The open channel structures facilitate the diffusion of reactants/products into/from the catalytic sites, respectively. This feature will break the diffusion limitation of the closed channel system and avoid the formation of cokes. 3D arrangement of the open channels provides more accessible active sites than the conventional structure.

4. Conclusions

Spherical nanostructured γ-Al_2O_3 can only be obtained from a stable reverse micelle emulsion using CTAB. CTAB reverse micelle template successfully limits the growth of particles directing the formation of spherical γ-Al_2O_3 consists of randomly arranged nanoplates in a spherical cage. The aggregated nanoplates provide a 3D open channel structure with more accessible active sites. Spherical nanostructured γ-Al_2O_3 open wide potential applications, notably in catalysis due to its high density closed packed structure, large surface area and high accessibility.

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