Sol-Gel Synthesis of Pure and Copper Oxide Coated Mesoporous Alumina Granular Particles

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A modified oil-drop sol-gel process is reported for synthesis of mesoporous spherical γ-Al_2O_3 granular particles and CuO-coated γ-Al_2O_3 granular particles of 1–3 mm in diameter. Various parameters affecting the granulation process were studied, and the optimum values of these parameters were identified for reproducible synthesis of the alumina granular particles. Under the optimum synthesis conditions, CuO-coated γ-Al_2O_3 granular particles could be synthesized directly from the pseudo-boehmite sol doped with $Cu(NO_3)_2$ by a solution–sol mixing method. The CuO-coated γ-Al_2O_3 granular particles prepared by the solution–sol mixing coating method exhibit better mechanical and sulfation properties than the similar sorbents prepared by the wet-impregnation method. The sol-gel derived granular CuO-coated γ-Al_2O_3 sorbents prepared by both coating methods have the same microstructure at lower CuO loading. © 1998 Academic Press

Key Words: Sol-gel; granulation; alumina; copper oxide; desulfurization; sorbent.

INTRODUCTION

Among several mesoporous ceramics, γ-alumina is perhaps the most common crystalline material used as a support body for catalysts or adsorbents. 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. For example, it was reported that the poor attrition resistance of granulized alumina supported copper oxide sorbents prepared by the conventional method was the major setback of the fluidized-bed flue gas desulfurization (FGD) process (1). Attrition of the catalysts or adsorbents in the moving beds or fluidized beds results in loss of catalyst or adsorbent material, generation of fine powder, and particulate pollution in the downstream. It also increases the process costs. Moreover, the change in the granule size might influence the properties of the catalysts or adsorbents.

Sol-gel derived alumina offers a number of advantages such as well-defined nanostructure, large surface area, and superior mechanical properties (2–5). However, it has been prepared primarily in the form of a thin film, membrane, or powder (2). For applications as catalysts or adsorbents in industrial processes, the sol-gel-derived alumina should be prepared in the form of spherical granules of 1–3 mm in diameter. A few studies were reported on 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 (6–10). This oil-drop method has been successfully used to synthesize spherical silica (SiO_2) or zeolite granules (11–15). The oil-drop method was also applied to prepare granular alumina supports from a suspension made from alumina powders (16–18).

Recently, we reported (19) preparation of sol-gel-derived nanostructured γ-Al_2O_3 granules by a granulation process that combines the Yoldas sol-gel process (3–5) and the oil-drop method. The sol-gel-derived mesoporous alumina granules of 1–3 mm in diameter exhibit large surface area, mesopore size, and mechanical properties (crush strength and attrition resistance) much better than alumina granules available from commercial sources. The excellent mechanical properties are derived from the unique microstructure of the granules. The sol-gel-derived monolith alumina granule consists of nanoscale γ-Al_2O_3 crystallites bound together by the bridges of the same material formed through coarsening or sintering. Our recent work showed that the new sol-gel granulation process can be effectively used for preparation of granular ceramic supports with excellent chemical, structural, and mechanical properties (19). However, effects of various parameters on the sol-gel granulation process were not investigated in the previous work.

As catalysts and adsorbent, the granular supports are often coated with metal or metal oxide active species (e.g., CuO for adsorbent for FGD). This is usually accomplished by the conventional wet-impregnation method (19–21). The wet-impregnation coating method involves (a) preparation of the support body, (b) bringing the support in contact with the liquid containing the active species precursor, (c) drying

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the coated support, and (d) calcination to convert the active species precursor to the final active species. Lin and co-workers (22) recently reported that the grain surface of sol-gel-derived ceramic membranes could be coated with metal oxides by a one-step solution–sol mixing method. In this method, coating is accomplished by mixing the solution containing the active species precursor with boehmite (or zirconia, titania) sol, followed by the steps of membrane formation, drying, and calcination. This method avoids additional drying and calcination steps required in the wet-impregnation method and thus is more efficient and energy saving than the wet-impregnation method. It may also offer some other advantages such as better dispersion of the active species on the surface of the support.

In the present work, the effects of various parameters involved in the sol-gel granulation process were more systematically studied. This work was part of our research effort in developing novel supported CuO sorbent/catalyst for simultaneous removal of SO_2 and NO_x from flue gas. The objective of this paper is to report on the preparation and properties of sol-gel-derived γ-Al_2O_3-supported CuO granular sorbent/catalyst particles by a one-step method. This represents the first effort of direct preparation of support/active-species granular particles of 1–3 mm in diameter by the sol-gel method. The sulfation and NO_x reduction catalytic properties of this new sorbent/catalyst will be reported in subsequent papers.

EXPERIMENTAL

The starting material for preparing the γ-Al_2O_3 granules was high-concentration (>1.0 M) boehmite sol (γ-AlOOH). Two methods were used to prepare the high-concentration boehmite sol. The first method is based on the exact Yoldas process. It included hydrolysis and condensation of 260 ml aluminum tri-sec-butoxide (ALTSB, 97%, Acros Oganic) in 1000 ml distilled water, and peptization with nitric acid in the amount that gave the H^+/Al^{3+} ratio of 0.07 (23, 24). The resulting sol at 1 M aluminum concentration was concentrated by evaporation on a hot plate. The second method, which avoids the evaporation step and is referred to here as the modified Yoldas process, was a direct preparation of the high-concentration boehmite sol. This method is described in more detail below using preparation of 2 M boehmite sol as an example.

The synthesis process started with slow addition of a total of 520 ml ALTSB to 1000 ml distilled water, which was well stirred and controlled at 80°C. Large, irregularly shaped clusters started to appear, and gradually precipitated in the flask during the hydrolysis and condensation process when the amount of ALTSB added exceeded 400 ml (equivalent to about 1.56 M). The slurry was then dispersed with addition of 140 ml of 1 M HNO_3 (that gave the H^+/Al^{3+} ratio of 0.07) and/or dilution with about 200 ml deionized water.
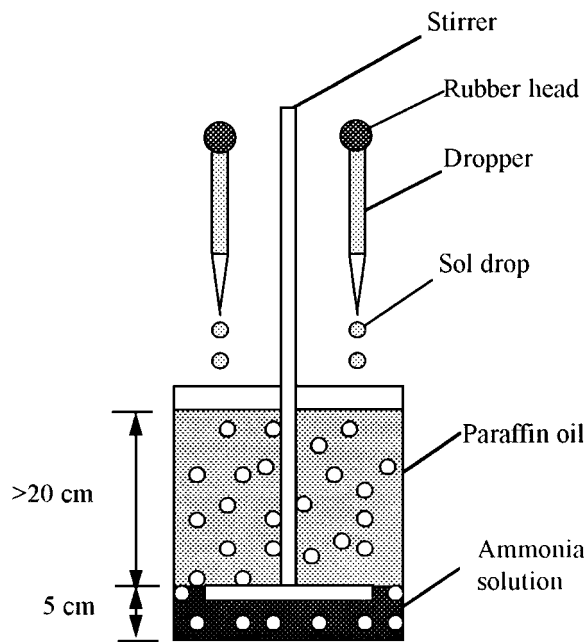

FIG. 1.   Schematic description of the oil-drop granulation process.

Continuous addition of 520 ml ALTSB in water took about 5 h. After that, the ALTSB/water mixture was vigorously stirred for half an hour and refluxed overnight (12 h) at 90–100°C.

Granular γ-Al_2O_3 and CuO-coated γ-Al_2O_3 particles were prepared by an oil-drop process schematically shown in Fig. 1. The 2 M boehmite sol was first mixed with a small amount of 1 M HNO_3 (acid/sol volume ratio of 1:5). The modified sol was stirred at 70–80°C with a magnetic strirrer. A dramatic decrease in the pH with the addition of HNO_3 substantially accelerated the gelation process of the sol. In the case of preparing CuO coated γ-Al_2O_3 particles, the modified 2 M boehmite sol was mixed with $Cu(NO_3)_2$ solution (with concentration varied from 0.52 to 9 M, depending on the required amount of coating) in the volume ratio of 6:1. After aging for half an hour at 60–70°C, the pure or Cu-doped 2 M boehmite sol became so viscous that it could not be stirred with the magnetic stirrer set at maximum power. It was then transferred to droppers as the starting material for the granulation process.

The granulation process included generating sol droplets by the droppers, shaping and partially gelating the droplets into spherical wet-gel granules in a paraffin oil layer (color: white; density: 0.7864 g/cm³; kinematic viscosity: 34.5 centistokes at 40°C; from Fisher Scientific), and consolidating the structure of the wet-gel granules in a 8 wt% ammonia solution layer. The temperature of the paraffin oil layer was varied from 25 to 100°C, and the ammonia solution layer was kept at room temperature. For preparing CuO/γ-Al_2O_3 granules, the ammonia solution was added with $Cu(NO_3)_2$ at the concentration identical to that in the

Cu-doped boehmite sol to prevent $Cu(NO_3)_2$ from being leached out of the wet-gel particles. The interface between the oil and ammonia solution was slowly stirred with a stirrer (at 18–50 rpm) to facilitate transport of the wet granules across the interface. After aging in the ammonia for at least 45 min, the spherical wet-gel particles were removed from the ammonia solution, carefully washed sequentially with water and alcohol, dried at 40°C for 48 h, and finally calcined in air at 450°C for about 4 h.

For comparison purposes, CuO/γ-Al_2O_3 samples were also prepared by the wet-impregnation method. This was done by immersing a given amount of the sol-gel-derived γ-Al_2O_3 granular particles in the $Cu(NO_3)_2$ solution for over 16 h, followed by the same drying and calcination procedures described above. The amount of active species coated was estimated from the weight of support, volume, and concentration of the $Cu(NO_3)_2$ solution used in the wet-impregnation step. The CuO/γ-Al_2O_3 samples, prepared either by the one-step solution–sol mixing method or by the wet-impregnation method, were further calcined in air at 550°C for 6 h to convert $Cu(NO_3)_2$ to CuO.

Pore and phase structure of the granular particles were respectively measured by adsorption porosimeter (Micromeritics, ASAP-2000) and XRD (Siemens D-50, with radiation of $CuK\alpha_1$). The pore structure data were obtained from nitrogen adsorption and desorption isotherms at liquid nitrogen temperature with the software provided by Micromeritics. The BET surface was calculated from the adsorption isotherm, and the pore size distribution was calculated from the desorption isotherm. The average pore diameter was obtained from the pore size distribution data.

The crush strength of individual spherical γ-Al_2O_3 particle was tested by a universal testing instrument (Instron 4465). The maximum force applied to break the sample particle was taken as the crush strength. Attrition tests were conducted in a rolling drum equipment. The particle samples together with a stainless steel cylinder ($\phi = 10$ mm, $L = 40$ mm) were put in a bottle of 40 mm in diameter and 70 mm in height. In each test, the bottle containing the sample was rolled at 75 rpm for 24 h. The sample was then removed from the bottle and sieved with a #20 sieve (850-μm opening). The attrition rate is the weight ratio of the portion that has passed through the sieve to the total amount of the sample used in each attrition test.

RESULTS AND DISCUSSION

Sol-Gel Granulation Process

To examine effects of aluminum concentration in the sol on the microstructure of the sol-gel derived alumina, eight samples of boehmite sol with aluminum concentration ranging from 0.8 to 2.3 M were prepared, as summarized in Table 1. The molar concentration in the second column of

TABLE 1

Summary of Eight Boehmite Sols with Different Aluminum Concentrations

Sample no.	Al molar concentration	Al_2O_3 (wt%)	Preparation method
1	0.8	3.8	Yoldas process
2	1.0	4.7	
3	1.1	5.1	
4	1.7	7.7	Modified Yoldas process
5	1.9	9.1	
6	2.0	9.6	
7	2.1	9.9	Evaporated from 1.2 M sol
8	2.3	10.8	

Table 1 is estimated from the amount of ALTSB and water used in preparing each sample. Al_2O_3 weight concentration in the third column was obtained by measuring the weight of the solid sample of 100 ml sol after drying and calcining. Samples with aluminum concentrations lower than 1.7 were prepared by the exact Yoldas process, and those with concentrations in the range 1.7–2.0 M (samples 4 and 5) by the modified Yoldas process. Samples with aluminum concentration higher than 2 M were prepared by evaporating the 1 M sample.

All the sols listed in Table 1 were stable, as indicated by the fact that no visible precipitates were observed within 30 days. Figure 2 gives the pH of the eight sols. The pH decreases slightly with the increase of aluminum concentration. Since the amount of the acid used increases proportionally with increasing aluminum amount (at ratio $H^+/Al^{3+} = 0.07$), it is expected that the pH of the sol should have weak dependency on the aluminum concentration.

Xerogel samples were obtained by drying respectively small amounts of the eight sols in petri dishes at 40°C for 48 h. The corresponding γ-Al_2O_3 samples were prepared by calcining the xerogel samples at 450°C for 3 h (heating rate of 30°C/h). Typical nitrogen adsorption and desorption isotherms of the xerogel sample are given in Fig. 3. The corresponding pore size distribution (calculated from desorption isotherm by Micromeritics software) is shown in Fig. 4. The surface area, pore volume, and average pore size of the alumina samples are plotted versus the aluminum concentration in the sol in Fig. 2. As shown, the surface area of all the eight samples is about 310 m²/g. The pore volume and pore diameter are in the range 0.3–0.4 ml/g and 4.1–4.6 nm, respectively. Different preparation methods and aluminum concentration of the sols have negligible effects on the pore structure of the alumina samples derived from the sols.

Highly viscous pseudo-boehmite sols, prepared by mixing HNO_3 in the boehmite sols with different aluminum concentrations, were used to generate the sol drops in the granulation process. It was found that only broken or
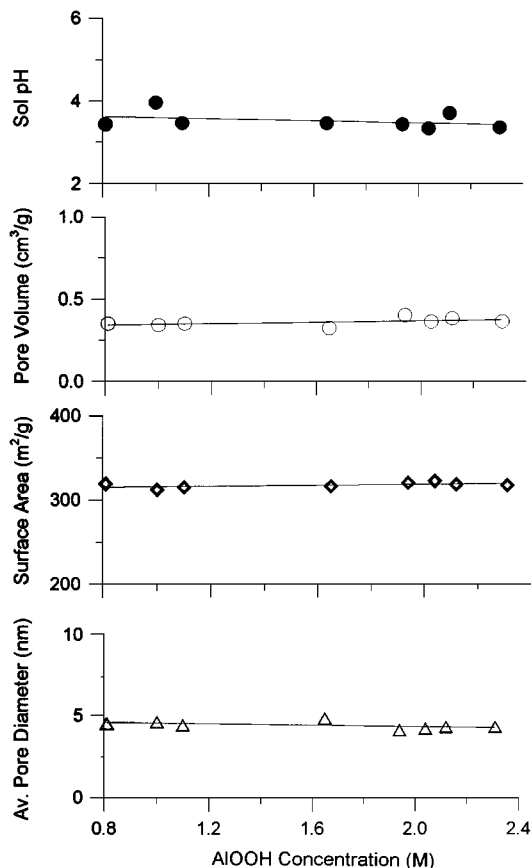
FIG. 2. pH of the sol and pore structure of the sol-gel-derived γ-alumina as a function of the aluminum concentration in the sol.

FIG. 3. Typical nitrogen adsorption and desorption isotherms measured by Micromeritics ASAP-2000. (Sample A in Table 5.)

lumped particles were obtained from the pseudo-boehmite sols with aluminum concentration lower than 1.5 M. On the other hand, granular particles prepared from the pseudo-boehmite sols with aluminum concentration higher than 2 M were more likely irregular in shape. Spherical alumina granular particles could be obtained from the pseudo-boehmite sols with aluminum concentrations in the range 1.5–2 M.

Whether good granular particles could be prepared from a boehmite sol also depends on the amount of acid used, and the aging time and temperature of the boehmite sol after the addition of HNO$_3$. In the case of preparing 2 M pseudo-boehmite sol, the aging time required was about 30 min at an aging temperature of 60–70°C and 25 min at 70–80°C. The aging time required decreases from above 200 to 10 min with the amount of HNO$_3$ added into 100 ml boehmite sol increasing from 10 to 60 ml. Broken or irregularly shaped particles were obtained from the pseudo-boehmite sol prepared with shorter aging time. It was also difficult for the drops to be formed from the pseudo-sol with longer aging time.

The oil layer was used in the granulation process for shaping the sol drops to spheres. It was found that the spheri-
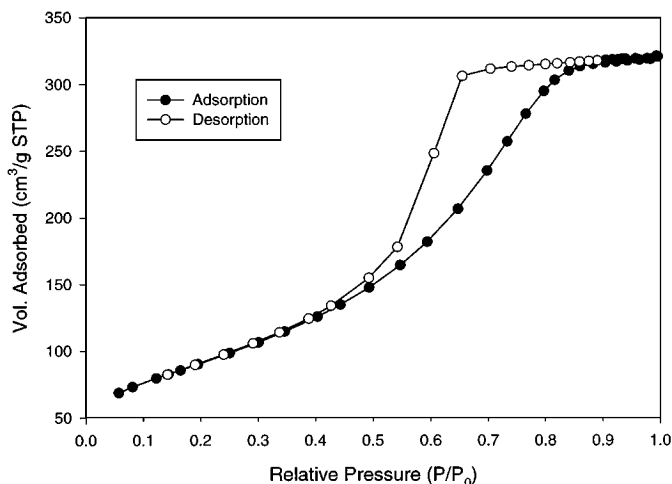
city of gel particles was improved with the increase of the oil temperature from 25 to 90°C. Varying the temperature above 90°C did not show much effect on the shape of the sol drops. The oil evaporates much faster at temperatures higher than 90°C. For the pseudo-sol aged at 60–75°C, good spherical particles could also be obtained with the oil layer kept at room temperature. However, at lower oil temperatures the spherical sol drops formed in the oil layer experienced difficulty in overcoming the surface tension on the interface of the paraffin oil and the ammonia solution. In this case the sol drops were easily accumulated above the interface rather than falling into the ammonia solution for further gelation. Transport of the sol drop across the interface could be facilitated by a stirrer placed at the interface, stirring slowly at 18–50 rpm.
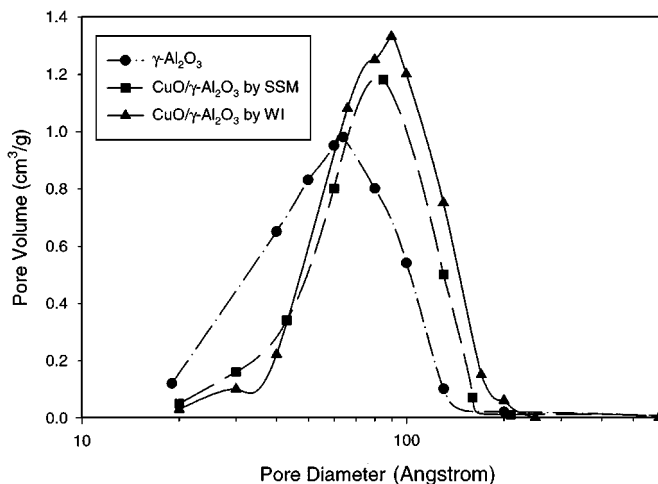

FIG. 4. Pore size distributions of granular samples of pure γ-Al$_2$O$_3$, CuO/γ-Al$_2$O$_3$ prepared by solution–sol mixing (SSM) method, and CuO/γ-Al$_2$O$_3$ prepared by wet-impregnation (WI) method.

TABLE 2

Effects of Ammonia Concentration on the Particle Appearance and Pore Structure (Sol Concentration: 1.8 *M*; Temperature: 25°C, Aging Time: 45 min)

Concentration of ammonia (wt%)	5	8	10	15	20	25
Appearance	good	good	good	general	fair	bad
Sphericity	fair	good	good	general	fair	bad
Surface area (m^2/g)	319	326	330	341	356	368
Average pore diameter (Å)	46.3	50.3	62.1	67.4	73.4	78.0
pore volume (%)	0.4	0.44	0.47	0.49	0.56	0.71

At a given temperature another critical parameter is the residence time of the gel particles in the oil layer. This is determined by the thickness of the oil layer. The sphericity of the particles improves with increasing oil thickness. For 2 *M* pseudo-boehmite sol the minimum height of the oil layer is about 60 cm. However, for 1.5 and 1.7 *M* pseudo-boehmite sol only 20-cm-high oil layer is required in order to obtain spherical drops.

The spherical sol (gel) particles stayed in the ammonia solution for about 45 min to allow for further gelation. The effects of the ammonia concentration on the results of the alumina granular particles are summarized in Table 2. Gel particles aged in the ammonia solution with ammonia concentration higher than 15 wt% exhibit rough surface and irregular shape, as shown in Fig. 5a. These particles were easily broken during subsequent washing and drying processes. The BET surface area, pore size, and pore volume of the final granular particles increase with the ammonia concentration. In terms of particle sphericity and appearance the best ammonia concentration appears to be in the range 8–10 wt%. The aging time for the gel particles (in the ammonia solution) is also an important factor determining the quality of the particles prepared. After aging in the ammonia solution (at concentration of 8 wt%) for less than 30 min the gel particles were soft and became dissolved in the solvent in the subsequent washing process. The minimum aging time at the 8 wt% ammonia solution is 45 min. Figure 5b shows the appearance of the good particles.

TABLE 3

Washing Solvents and Procedure

Washing liquid	Amount (l)	Cycles	Washing time (min/per cycle)
Cool water	2	3	5
Hot water	2	2	5
Alcohol (40%)	1	2	5
Cool water	2	2	5

TABLE 4

Optimum Conditions for Preparing γ-Al$_2$O$_3$ Granular Particles

Parameters	Value
Boehmite concentration in the sol (*M*)	1.8
pH of the sol	3.8
Volume of 1 *M* HNO$_3$ added per 100 ml sol (ml)	20
Gelation time for preparing pseudo-sol (min)	30
Thickness of the paraffin oil (cm)	20
Ammonia concentration (vol%)	8
Aging time of sorbent particles in ammonia (min)	45

The established solvent and washing procedures are given in Table 3. It was found that the wet-gel particles removed from the ammonia solution should first be washed very carefully with cool water. When the wet-gel particles were first washed with hot water or alcohol, the particles were softened or even broken during washing. After being washed sequentially with cool water, hot water, and alcohol, the gel particle should be washed again with cool water, as otherwise the particles were found to be broken during the subsequent drying process.

CuO/γ-Al$_2$O$_3$ Granular Particles

Six batches of the γ-Al$_2$O$_3$ granular particles were prepared under optimum conditions listed in Table 4. All particles were in the size of about 1.5 mm with good sphericity. The samples appear translucent. Table 5 gives the surface area, pore size, and pore volume of these samples, which are within the narrow range 320–330 m^2/g, 62–74 Å, and 0.45–0.50 ml/g, respectively. This indicates good reproducibility of the granulation process. The granular γ-Al$_2$O$_3$ particles have similar surface area, but larger pore size and pore volume, as compared to xerogel γ-Al$_2$O$_3$ samples (see Fig. 2) prepared by drying the boehmite sol in a petri dish and calcination under the same conditions as for granular samples. This is because the gelation process and environment for preparing the granular particles are quite different from those for the xerogel samples.

TABLE 5

Pore Structures of γ-Al$_2$O$_3$ Granular Particles (Particle Diameter: 2 mm)

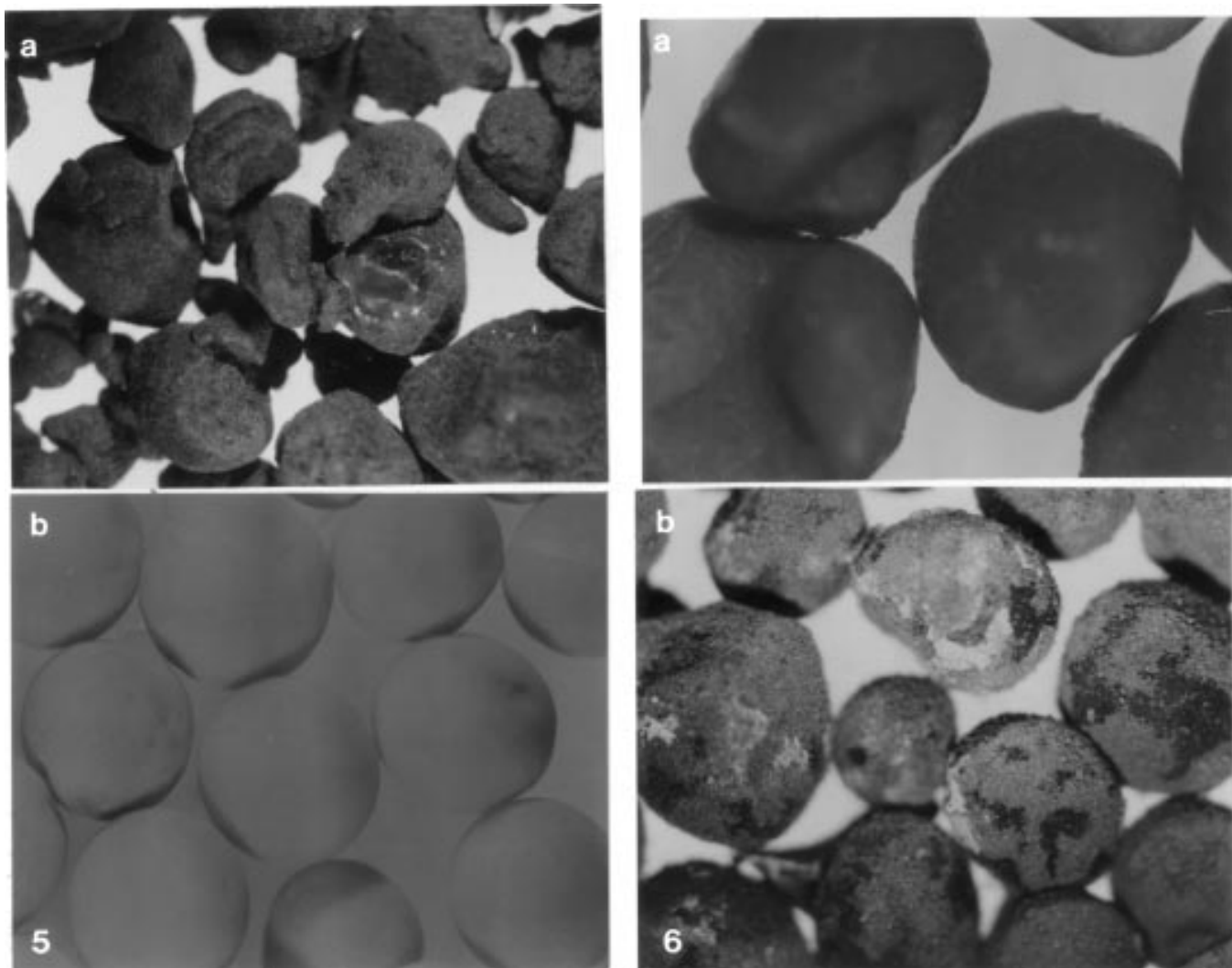| Sample ID	Surface area (m^2/g)	Average pore diameter (Å)	Pore volume (ml/g)
A	325.2	62	0.50
B	327.6	70	0.50
C	332.7	68	0.57
D	326.8	72	0.52
E	331.6	74	0.45
F	321.5	68	0.50

FIG. 5.   Appearance of bad (a) and good (b) spherical γ-Al$_2$O$_3$ granules (particle diameter = 1.5–3.0 mm).

FIG. 6.   Appearance of CuO/Al$_2$O$_3$ samples prepared by the wet-impregnation method: (a) with CuO loading of 7.7 wt% (particle diameter = 1.5–3.0 mm) and (b) with CuO loading of 17.0 wt% (particle diameter = 1.5–2.0 mm).

CuO/γ-Al$_2$O$_3$ granular particles with different CuO loading were prepared from the six samples listed in Table 5 by the wet-impregnation method. Table 6 lists the pore structure of the six CuO/γ-Al$_2$O$_3$ samples with different amounts of CuO. For the samples with CuO loading smaller than 8 wt%, the particles exhibit gray color with smooth surface, as shown in Fig. 6a. The particles of the samples with CuO loading exceeding 8 wt%, however, show gray color with a rough surface, as shown in Fig. 6b. XRD patterns of the four CuO/γ-Al$_2$O$_3$ samples with different CuO loading are given in Fig. 7. As shown, XRD peaks of CuO crystallites (tenorite and monoclinic, at 2θ of 35.6° and 38.8°) appear to be present in the samples with CuO loading of about 9 wt%. According to the monolayer loading theory (25), this indicates that in this study only a limited amount of

CuO (<9 wt%) could be well dispersed on the internal pore surface of the alumina support by the wet-impregnation method used here. Excessive CuO may crystallize and is present on the external surface of the particles.

As shown in Table 6, the surface areas of the CuO-coated γ-Al$_2$O$_3$ samples prepared by the wet-impregnation method are about 80–100 m^2/g smaller than those of the uncoated alumina samples (Table 5). Moreover, coating CuO on γ-Al$_2$O$_3$ results in about a 25% increase in the average pore size. The pore volumes of the coated samples are the same as those of the uncoated ones. The pore size distributions of CuO-coated γ-Al$_2$O$_3$ sample are compared with those of uncoated samples in Fig. 4. As shown, the coated CuO seems to fill the smaller (micro) pores of γ-Al$_2$O$_3$, resulting in an appreciable decrease in the number

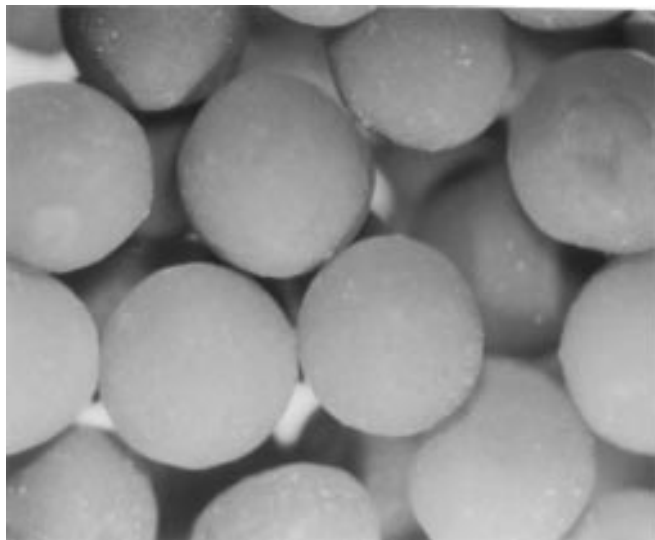**FIG. 8.** Appearance of CuO/γ-Al$_2$O$_3$ granular particles prepared by the solution–sol mixing method (9 wt% CuO, particle diameter = 1.5–2.5 mm).

FIG. 7. XRD patterns of CuO/γ-Al$_2$O$_3$ samples prepared by the wet-impregnation method.

of smaller pores and, consequently, an increase in the average pore size. Deng and Lin (24) reported similar findings on CuO coated γ-Al$_2$O$_3$ powders (not granules) prepared by the sol-gel method. Different from CuO coated γ-Al$_2$O$_3$ powders whose surface area decreases with increasing CuO loading, the surface areas of the CuO-coated γ-Al$_2$O$_3$ granules remain essentially constant with respect to the different loading amount of CuO.

CuO/γ-Al$_2$O$_3$ granular particles with CuO loading up to 18.3 wt% were also prepared by the one-step solution–sol mixing method under the conditions summarized in Table 4. The only difference between the preparation of pure γ-Al$_2$O$_3$ granular particles and CuO/γ-Al$_2$O$_3$ granular particles is that for the latter the starting sol was Cu(NO$_3$)$_2$ doped pseudo-boehmite sol, as described under Experimental. Table 7 summarizes the eight samples prepared by the one-step solution–sol mixing method. The color of the

wet samples (before drying) was blue. The color became darker as CuO loading increased. The color of the final calcined samples was green. Except for the last sample, with CuO loading of about 18.3 wt%, all samples show good sphericity and integrity.

Figure 8 shows the appearance of CuO/γ-Al$_2$O$_3$ sample prepared as such. XRD patterns of four samples with CuO loading up to 18.3 wt% are shown in Fig. 9. The particles of these four samples exhibit a smooth surface, as shown in Fig. 8. No XRD peaks for CuO crystallites are observed in Fig. 9. These indicate that CuO coated is well dispersed on the grain surface of these particles. It appears that the solution–sol mixing coating method could disperse more CuO on the grain surface of the alumina support than the wet-impregnation method.

TABLE 6

The Pore Structure of CuO/γ-Al$_2$O$_3$ Granular Particles Prepared from γ-Al$_2$O$_3$ Particles Listed in Table 5 by the Wet-Impregnation Method

Sample ID	CuO (wt%)	Surface area (m^2/g)	Average pore diameter (Å)	Pore volume (ml/g)
IM-A	4.2	241.2	81	0.49
IM-B	5.8	232.6	84	0.49
IM-C	6.6	232.2	82	0.48
IM-D	9.3	238.9	80	0.46
IM-E	13.4	236.8	83	0.43
IM-F	17.0	233.2	81	0.46

TABLE 7

Pore Structure and Appearance of CuO/γ-Al$_2$O$_3$ Granular Particles Prepared by the Solution–Sol Mixing Method

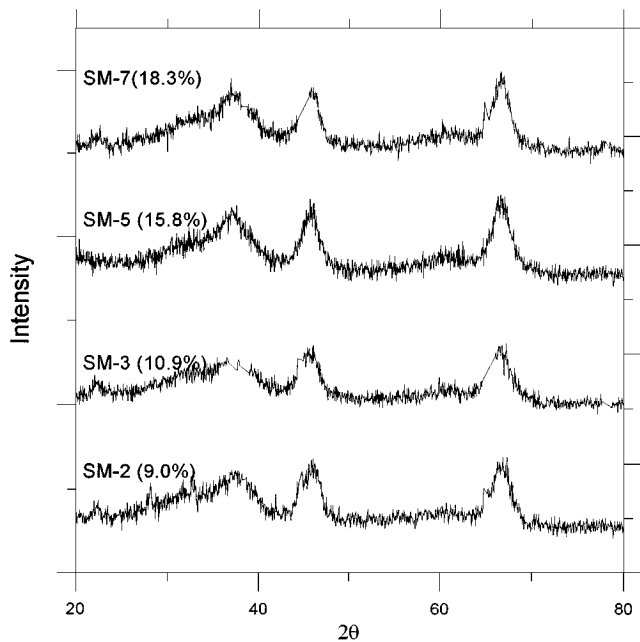| Sample ID	CuO (wt%)	Surface area (m^2/g)	Average pore diameter (Å)	Pore volume (ml/g)
SM-1	8.4	248.5	74.9	0.48
SM-2	9.0	243.6	74.8	0.45
SM-3	10.9	254.2	80.7	0.45
SM-4	13.5	243.2	74.2	0.46
SM-5	15.8	249.3	75.8	0.47
SM-6	17.6	245.0	78.2	0.46
SM-7	18.3	244.2	82.8	0.51

FIG. 9. XRD patterns of CuO/γ-Al$_2$O$_3$ granular particles prepared by the solution–sol mixing coating method.

The pore structure data of the CuO/γ-Al$_2$O$_3$ samples prepared by the solution–sol mixing method are summarized in Table 7. Compared to the undoped alumina granules, these samples have a smaller surface area and larger pore size, but similar pore volume. The pore structure of the CuO/γ-Al$_2$O$_3$ samples prepared by the solution–sol mixing method is very close to that of CuO/γ-Al$_2$O$_3$ granular samples prepared by the wet-impregnation method. This is more obvious if one compares the pore size distributions of the CuO/γ-Al$_2$O$_3$ samples prepared by the two coating methods, which are given in Fig. 4. These suggest that doping Cu(NO$_3$)$_2$ in the boehmite sol did not alter the structure of particles in the sol.

The exact location of CuO in the CuO/γ-Al$_2$O$_3$ particle is not certain. In the solution–sol mixing method, Cu(NO$_3$)$_2$ is mixed with boehmite sol, which contains aggregates of primary boehmite crystallites. Cu(NO$_3$)$_2$ could be adsorbed uniformly on the grain surface of the boehmite crystallites during the aging and drying steps. Cu(NO$_3$)$_2$ is converted to CuO in the calcination step in which boehmite transforms to γ-Al$_2$O$_3$. It can be assumed that the majority of CuO coated remains on the grain surface of γ-Al$_2$O$_3$ crystallites after calcination.

Table 8 summarizes the attrition rate and crushing strength of three CuO/γ-Al$_2$O$_3$ granular particles (prepared by the solution–sol mixing method) after heat treatment at different temperatures for 6 h. As shown, the surface area decreases and the pore size increases with the heat-treatment temperature, due to sintering of ceramic (24). The attrition rate decreases and the crushing strength increases with the heat-treatment temperature.

TABLE 8

Effects of Sintering Temperature on Mechanical Properties of 9 wt% CuO/γ-Al$_2$O$_3$ Granular Particles Prepared by the Solution–Sol Mixing Method

Sample ID	Temperature (°C)	BET surface area (m^2/g)	Average pore diameter (Å)	Attrition weight loss (wt%)	Crushing strength (N/particle)
SM-2	450	243.6	74.8	0.126	89.3
SM-2	550	218.9	88.3	0.113	113.8
SM-2	650	206.8	97.6	0.109	116.9

As expected, the sintering enhances the mechanical properties of the sol-gel derived granules. The attrition rate and the crushing strength of the samples with different amount of CuO and preparation methods are compared in Table 9. Granular particles with CuO coated obviously have a lower attrition rate and a higher crushing strength than the uncoated alumina granules. Furthermore, for samples coated with same amount of CuO, those prepared by the solution–sol mixing method appear to have better mechanical properties than those prepared by the wet-impregnation method.

In our previous studies (19) we also found that our sol-gel-derived pure γ-Al$_2$O$_3$ granular particles have the crushing strength and attrition resistance 3–5 times those of the pure γ-Al$_2$O$_3$ granules available from Alcoa. The pore structure and mechanical properties of a 7 wt% CuO/γ-Al$_2$O$_3$ sorbent prepared by UOP were measured in this work for comparison. The UOP sorbent has surface area, pore volume, and average pore diameter of 158 m^2/g, 0.60 cm^2/g, and 152 Å. Its crushing strength and attrition rate are 24 N/particle and 0.64 wt%, respectively. Compared to the data given in Table 8, the mechanical properties of the sol-gel-derived CuO/γ-Al$_2$O$_3$ are much better than those of a similar sorbent available from the commercial source.

TABLE 9

Comparison of Mechanical Properties of CuO/γ-Al$_2$O$_3$ Granular Particles with Different CuO Loading (Calcined at 450°C)

Sample ID	CuO (wt%)	Attrition weight loss (wt%)	Crush strength (N/particle)
SD-0	0	0.33	96.1
SD-1	0	0.13	116.9
SM-1[a]	8.4	0.123	152.9
SM-2[a]	9.0	0.121	119.5
SM-3[a]	10.9	0.105	86.1
SM-6[a]	17.6	0.122	88.4
IM-B[b]	5.3	0.132	100
D-1[b]	6.0	0.134	86.9

[a] CuO was coated by the solition–sol mixing method.
[b] CuO was coated by wet-impregnation method.

The sorption capacity of CuO/γ-Al_2O_3 for sulfur dioxide was measured by passing air containing 2000 ppm (v%) SO_2 (at 8.9 mL/min) through a fixed bed packed with 0.5 g of each of several sorbents prepared by the one-step solution–sol mixing method and wet-impregnation method (all with CuO loading of 7–9 wt%). Details about the fixed-bed experiments are given elsewhere (26). SO_2 sorption capacity was calculated from the SO_2 breakthrough curves. At 400°C the sample prepared by the solution–sol mixing method (SM-1) has the SO_2 sorption capacity about 1.5 mmol/g, about 50–100% larger than the sorbents (with similar CuO loading) prepared by the wet-impregnation method. This sorbent (SM-1) went through 15 cycles of sulfation (with air containing 2000 ppm SO_2), reduction (regeneration) (with methane), and oxidation (with air). The SO_2 adsorption capacity of this sorbent decreased by about 0.5% after these cycles for the period of 1 month. These results indicate that the sorbent was rather stable, and that CuO coated by the solution–sol mixing method has better sulfation properties and stability than that coated by the wet-impregnation method.

CONCLUSIONS

Mesoporous spherical γ-Al_2O_3 granular particles could be prepared by an improved sol-gel oil-drop granulation process. The quality of the γ-Al_2O_3 particles depends strongly on the preparation conditions. Critical parameters identified include boehmite concentration, aging time and conditions for preparing pseudo-boehmite sol, oil layer thickness, and aging conditions in ammonia solution. Under the optimum conditions identified, CuO coated γ-Al_2O_3 granular particles could be synthesized directly from the pseudo-boehmite sol doped with $Cu(NO_3)_2$ by the one-step solution–sol mixing coating method.

The solution–sol mixing coating method allows for more CuO to be uniformly dispersed on the γ-Al_2O_3 grain surface as compared to the wet-impregnation method. This method is also more efficient and energy-saving as compared to the wet-impregnation coating method. Furthermore, the CuO coated γ-Al_2O_3 granular particles prepared by the solution–sol mixing coating method exhibit better mechanical and sulfation properties than the similar sorbents prepared by the wet-impregnation method.

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