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The utilized of aluminium (Al) for boehmite as catalyst: Brief review

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Abstract
Boehmite is one of the aluminium derivatives that consists of oxygen and hydroxyl groups. Boehmite is a very profitable material with a promising future, notably as a catalyst for the production of other chemicals. Surface modification of boehmite can be done with different functional groups to produce supported-catalysts, catalysts, adsorbents, reagents, membranes, coatings, optical materials, corrosion inhibitors, and composite materials. Synthesis process influences the properties of boehmite. Specific properties are needed to produce a specific application of boehmite, as every application requires specific properties. The shape, structure, and morphology of the boehmite depend heavily on the treatment and the condition of the process. To manufacture high-quality boehmite with economic and environmental friendly, it is necessary to evaluate the effectiveness of the production process. This review provides a brief explanation of the publicly available information published in recent years on the synthesis of boehmite with various synthesis method.

Keywords: Boehmite, catalyst, nanomaterial, synthesis method

1. Introduction

To increase process efficiency, catalyst is used in the majority of chemical manufacturing. The industry depends heavily on catalysts for chemical processes. Approximately 85-90% of chemical products are synthesized with catalytic process [1]. Catalysts offer a different and more energy efficient technique for producing materials and other chemical products. Homogeneous, heterogeneous, and enzyme categories are used to categorize catalysts [2]. The solubility of homogeneous catalysts is a cause of their high catalytic activity and selectivity [3]. Because homogenous catalysts are difficult to extract from the finished products, their use has been restricted. If the catalysts are not thoroughly removed, it results in the impurity of the final products. As a result of their insoluble and recoverable qualities, heterogeneous catalysts have received a lot of attention. Heterogeneous catalysts are less harmful to the environment since they are simple to handle, highly resistant to high temperatures, and have a lengthy deactivation process. Because of its characteristics and simplicity of modification, boehmite (γ-AlOOH) is one of the most beneficial minerals to utilize as a catalyst among the different materials available [4]. What's more, boehmite possesses a stable orthorhombic structure with a high density of hydroxyl groups on its surface, allowing for surface modification with different functional groups. Because of its characteristics and simplicity of modification, boehmite (γ-AlOOH) is one of the most beneficial minerals to utilize as a catalyst among the different materials available [4]. What's more, boehmite possesses a stable orthorhombic structure with a high density of hydroxyl groups on its surface, allowing for surface modification with different functional groups to produce expensive supported-catalysts, catalysts, adsorbents, reagents, biologically active compounds, cosmetic products, membranes, coating, optical materials, corrosion inhibitor, and composite reinforcement material in ceramic [5-7]. The method for producing boehmite plays an important role in the final products and it is used for further applications as different applications require different properties of products. Numerous techniques are now available to generate boehmite with specified properties that are also affordable and environmentally beneficial.

This review offers an important synopsis of the most recent advancements in the thorough investigation of the synthesis of boehmite using a variety of techniques. It examines the procedures used to create boehmite with the desired structures and properties, including the efficiency of the synthesis process and how it affects the final products.

2. An overview on boehmite

Aluminum hydroxide has been known for having four structural forms: boehmite (Gamma-monohydrate) and diaspore (Alpha-mono-hydrate), trihydrate, gibbsite (gamma trihydrate), and bayerite (alpha trihydrate) [8]. A study of the structure of boehmite was carried out by Johann Bohm (1925) [9]. X-ray technology has been used to evaluate boehmite's structure. These investigations reveal that the mineral is made up of two layers that are connected by a hydrogen connection between hydroxyl groups. The knowledge about structure and morphology of boehmite is important to understanding more.

2.1 1D, 2D, 3D of Boehmite Nanostructures

Nanomaterials can be classified as per the size and dimensions. There are four types of nanomaterials such as zero-dimension, one dimension, two dimensions, and three dimensions [10]. The chemical and physical properties of boehmite are strongly dependent on the experimental factors of its synthesis. Boehmite can be prepared by different synthetic methods which have different morphologies; including, hollow micro-sphere, nanorods, nanofibers, boehmite layered nanostructures, nano leaves, nanoflower, the butter-shaped three-quarters, 3D nanosheets, porous boehmite, and flake-like boehmite [8].

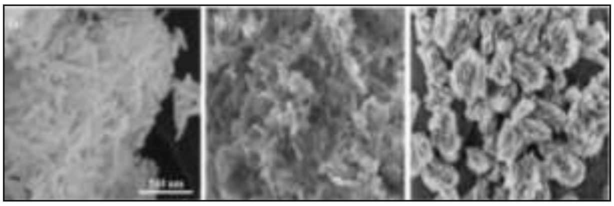

Fig 1: Structure of Boehmite; (a) 1D nanorods [11], (b) 2D nanosheets [12], (c) flower-like structure [13]

Chen *et al*. (2008) [14] studies about the effect of pH to structure of boehmite. The dominant morphology of the prepared particles in acidic conditions is nanorod, and the structure of the prepared particles in the basic environment is 2D nanoflake. Li's research group (2006) [15] reported that solvent has a special role in the structure of the nanosheet. The morphology of the particles is changed in different alcohols. Also, the morphology of the prepared boehmite depended on different temperatures [16].

2.2. Mechanism of Crystal Growth

A spontaneous morphological evolution method in nanoparticle synthesis driven by Ostwald ripening [17]. Ostwald ripening often refers to a process that involves the relocation of matter and involves the evolution of an inhomogeneous structure over time in solid solutions or liquid sols. The larger particles are more energetically favorable than the smaller ones, which results in an apparent higher solubility for the smaller ones. This leads to the ripening process [18]. Amorphous aluminum oxide changed into both small and large boehmite nanoparticles as the temperature was raised. Then, as some large nanoparticles were spontaneously transferred onto the surfaces of some small nanoparticles, the small nanoparticles gradually dissolved to create free ions in the solution, leading to the production of the uniform and well-developed 3D flower-like structure [13, 19]. Due to the instability of the original amorphous phase, slower phase transformations could generate more thermodynamically stable polymorphs of boehmite. The Ostwald ripening process, which is characterized by the growth of larger crystallites at the expense of the dissolution of smaller and less stable matrical products due to a decrease in surface energy, is what caused the increase in the quantity and average crystal size of the laminar boehmite particles [20].

3. Method for the synthesis of boehmite

Boehmite presented in natural as orthorhombic crystal while synthetic boehmite presented in amorphous or nanocrystalline [21]. The method for synthesis of boehmite is important not only to control the morphology and particles size but also crucial to its stability property to achieve long time stability of their dispersion [22]. The activity of boehmite as catalyst is strongly dependent on the method used in their preparation [23]. Recent studies explain influential parameters on synthesis of boehmite are crystal's shape, particle size, and surface area [12].

3.1 Hydrolysis Method

Boehmite can be made through hydrolysis. Hydrolysis is a process between a chemical compound and water to create two or more compounds, break chemical bonds, or combine two molecules into a single bigger molecule [24]. The hydrolysis process has the benefit of using inexpensive, environmentally acceptable materials [25]. The temperature was low during operation, but it took too long for the products to be synthesized.

Milanovic *et al*. (2018) [25] carried out the synthesis of boehmite at room temperature with the hydrolysis method. Sodium aluminate was used as a precursor and glucose was used to prevent the nucleation of gibbsite. The reaction was regulated using a pH ratio of 12-10, 8 and 10,8-9,5. Synthesized boehmite powders have an average particle size of less than 5 nm and a high surface area. It is possible to use glucose to produce boehmite with mesoporous structures. It was found that higher pH produces a higher surface area and a larger pore volume of boehmite.

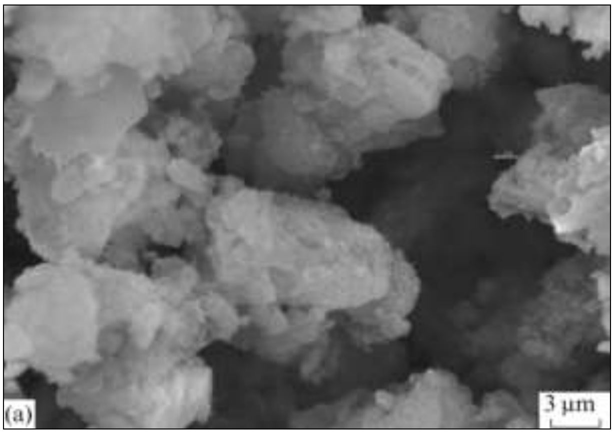

Fig 2: SEM image of boehmite mesoporous [25]

Stefanic and Music (2011) [12] synthesized boehmite with aluminum sec-butoxide as a precursor. Boehmite nanoparticles were prepared by rapid hydrolysis. The reaction was carried out in acidic or alkaline conditions. The temperature ranges from 90 to 120 °C. The results show that pH, temperature, and reaction time affect the synthesized boehmite as the particle size of boehmite is generally larger with the increase of those parameters. Rapid hydrolysis produces nano size boehmite.

3.2. Solvothermal Method

Nanoscale materials are frequently produced using solvothermal methods [26]. The solvent is boiled using this approach at temperatures higher than its boiling point and at pressures more than 1 bar [27]. In an organic solvent, precursors are combined; templates may be present or absent [27, 28]. Due to its adjustable parameter changes and operating conditions on material synthesis, solvothermal is touted as an effective technique [22]. To create boehmite via the solvothermal process, ethanol is frequently used as a solvent [22, 28, 29].

Synthesis of boehmite with a solvothermal method was carried out by Abdollahifar *et al.* (2018) [22]. As precursors, aluminum nitrate hydrate and aluminum chloride were used, and the solvent was 96% ethanol. The evaluated parameters are precursors, and pH in the number of 5 and 11. Boehmite nanoparticles are presented in an orthorhombic structure, a spherical shape, and in a single phase. Anions affect the crystallinity and morphology of boehmite. Aluminium nitrate produces boehmite with a higher crystallinity than aluminium chloride. Lower pH produces a higher surface area for products from both precursors. The researchers claimed that the solvent has a more significant effect on the characteristics of products.

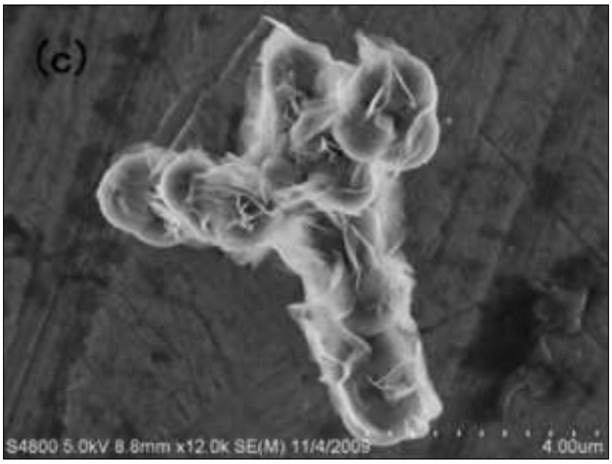

Fig 3: SEM image of flower-like boehmite [29]

Li *et al.* (2010) [29] prepared a synthesis of boehmite with flower-like morphology via simple solvothermal method. No surfactant was used in this research. Aluminium chloride hydrate is used as a precursor and mixed ethanol-toluene is used as solvent. The experiments were regulated using a volume ratio of toluene/ethanol. The Boehmite produced in this research is presented in an orthorhombic structure with high crystallinity. The particle size is smaller in the reaction with a low reaction temperature. Several boehmite nanosheets are joined to construct a flower-like morphology. Toluene has a more significant influence on the morphology of boehmite. Crytallites were homogeneously deposited with other particles in the absence of tolune. In the presence of toluene, armophous aluminium hydroxide adsorbs toluene, which causes a decrease in surface free energy.

In the absence of a template, Cai *et al.* (2013) [28] synthesized Boehmite by a solvothermal process. Aluminium chloride is used as a precursor, and ethanol and trisodium citrate dihydrate is used as solvent. The results show that boehmite produced with the solvothermal method has high purity and nanosized particles with a nanorod structure. The reaction could be shown as follows:

$$Al^{3+} + 148C_2H_5OH \rightarrow Al\,(OC_2H_5)_3 \cdot 145\,C_2H_5OH + 3H^+ \quad (1)$$

$$Al^{3+} + n\text{citrate}^{3-} \rightleftharpoons [Al\,(\text{citrate})_n]^{-3(n-1)} \quad (2)$$

$$Al^{3+} + H^+ + \text{citrate}^{3-} \rightleftharpoons AlH(\text{citrate})^+ \quad (3)$$

$$Al^{3+} + 2\text{citrate}^{3-} \rightleftharpoons Al\,(\text{citrate})_2{}^{3-} \quad (4)$$

$$Al\,(OC_2H_5)_3 \cdot 145C_2H_5OH + 3H_2O \rightarrow Al(OH)_3(\text{amorphous}) + 148C_2H_5OH \quad (4)$$

$$Al^{3+} + 3H_2O \rightarrow Al\,(OH)_3(\text{amorphous}) + 3H^+ \quad (5)$$

$$Al\,(OH)_3\,(\text{amorphous}) \rightarrow \gamma - AlOOH + H_2O \quad (6)$$

The concentration of trisodium citrate dihydrate plays an important role in the formation of the boehmite. The increase in trisodium citrate dihydrate concentration results in a well-defined hollow microsphere with a 600 nm thickness. Trisodium citrate dihydrate acts as a shape controller, stabilizer, and dispersant. Aluminium is coordinated with citrate to form A-citrate complexes that prevent amorphous aluminium hydroxide from precipitating. The unstable Al-citrate is assembled to form nanorods due to hydrogen bond interaction and with further transformation into stable microscophere s to decrease the surface energy under certain conditions.

3.3. Hydrothermal Method

Due to its low cost and environmentally favorable production technique, hydrothermal is the most widely used technology. The advantage of the hydrothermal method over solvothermal is that water, which is more affordable and environmentally friendly than other solvents, is employed as the process's solvent [30]. Boehmite is produced by a hydrothermal process as 1D nanostructures [11]. To acquire a given crystal orientation, boehmite particles can be adjusted by modifying hydrothermal conditions and solution. The disadvantage of this process is the lengthy period required to produce boehmite.

Synthesis of boehmite was carried out from alumina sols by He *et al.* (2022) [11] via hydrothermal methods. Aluminum sec-butoxide (ASB) was used as precursor to produce alumina sols. pH of alumina solution was evaluated. Temperature and time of hydrothermal process was evaluated. The temperature range in 160, 200, and 240 °C and the process were performed for 1, 2, 4, and 8 days respectively. The optimal condition for preparing boehmite is at 160 °C and 4 days. One of the causes for limiting the growth of boehmite in the 1D direction is the excessive hydrothermal temperature. The solubility of boehmite increases with greater hydrothermal temperatures while the relative solvent saturation decreases, resulting in larger size particles. Boehmite's structure is influenced by time; as time passes, it gets longer and coaser. Additionally assessed was the impact of the acetic acid employed in the hydrothermal treatment. The directed control of boehmite is accomplished by the use of acetic acid as a shape-directing agent. Along with an increase in alcohol content, larger boehmite crystal were also created. The creation of isotropous granular morphology and suppression of 1D growth occur when too much alcohol is introduced, resulting in bigger crystals with slower coagulation. Boehmite growth can be enhanced by stirring patterns in the hydrothermal reactor.

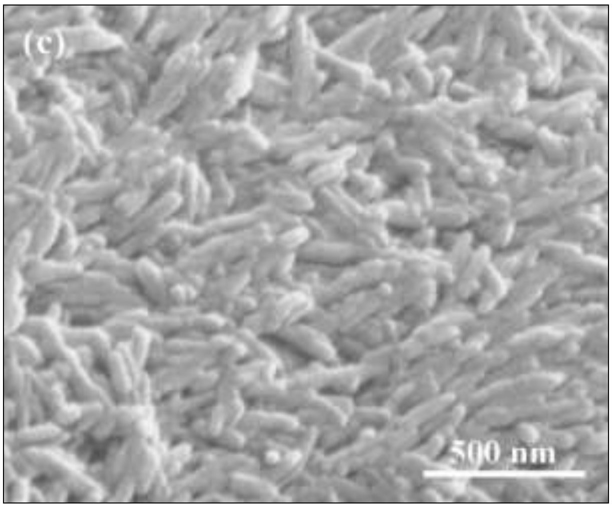

Fig 4: SEM image of boehmite nanorods [11]

Kozerozhets *et al*. (2020) [31] carried out hydrothermal method for synthesis of boehmite nanosized powder. γ-Alumina is used as precursor with hydrochloric acid and water performs as solvents. The optimal condition to produce boehmite are at 170 °C and 24 hours. Boehmite appears as large agglomerates of particles with an average crystal size of 20 nm. This experiment demonstrates that regardless of the temperature of synthesis, boehmite powder has comparable characteristics. The characteristics of the boehmite created in this experiment are suitable as a sorbent for wastewater, an additive to paints and varnishes, and as a compound to enhance the capabilities of thermal insulation.

3.4. Sol-Gel Method

Sol describes colloidal suspensions of solid particles in the liquid phase that contain small enough solid particles to exhibit Brownian movements. A network of solids that contains a combination of hardly distributed liquid is referred to as a "gel." Typically, the sol-gel technique is a way to make solids at low temperatures by condensation and hydrolytic processes, such as ceramics [32, 33]. The creation of nanomaterials using the sol-gel method is more expensive than using other techniques, which may make them less appealing to researchers. Sol-gel method also need a quite long time until the product is perfectly formed. However, numerous attempts to create boehmite using this method have been made.

Boehmite was synthesized via sol-gel method by Lueangchaichaweng *et al*. (2019) [23]. Aluminium source was obtained from aluminium tri-sec-butoxide. Ammonia solution diluted with absolute ethanol is used as solvent. Boehmite obtained from this experiment has small size and high surface area with orthorhombic structure. The product has similar dimensionality to the length of the nanorods.

Hosseini *et al*. (2019) [34] carried out sol-gel method to produce boehmite nanoparticles that used for biodiesel production from soybean oil. Aluminium nitrate hydrate is used as precursor and the reaction takes place in alkaline condition in the presence of sodium hydroxide and distilled water as solvents. The sol-gel method is relatively expensive to prepare nanomaterials, which may be less interesting to researchers than other methods. But, a wide variety of works have been done to synthesize boehmite using this technique.

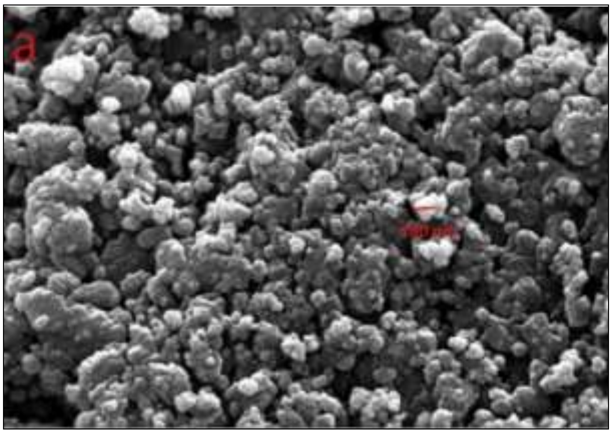

Fig 5: SEM image of boehmite nanoparticles [34]

4. Conclusion

The path of inventive synthetic techniques, which primarily concentrate on environmental issues of chemical or organic synthetic reactions such as the use of green materials and catalysts, is changing the course of organic synthesis in the modern day. The exceptional of mechanical and chemical stability of boehmite make them desirable choices. The design and creation of a specific organic reaction-specific catalyst is the most crucial component of boehmite-based catalysis, considering the potential for commercial applications, the mechanistic process, and the viability of performing reactions. This review describes numerous processes for producing boehmite. The used of mineral sources are also an interesting subject for further research. However, many of the offered tsechnologies still need to be improved in order to be practical and economical for the production of boehmite.

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