Granulation of Sol-Gel-Derived Nanostructured Alumina

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A sol-gel granulation process was developed to prepare porous nanostructured γ-alumina granules as supports for catalysts and adsorbents. The process, which starts with an aqueous sol of gelatinous boehmite, involves droplet formation, gelation in paraffin oil, conditioning in ammonia solution, and drying and calcination in air under controlled conditions. The γ-Al_2O_3 granules prepared are 1–3 mm-dia. spherical particles with large surface area (380 m^2/g) and pore volume (0.5 cm^3/g), uniform pore-size distribution (20–60 Å), and controllable average pore size (35 Å). These sol-gel-derived granules have excellent mechanical properties with crush strength (>100 N per granule) and attrition resistance (< 0.01 wt. %/h), much better than the commercial alumina and zeolite granules. Supported CuO sorbents were prepared on these granules for SO_2 removal applications. The alumina-supported CuO sorbents contain higher loading of well-dispersed CuO and better sulfation properties than similar sorbents reported in the literature.

Introduction

The performance of solid catalysts and adsorbents critically depends on the size, shape, pore texture, and mechanical strength of the support bodies. The shapes and sizes of the commonly used catalysts and adsorbents in industry usually include (Cahen et al., 1979) (1) pellets or cylinders (diameter 3–7 mm; length 3–7 mm); (2) extrudates (diameter 1.5–5 mm; length 2–8 mm); and (3) spheres (diameter 1.5–5 mm). Support bodies, catalysts and adsorbents of different shapes and sizes are being manufactured on an industrial scale by (1) extrusion, (2) granulation, (3) spray drying, (4) tabletting, and (5) sol-gel process. Extrusion and granulation are relatively inexpensive processes, and tabletting is the most expensive process. Although the sol-gel process is relatively expensive, it is a very promising and attractive process for fabrication of supports, catalysts, and adsorbents because the sol-gel process has a much better control of both physical and chemical properties of the processed materials.

Catalysts or adsorbents used in the moving beds or fluidized beds are practically produced as spherical granules by granulation, spray drying, and sol-gel processes. Granulation technique relies upon the buildup of the smaller particles into spheres by means of a rolling, or "snowball" technique. The production costs for this type of process are low, but the spheres are irregular and the particle sizes are randomly distributed. In the spray-drying process, feed solids in a fluid state are dispersed in a gas and converted into solid granules by heat or mass transfer. The spheres manufactured by the spray-drying technique are about 50 to 200 μm. They have good attrition resistance, but their sizes are so small that entrainment loss of solid particles with the gas flow in fluidized beds is very significant. A few studies were reported on the preparation of large spherical granules (typically in the range of 100 μm to 5 mm) by gelation of individual droplets generated from colloidal suspension by the so-called "oil-drop" method (Capes and Fouda, 1984; Lapes, 1986; Komarneni and Roy, 1985; Trüdinger et al., 1990; Ramsay, 1994; Marella et al., 1995). This oil-drop method, as reported mainly in the patent literature, has been successfully used to synthesize spherical silica (SiO_2) or zeolite granules (Yakov et al., 1978; Spek and van Beem, 1982; Barten et al., 1987; van der Grift et al., 1991; Kiel et al., 1992). Preparation of granular alumina supports by the oil-drop method starting from a suspension made of alumina powders was also reported recently (Shepeleva et al., 1991; Svoboda et al., 1993; Duisterwinkel and Frens, 1995). The spheres manufactured by individual

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shaping (oil-drop method) are more expensive. However, their shape and calibration are quite regular.

It was reported that the poor attrition resistance of alumina-supported copper oxide sorbents was the major setback of the fluidization flue-gas desulfurization (FGD) process (Cull, 1978; Yeh et al., 1985). The attrition of the adsorbents or catalysts in the moving beds or fluidized beds will result in loss of catalyst or adsorbent material, generation of fine powder and particulate pollution downstream, and an increase in process costs. Moreover, the change in the granule size might influence the properties of the catalyst or adsorbents. In order to reduce the mechanical attrition of the solid catalysts or adsorbents in the moving beds or fluidized beds, it is ideal that these spheres have a smooth surface and high mechanical strength. In some environments, such as the flue-gas desulfurization process, the catalysts/adsorbents have to be exposed to some caustic fluids or oxidative and reductive atmospheres at high temperature. Chemical and thermal attrition of the support body and active species of the catalysts/adsorbents may be very significant. Thus it is also required that the catalysts/adsorbents have high thermal- and chemical-attrition resistance in these situations.

γ-Alumina is perhaps the most common crystalline material used as a support body for catalysts or absorbents. Preparation of porous γ-alumina granules with excellent mechanical properties and desirable pore structure is of great importance to the development of novel catalysts and adsorbents for various applications such as the flue-gas desulfurization process. The superior mechanical properties can be derived from the microstructure of the granules, which is defined by compacting nanoscale γ-Al_2O_3 crystallite particles bound together by the bridges of the same material formed through coarsening or sintering. To attain high surface area of the granules it is preferable that the γ-Al_2O_3 crystallites be within a few nanometers. Sol-gel-derived γ-Al_2O_3 prepared by the Yoldas process (Yoldas, 1975; Leenaars et al., 1984; Lin et al., 1994) exhibits the desired nanoscale microstructure.

This article reports preparation of sol-gel-derived porous nanostructured γ-Al_2O_3 granules based on a granulation process that combines the Yoldas process and the oil-drop method. Our main objective is to develop a method to prepare porous alumina granules with excellent mechanical properties (high crush strength and attrition resistance) and desired pore structure (large surface area and meso pore size). Preparation and sulfation properties of CuO sorbent supported on the γ-Al_2O_3 granules are also reported to illustrate application of these granules as support for catalysts and adsorbents. The supported CuO sorbents have potential for use in flue-gas desulfurization process. The principle of the sol-gel granulation process developed in this work may also be applied to the preparation of other spherical supports, catalysts, and adsorbents from gel-forming precursors.

Experimental Studies

Synthesis of spherical γ-alumina supports and supported CuO sorbents

Figure 1 shows the formation of spherical supports and adsorbents by the sol-gel granulation method. Procedures of the process include generating sol droplets by a dropper, shaping and partially gelating the droplets into spherical wet-gel granules in a paraffin oil-layer, and converting the wet-gel granules into solid gel granules by gelating and aging them in an ammonia layer. A reaction column (ID: 50.8 mm) filled with 1.0 m paraffin oil and 0.15 m ammonia solution was used as the γ-Al_2O_3 gelation medium. The paraffin oil-layer (white, density: 0.7864 g/cm^3, kinematic viscosity: 34.5 centistokes at 40°C, Fisher Scientific) was heated at 90–100°C during the granulation experiments, and the ammonia solution layer (15% NH_3) was kept at room temperature.

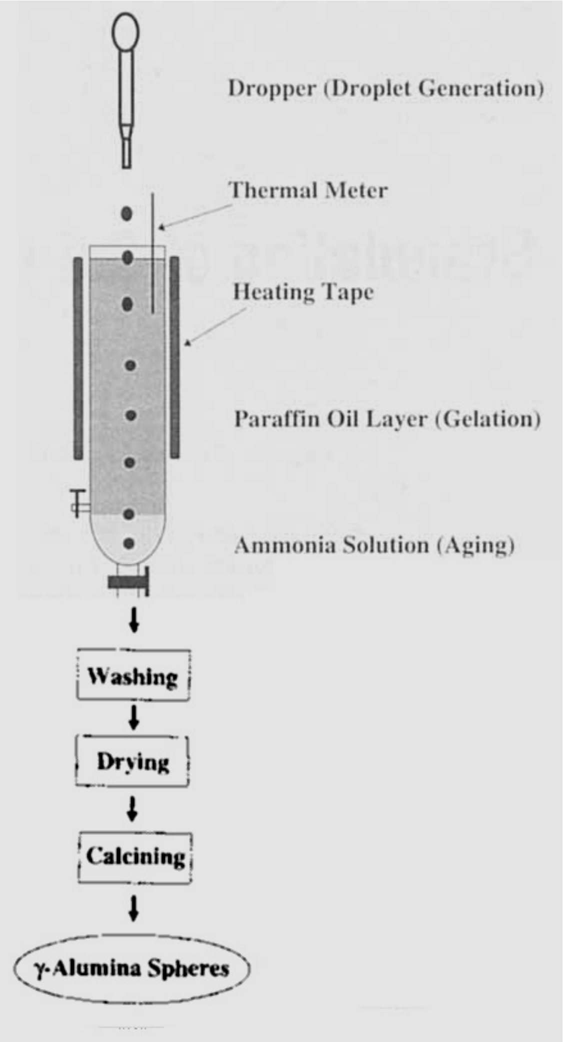


Figure 1. Sol-gel granulation method.

The sol-gel fabrication of the spherical γ-alumina granules started with an aqueous sol of pseudoboehmite (gelatinous boehmite). The first step was to prepare 2 M boehmite sol (γ-ALOOH) using the Yoldas's process (Yoldas, 1975). The 2 M boehmite sol was synthesized by dissolving alumina-tri-secondary butoxide (97%, Janssen) in the deionized water while stirring vigorously at an initial temperature of 75°C. After heating at 90°C for 1 h, the resulting slurry with γ-ALOOH precipitates was peptized with 1 M HNO_3. The peptized sol was refluxed at 90 ~ 100°C for 10 h to yield a stable boehmite sol. The pseudoboehmite sol was prepared by adding nitric acid or nitric acid mixed with urea into the 2 M boehmite sol to adjust the pH of the boehmite sol. Different pH values of the starting boehmite sol ranging from 1.45 to 9.55 were applied in this work. The final pseudoboehmite sol used in the sol-gel granulation processes was then obtained by heating and stirring the sol at 50°C for 1 h. In some granulation experiments, a water-soluble organic monomer (acrylic acid) was also added into the pseudoboehmite sol as a polymerization initiator before dropping the sol into the oil layer.

The starting pseudoboehmite sol was dispersed into droplets by a dropper. The droplets were then suspended in the immiscible paraffin oil layer. The droplets in spherical shape (due to the surface tension) transformed to wet-gel granules while falling through the oil layer as a result of partial gelation. A small amount of surfactant (liquid soap) was added to the oil layer to facilitate the formation of a thin oil film around the surface of the wet-gel granules. This oil film would protect the integrity of the wet-gel granules while they were falling into the ammonia solution underneath the oil layer. During aging in the ammonia layer, ammonia would penetrate through the oil film to neutralize the acid in the partially gelated sol in the wet-gel granules. Thus, the wet-gel granules were further gelated, aged, and became solid granules in the ammonia layer. The wet-gel solid granules formed from this process were then withdrawn from the forming reactor, and washed with water and ethanol to remove most of the oil and water. The wet-gel granules were dried in an oven at 40°C and high humidity for more than 10 h, followed with calcination at 450°C for 3 h under controlled heating and cooling rates. Boehmite was converted to γ-alumina during the calcination step (Leenaars et al., 1984; Chang et al., 1994; Lin et al., 1994). Droppers of different sizes were used to control the particle size of the final granules.

The effects of sintering temperature on the pore structure and mechanical properties of the γ-alumina granular supports were investigated by comparing the initial pore and mechanical properties of the sample to those after heat-treatment at different temperatures. The γ-alumina granular supports were heated in the furnace in air at 600 or 700°C for 30 h with a heating rate of 30°C/h and a cooling rate of 100°C/h. This experiment was designed to study the thermal stability of the pore structure and stiffness of matrix of the γ-alumina granular supports.

A wet-impregnation method was used to prepare the γ-alumina-supported copper oxide sorbents. The precursor solution for active species CuO was prepared by dissolving $Cu(NO_3)_2$ (ACS grade, Fisher Scientific) in water. In coating the active species, the sol-gel-derived γ-alumina granular supports, after heat-treatment at 200°C for several hours, were brought into contact with the solution containing the active species for more than 16 h. The impregnated samples were dried in a vacuum oven at 200°C for more than 10 h, and calcined in a furnace at 550°C under air atmosphere for 6 h to convert $Cu(NO_3)_2$ into copper oxide. The weight ratio of the active species (CuO) to the support in the final sorbents was estimated from the weights of support, volume, and concentration of Cu^{2+} in the solution used in the wet-impregnation step.

Property study

The appearance, calibration, sphericity, and diameter of the prepared spherical γ-alumina granules were examined by light microscopy (Olympus, type SZH). A nitrogen adsorption porosimeter (Micromeritics, ASAP 2000) was used to determine the pore-texture data, including the BET surface area, pore volume, pore-size distribution, and average pore size of these γ-alumina supports and sorbents. The nitrogen adsorption and desorption isotherms were measured automatically at liquid-nitrogen temperature (77.5 K). Pore-size distribution and mean pore size were calculated from nitrogen desorption isotherms using the BJH method with the software provided by Micromeritics. The crystalline structure of the supports and sorbents and the dispersion of the active species on the surface of the support were examined by an X-ray diffractometer (Siemens D-50, with radiation of CuKα1).

The crush strength of individual granular γ-alumina supports and sorbents of different sizes prepared in this work and some commercial supports and adsorbents were experimentally determined by a universal testing instrument (Instron 4465). During these experiments, a single granular support or adsorbent was placed between two smooth and parallel compression surfaces made of steel. One of the flat surfaces was mounted on the base of the loading frame of the instrument and the other flat plate was attached to a crosshead that moved toward the granule at a controlled speed of 2 mm/min. A compression load cell (force sensor, 0–400 lb) mounted on the moving crosshead was used to measure the force acting on the particle. Both the load force and displacement of the sphere were recorded by a computer. At the end of the test, the granule crushed or collapsed when the force applied on the granule was large enough, and an abrupt decrease of the force signal was detected. The maximum force load applied to break the granule was taken as the side crush strength.

Several attrition test methods are available to measure the attrition tendency of fluidized solids or moving solids in a drum (Doolin, 1993; Lee et al., 1993; Spek and van Beem, 1982). Many of these tests assign a number of the rate of attrition based on a practical engineering measure. For example, the percentage of particles reduced to less than a certain size in a specific time within a specific test apparatus may be used as an index describing the attrition propensity of the particulate solids. Among the established attrition test methods, the Peter Spence method is a simple and practical one (Spek and van Beem, 1982).

Figure 2 shows the Peter Spencer attrition setup applied in this work to measure the attrition rate of the alumina supports and sorbents. It consists of a motor, a motor controller, and a stainless-steel attrition testing tube (315 mm long, 10 mm ID) mounted at a point about 80 mm from the center. The tube rotated about an axis normal to the length at a controlled speed ranging from 20 to 200 rpm. In the attrition

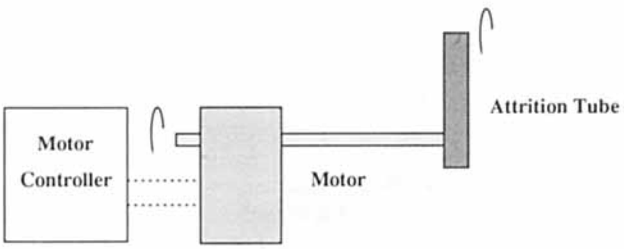


Figure 2. Peter Spence attrition apparatus.

Table 1. Experimental Conditions for Sulfation, Regeneration and Oxidation Stages in Figure 7

Stage		Flow Rate mL/min	SO_2 vol. %	CO_2 vol. %	CH_4 vol. %	Air vol. %	N_2 vol. %
A	Sulfation	600	0.8	0	0	99.2	0
B	Regeneration	500	0	0	10	0	90
C	Oxidation	500	0	0	0	100	0
D	Carbonation	600	0	15%	0	85	0
E	Sulfation with CO_2	600	0.8	15%	0	84.2	0

test performed in this work, about 5 g of granules were placed in the testing tube and tested at rotation speed of 60 rpm for 24 h. Thereafter the powder material generated during the attrition experiments was sieved off over a No. 35 sieve with mesh opening of 500 μm. The weight loss percentage rate (wt. %/h) calculated by the following equation was used as attrition index:

$$\text{Attrition index} = (\text{initial weight} - \text{remaining weight}) / \text{initial weight/time} \times 100\%$$

A microelectronic recording balance system (Cahn C-1000) described elsewhere in detail by Deng and Lin (1995b, 1996) was employed to determine the desulfurization properties of the γ-alumina-supported copper oxide granular sorbents. About 100 mg of sorbent particles were put in the sample basket made of stainless-steel sheet, which was suspended in a vertical quartz tube 2 in. in diameter. The transit weight change of the sample exposed to various gas streams was measured. Gas flows from certified gas cylinders were controlled by the mass-flow controllers and blended to generate desired sulfation, regeneration, and oxidation gas mixtures. Sulfation curves were measured at 500°C with an air stream containing 0.8% SO_2 at a total flow rate of 600 mL/min. The sulfated sorbents were regenerated at 500°C with a gas mixture containing 10% CH_4 and 90% N_2 at a total flow rate of 500 mL/min. Oxidation of the regenerated sorbents was carried out in the balance at the same temperature with a flow of air at flow rate of 500 mL/min. The experimental conditions are summarized in Table 1.

Results and Discussion

Optimal preparation conditions

Experiments showed that it is difficult to form unbroken γ-alumina wet-gel granules of relatively large size (1–3 mm) by the sol-gel granulation method, starting from 1 M boehmite sol commonly used to synthesize γ-alumina nongranular powdered supports and membranes (Deng and Lin, 1995a, 1996; Lin et al., 1994). Apparently the particulate concentration (6 wt. % of AlOOH) of the 1 M boehmite sol was too small for partial gelation of the sol in the droplets while falling through the oil layer. So in this work 2 M boehmite sol was synthesized and used to form the starting pseudoboehmite sol. In order to determine the solid concentration of AlOOH in the pseudoboehmite sol prepared in this work, 5 g of pseudoboehmite sol was dried and calcined under the standard conditions for preparing γ-Al_2O_3 (Chang et al., 1994), and about 0.735 g of γ-Al_2O_3 was obtained. From this experimental result the solid concentration of AlOOH in the pseudoboehmite sol prepared in this work was estimated to be 17.3 wt. %.

Table 2 summarizes several different γ-alumina granule samples prepared by the sol-gel granulation method using the pseudoboehmite sol derived from 2 M boehmite sol under various experimental conditions. As shown in Table 2, the optimal pH range of the pseudoboehmite sol for obtaining integral wet-gel granules was found to be 1.55 ~ 1.75. Samples AL-S-2 and AL-S-3 prepared from the pseudoboehmite sol with a pH of 1.65 were found to be the best in terms of the granule integrity and sphericity. The difference between these two samples was that sample AL-S-3 was prepared from the pseudoboehmite sol with the addition of 0.5 wt. % acrylic acid. It is believed that introduction of the organic monomer as a polymerization initiator could promote the formation of rigid bonds among the particles in the granule (Cahen et al., 1979). After calcination at 450°C for 3 h sample AL-S-2 was translucent, but sample AL-S-3 was light brown, which changed to translucent after heat-treatment at 600°C for more than 2 h. It will be shown in the following sections that these two samples have identical pore structure and similar mechanical properties. So the addition of organic monomer to the starting pseudoboehmite sol has not significantly improved the pore structure, integrity, and hardness of the granules obtained.

Other samples (AL-S-1, AL-S-4 to AL-S-6) obtained from the pseudo boehmite sol with pH values beyond the optimal range (1.55–1.75) determined in this work did not have the required integrity. This clearly shows that the pH value of the starting pseudoboehmite sol or the addition of acid or base to the starting sol is very critical to the formation of the integral and rigid spheres by the sol-gel granulation method. Although the addition of urea to the pseudoboehmite sol can enhance the gelation of the droplet in the oil layer by increasing the pH of the droplet due to the formation of ammonia by the decomposition of the urea, the residual urea in the wet-gel granules was difficult to remove and would have a detrimental effect on the integrity of the granules formed.

Table 2. Preparation Conditions of Spherical γ-Alumina Granules

Samples	pH of Sol.	Addition of Additive	Sphericity of Wet Particle	Sphericity of Dry Spheres
AL-S-1	1.45	None	Broken	N/A
AL-S-2	1.65	None	Good	Good
AL-S-3	1.65	0.5 wt. % acrylic acid	Good	Good
AL-S-4	1.77	None	Fairly good	Fairly good
AL-S-5	2.10	5.0 wt. % urea	Fairly good	Broken
AL-S-6	9.55	None	No large spheres	N/A

The γ-alumina granules (Sample AL-S-5) made from the pseudoboehmite sol with addition of urea exhibit poor mechanical strength.

After aging in the ammonia solution and being separated from the liquid medium the alumina wet-gel granules became rigid enough to be transported, washed, and dried. The washing step is necessary to remove those impurities such as ammonium nitrate, nitric acid or ammonia, and hydrocarbons in the wet-gel granules before the drying process. Trüdinger et al. (1990) have described a very comprehensive washing and drying method for the sol-gel preparation of titania and zirconia microspheres. It was found in this work that removing hydrocarbons from the wet-gel granules by washing with ethanol was necessary in order to obtain perfect alumina spheres with the desirable pore structure and mechanical properties. The wet-gel solid granules shrank about two times in diameter after drying and calcination. By changing the size of the dropper, spherical γ-alumina granules with different diameters ranging from 1 to 3 mm were prepared. Among these samples a large quantity of the spherical γ-alumina granules with diameter of around 1.75 mm was prepared and used as supports for granular copper oxide sorbents.

Sphericity and pore structure

Some of the γ-alumina spheres obtained were examined by light microscopy. A microscopic view of the granules prepared in this work is shown in Figure 3. A close look at a single granule, as shown in Figure 3a, clearly reveals that the γ-alumina granule (diameter: 1.75 mm) obtained is a spherical particle with smooth surface that does not have any cracks or protrusions, and particle fragments. Figure 3b shows that the multiple granules prepared under the same experimental conditions are nonaggregated spherical particles without lumps. The particle sizes of these granules are uniform. The smooth spherical shape and narrow particle-size distribution provided the necessary homogeneity of γ-alumina support for catalysts or absorbents for use in fixed-bed, moving-bed, or fluidized-bed reactors. Experiments performed in this work showed that it was easy to make good spherical and smooth γ-alumina granules with diameters smaller than 3 mm using the sol-gel granulation method developed in this work. Bigger particles had the tendency to deform during the washing and drying stages. It will be much easier to control the particle size and obtain more uniform particles when this method is scaled up for the production of the γ-alumina granules or other granular supports, since calibrated orifices of different sizes can be used and the generation of sol droplets can be performed by spraying the starting sol into the oil layer.

The nitrogen adsorption isotherms of all the samples are of Type IV, as shown in Figure 4a for sample AL-S-2. The desorption hysteresis loop indicates that these sorbents have a mesoporous pore-size distribution, as shown in Figure 4b for sample AL-S-2. The BET surface area, pore volume, average pore size, and pore-size distribution range for these sorbents are in Table 3. All the sorbents have a narrow pore-size distribution (20 ~ 60 Å) with an average pore diameter of around 35 Å. These results show that the pore structure of the γ-alumina granules prepared in this work is similar to that of the γ-alumina powders or membranes prepared from 1 M boehmite sol reported previously (Leenaars et al., 1984; Deng and Lin, 1995a, 1996; Lin et al., 1994). The single-model pore-size distribution also indicates that the granules may not contain aggregates of γ-Al_2O_3 primary particles.

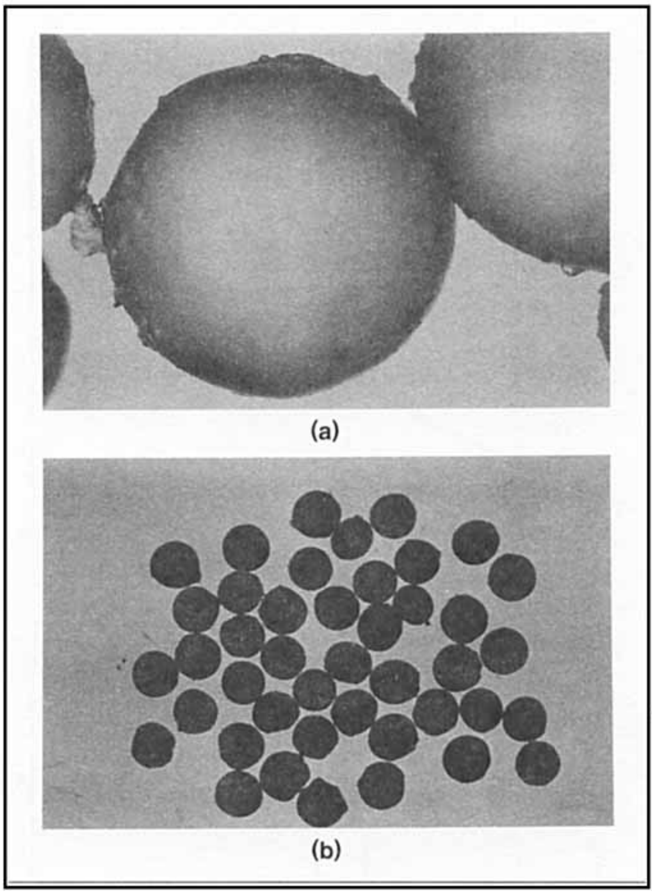
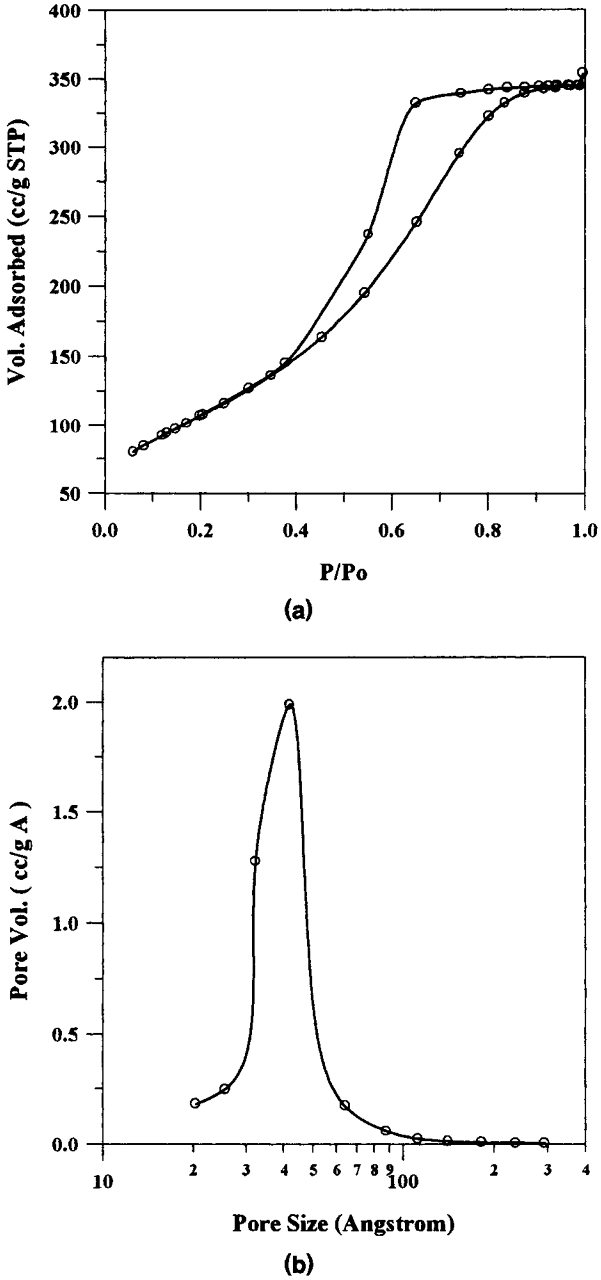


Figure 3. Microscopic view of spherical γ-alumina granules: (a) single granule; (b) multiple granules).

As shown in Table 3, the BET surface area, pore volume, pore-size range, and median pore size are the same for samples AL-S-2 and AL-S-3. This indicates that the γ-alumina granules prepared by the sol-gel granulation method were reproducible, and the addition of a small amount of organic monomer to the starting pseudoboehmite had negligible effect on the pore structure of the γ-alumina granules. The pore structure of the γ-alumina granules prepared in this work were mainly determined by the properties of the starting pseudoboehmite sol, and the drying and calcining conditions. The BET surface area (>380 m^2/g) obtained on the γ-alumina granules prepared in this work is about 30–90% larger than the reported values of the BET surface area (200 ~ 300 m^2/g) of γ-alumina spheres prepared by other methods (Cahen et al., 1979; Shepeleva et al., 1991; Svoboda et al., 1994).

Sample AL-P-7 was prepared by directly drying the starting pseudoboehmite sol in a petri dish at 40°C and about 50% relative humidity, followed by calcination at 450°C in air for 3 h (Chang et al., 1994; Lin et al., 1994). It is γ-alumina in small pieces (size 10–500 μm), and is referred to as the powder sample. As compared with the γ-alumina granules ob-



(a)

(b)

Figure 4. (a) Nitrogen adsorption isotherm on spherical alumina granular sample AL-S-2; (b) its corresponding pore-size distribution.

tained by the sol-gel granulation method shown in Table 3, sample AL-P-7 has a smaller BET surface area and pore volume. Several stages involved in the forming of the granules might contribute to an improvement in the pore structure of the γ-alumina granules. The interfacial energy of the gel particles would be reduced and less shrinkage would be expected when the pseudoboehmite sol droplets are gelled in the hot paraffin oil layer. Aging the particles in the ammonia solution might change the surface properties and enhance the pore structure of the wet-gel particles, since ammonia is an unusual interfacial solvent. Using alcohol to extract oil and water during the washing stage might also reduce the interfacial energy during the drying process of the alumina particles.

Table 3. Pore Texture Data of the Sol-Gel-Derived γ-Alumina Supports

Samples Number	Form	BET (m^2/g)	Pore Vol. (cm^3/g)	Pore Size (Å)	Median Pore (Å)
AL-S-2	Granule	388.9	0.50	20-60	35.3
AL-S-3	Granule	384.8	0.48	20-60	34.0
AL-P-7	Powder	351.3	0.40	20-50	31.3

Crush strength and attrition resistance

Several supports and adsorbents, including the sol-gel-derived spherical γ-alumina granules prepared in this work, a commercial γ-alumina support (LD-135, in spherical shape, made by Alcoa), and two commercial zeolite adsorbents (DAY zeolite made by Degussa AG, and silicalite by Union Carbide Co., both cylindrical in shape), were tested for their crush strength. Figures 5a and 5b show the typical deformation (load-displacement) curves obtained in the crush-strength test for some commercial adsorbents and the sol-gel-derived spherical γ-alumina supports. As shown in Figures 5a and 5b, all the particles tested in this work are elastic. They follow basically the same type of deformation curves, but the maximum deformation distances are quite different for different samples. The sol-gel-derived γ-Al_2O_3 granules exhibit the largest relative deformation distance (40–70%) (deformation distance divided by the diameter). This is possibly the reason that the sol-gel-derived γ-Al_2O_3 granules have the highest crush strength and attrition resistance among these samples. Silicalite is very brittle, so no sharp deformation peak was was found in its deformation curve, as shown in Figure 5a.

All the spherical γ-alumina granules of different diameters have the same type of load-displacement curve, and the initial part of all the load-displacement curves (at low load) follows the same trajectory. As shown in Figure 5b the side crush strength (the maximum load to crush a particle) is proportional to the diameter of the granules tested in this work. The experimental side crush strengths of the sol-gel-derived alumina granules are compared with commercial samples in Table 4. As shown in Table 4, the largest crush strength obtained on the γ-alumina granules (diameter = 2.6–2.8 mm) prepared in this work is 190 N, about 4.5 times as large as that of the commercial alumina granular support (LD-350, diameter = 4–4.6 mm). The crush strengths of the two commercial zeolite adsorbents (extrudates) are less than 40 N, much smaller than that of the γ-alumina granules (diameter > 1.5) prepared in this work.

Attrition rate is one of the critical mechanical properties for adsorbents or catalysts used in moving or fluidized beds. The attrition resistance is also important for pellet adsorbents or catalysts used in fixed beds, since attrition also occurs during transportation of pellets, filling, and withdrawing pellets from the reactor. Several different mechanisms that have been identified to account for attrition of adsorbents used in the FGD process include static mechanical stress, kinetic stress, thermal stress, and chemical stress (Wolff et al., 1993). Among these different mechanisms, the attrition caused by mechanical stresses makes the most significant contribution. Two types of particle degradation are usually observed in the mechanical attrition of solid particles: "fracture" or deep disintegration of the adsorbent or catalyst particles, and "grinding" or the abrasive removal of the particle skin. Particle fracture yields an assortment of fragments from small size to large size (Doolin et al., 1993). The grinding mechanism leaves behind a particle reduced in size and quantity of fine particles. The forces to which the adsorbent or catalyst particles are exposed in the moving bed or fluidized bed unit involve mechanical motion between any given particle–particle or particle–wall interactions and high-speed-velocity impingement during movement of particles from vessel to vessel. These forces will result in both particle fracture and grinding in the moving beds and fluidized beds.

In attrition experiments, each granule sample after the attrition run was examined for its breakage and formation of particle fragments and fine powder. No breakage and particle fragments were found in all of the samples except for silicalite. Most of the silicalite extrudates were found broken into small particles and a certain amount of fine powder was generated after the attrition test. This may indicate that the attrition of silicalite pellets followed both particle fracture and abrasion mechanisms, and that the attrition of other granules follows the abrasion mechanism only. The attrition index of the sol-gel-derived spherical γ-alumina granules along with the commercial supports and adsorbents determined by the Peter Spence method are summarized in Table 4. Among all the samples listed in Table 4, the sol-gel-derived spherical γ-alumina granules prepared in this work have the smallest physical attrition index: 0.033 wt. %/h, about one-fifth of that of the commercial alumina granule (LD-350 of Alcoa). This clearly demonstrates that the sol-gel-derived spherical γ-alumina granules have exceptional attrition resistance. These results also indicate that the attrition of the sol-gel-derived γ-alumina granules prepared in this work follows the "fracture" mechanism (Doolin et al., 1993). In this case the attrition of the sol-gel-derived alumina granules is extremely low if the mechanical stress is not large enough to break the particles in the attrition test.

Results of the effects of heat treatment on the pore structure and mechanical properties of spherical γ-alumina granules prepared in this work are summarized in Table 5. The heat-treatment results in a decrease in surface area and an increase in the pore size of the γ-alumina granules. This trend is the same as that of sol-gel-derived γ-alumina membranes

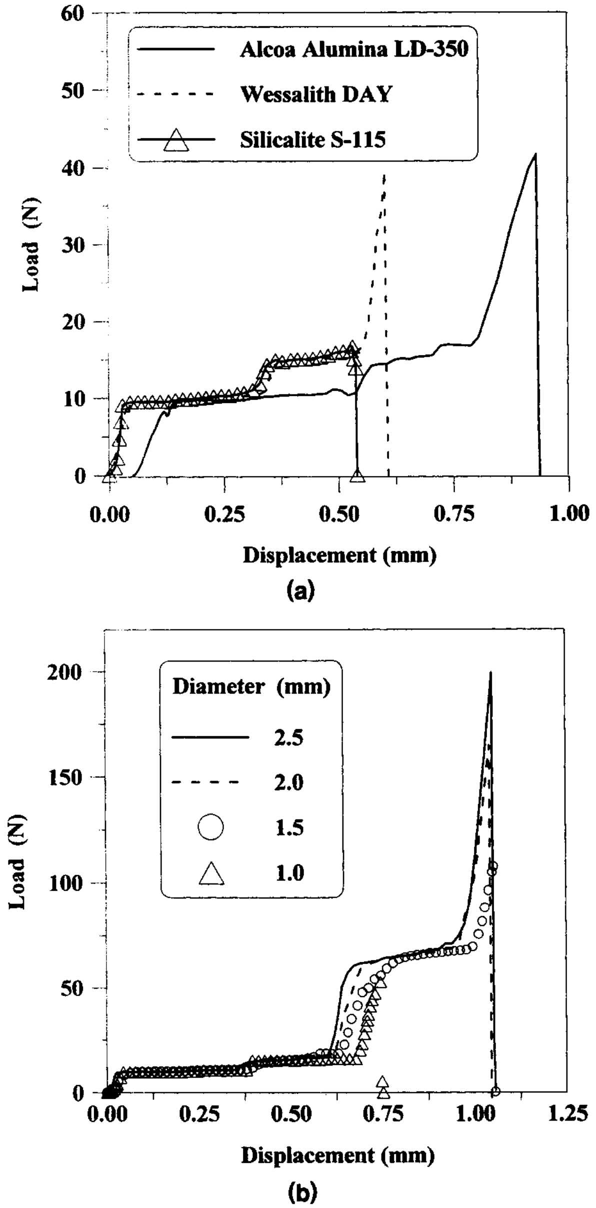


Figure 5. Deformation behavior for: (a) commercial adsorbents; (b) sol-gel-derived γ-alumina granules.

Table 4. Side Crush Strength and Attrition Index of Spherical γ-Alumina Granules and Some Commercial Adsorbents

Samples	Dia. (mm)	Avg. Dia. (mm)	Load (N)	Avg. Load (N)	Attrition Index (wt. %/h)	Attrition Wt. Loss (wt. %)
AL-S-2	2.6–2.8	2.7	175–203	190		
AL-S-2	2.0–2.5	2.2	158–165	160		
AL-S-2	1.5–2.0	1.75	93–129	112	0.033	0.785
AL-S-2	1.0–1.5	1.2	47–87	65		
AL-S-2	1.0–2.5	1.5	47–165	90		
AL-S-3	1.5–2.0	1.75	95–133	115		
AL-LD-350 (Alcoa)	4–4.6	4.25	35–49	42	0.177	4.25
Wessalith DAY (Degussa AG)	3.5–3.7	3.6	36–47	40	0.073	1.75
Silicalite (S-115) (Union Carbide)	1.4–1.6	1.5	10–24	16	0.575	13.8

Table 5. Temperature Effects on Pore Structure and Mechanical Properties of Spherical γ-Alumina Granular Supports and Sorbents

Samples	Temp. (°C)	BET Surface Area (m^2/g)	Pore Size (Å)	Avg. Pore Size (Å)	Crush Strength (N)	Attrition Index (wt. %/h)	Attrition Wt. Loss (wt. %)
AL-S-2	450	388.9	20–60	35.3	112	0.0327	0.785
AL-S-2	600	249.7	20–90	50.8	110	0.0076	0.182
AL-S-2	700	212.6	20–100	59.6	121	0.0060	0.144
CuO/γ-Al_2O_3	550	227.8	20–90	53.9	115	0.0088	0.211

(Chang et al., 1994; Lin et al., 1994). But the BET surface area of the γ-alumina granules decreases more rapidly and the pore-size distribution becomes wider after the heat treatment at the same temperatures as compared to the γ-alumina membranes. This is because the preparation procedures for the granules are different from those for membranes. The concentration of starting boehmite sol for granule preparation was 2 M, which is two times as concentrated as that for membrane preparation. Besides, the gelation of the granules in the ammonia solution would give the granules larger porosity due to the smaller interfacial energy, which would result in lower surface activation energy for sintering. The activation energy for sintering of the spherical γ-alumina granules, calculated from the surface-area data given in Table 5 using a surface-diffusion model (Lin et al., 1994) is 60 kJ/mol, about one-half that for the sol-gel-derived γ-alumina membrane or powder (Deng and Lin, 1996).

As shown in Table 5, the attrition resistance of the γ-alumina granules increases with the heat-treatment temperature, consistent with the reported experimental results on the attrition of alumina-based adsorbents and catalysts after heat treatments (Doolin et al., 1993; Wolff et al., 1993). This is basically because sintering at high temperatures made the bridging bonds between particles in the γ-alumina granules stronger. The crush strength is essentially the same for these γ-alumina granular supports before and after heat treatments.

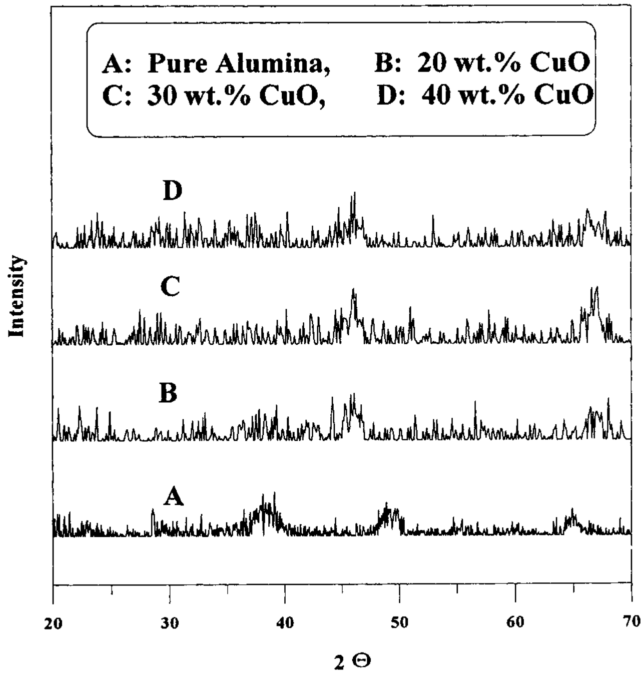


Figure 6. X-ray diffraction patterns for alumina granular support and supported copper oxide granular sorbents.

The excellent mechanical strength, high attrition resistance, and desirable pore structure of the spherical γ-alumina granules prepared in this work are the unique properties of sol-gel-derived ceramics. In synthesizing these granules, plate-shaped boehmite primary particles were formed and grew via the hydrolysis and condensation of aluminum alkoxide in aqueous solution (Leenaars et al., 1984). The particles reached a final uniform nanoscale size (about 5 nm) (Leenaars et al., 1984) due to the Ostwald ripening mechanism (Brinker and Scherer, 1990). The boehmite particles were connected during the partial gelation process while the sol droplets were falling through the oil layer. Complete gelation occurred when aged in the ammonia solution. After removal of the solvent, the structure of the solid beohmite gel granules was consolidated by calcination in air at 450°C. The boehmite particles also transformed to γ-alumina crystallites during the calcination step. The final granules consisted of nanoscale primary γ-alumina particles of rather uniform size. These uniform particles are strongly bound together by the alumina bridges formed in the calcination step, and, as a result, the granules become mechanically very strong.

Properties of granular alumina-supported CuO sorbents

In the preparation of sorbents for flue-gas desulfurization monolayer dispersion is highly desired in order to maximize the amount of active species that can react with SO_2, and hence to enhance their sorption capacity for SO_2. According to the monolayer model proposed by Xie and Tang (1990), about 40 wt. % of the CuO can be coated on the surface of the γ-Al_2O_3 support with a BET surface area of 350 m^2/g. Sorbents containing about 20, 30 and 40 wt. % of CuO were prepared to explore the monolayer coating amount on this specific γ-alumina support. The XRD patterns of these three CuO sorbents and a pure alumina sample are shown in Figure 6. No XRD peak of CuO was detected in all these samples. Based on the XRD results shown in this figure it is reasonable to conclude, according to Friedman et al. (1978) and Xie and Tang (1990), that 40 wt. % or less of CuO can be coated as a monolayer or submonolayer on the surface of the spherical γ-alumina granular supports. According to our previous studies (Deng and Lin, 1996), about 20–30 wt. % of CuO could be coated on the surface of sol-gel-derived γ-alumina powder supports in monolayer form, and the CuO sorbent containing 20 wt. % of CuO gave the best

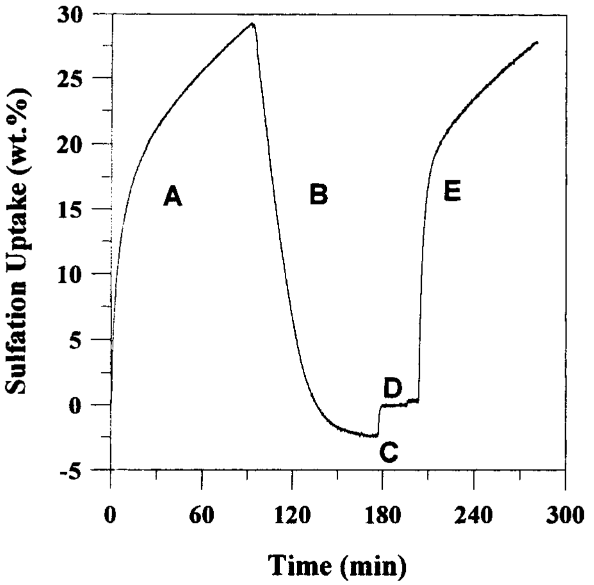


Figure 7. Sulfation, regeneration and oxidation uptakes on granular sorbents at 500°C.

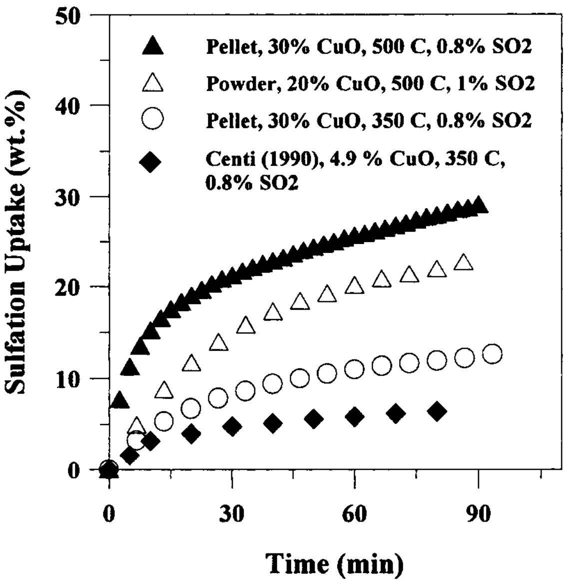


Figure 8. Comparison of sulfur uptakes on different supported copper oxide sorbents.

desulfurization performance. The higher monolayer loading of CuO achieved on these granular sorbents is due in part to the larger specific surface area of the granular support (380–400 m^2/g) compared with the powder support.

The sulfation, regeneration, and oxidation properties of the sol-gel-derived nongranular-alumina-supported CuO sorbents in powder form were systematically investigated in our previous work (Deng and Lin, 1996). In the present work the desulfurization experiments reported were carried out on the granular CuO sorbent containing 30 wt. % CuO. The experimental results of the sulfation, regeneration, and oxidation of the γ-alumina-supported CuO granular sorbents at 500°C are presented in Figure 7. The specific conditions for each experimental step (A to E) shown in Figure 7 are listed in Table 1. In Figure 7, Curve A corresponds to the formation of solid $CuSO_4$ on the sorbent surface through a sulfation reaction between CuO and SO_2 (with O_2). The sulfation results in about 30% weight gain of the sorbent, equivalent to 3.75 mmol/g sorption capacity for SO_2. The sulfated sorbent can be completely regenerated using a methane and nitrogen mixture, as shown by Curve B. Curve C shows the weight gain of the sorbent due to the oxidation of copper formed in the regeneration step. Carbon dioxide does not interact with CuO, as shown in Curve D. Curve E corresponds to weight gain in the second sulfation step, which is identical to Curve A. This indicates that the sorbent is highly recyclable.

The sulfation, regeneration, and oxidation curves observed on the granular sorbent are similar to those on the powder sorbents (Deng and Lin, 1996). Figure 8 presents a comparison of the sulfation uptake curves of the sol-gel-derived granules, powder-supported CuO sorbents, and a similar alumina-supported CuO sorbent reported in the literature (Centi et al., 1990, 1992, 1995). The granular CuO sorbent tested in this work has the largest loading of CuO (30 wt. %), and therefore the largest sorption capacity of SO_2 (e.g., 25 wt. % in 75 min at 500°C) as compared with other CuO sorbents. The absolute sulfation rate on the granular CuO sorbent tested in this work is also the largest among these CuO sorbents compared in Figure 8.

Conclusions

A sol-gel granulation method was developed to prepare spherical γ-alumina-granular support and -supported copper oxide granular sorbents for flue-gas desulfurization. The sol-gel granulation method is based on a modified Yoldas process and the oil-drop method. Due to their nanoscale microstructure, the prepared spherical γ-alumina granules exhibit (1) the desirable pore structure, including large surface area (380 m^2/g) and pore volume (0.5 cm^3/g), narrow pore size distribution (20–60 Å), and controllable average pore size in the mesopore range (35 Å); and (2) excellent mechanical properties, including high crush strength (>100 N per granule) and attrition resistance (0.033 wt. %/h). The pore structure and mechanical properties of the sol-gel-derived alumina granules are better than those of commercial alumina and zeolite granules. The sol-gel granulation technique developed in this work can be applied to the preparation of other spherical granular supports, catalysts, and adsorbents.

The prepared γ-alumina-supported copper oxide granular sorbents exhibit similar properties as the sol-gel-derived alumina-supported copper oxide sorbents in power form. In comparison with the sol-gel-derived sorbents in powder form, or other similar sorbents reported in the literature, the spherical γ-alumina-granular-supported copper oxide granular sorbents prepared in this work have (1) higher loading (30–40 wt. %) of CuO dispersed in the monolayer or submonolayer form; and (2) larger SO_2 sorption capacity (> 35 wt. % at 500°C) and faster sorption rate. With the favorable desulfurization properties, desirable pore texture and excellent mechanical properties, the granular γ-alumina-supported copper oxide sorbent prepared in this work has the potential for use as a sorbent in a fluidized-bed flue-gas desulfurization process.

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