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ADSORPTION AND DESORPTION OF SULFUR DIOXIDE ON NOVEL ADSORBENTS FOR FLUE GAS DESULFURIZATION

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Y. S. Lin (Project Manager)
Assistant Professor of Chemical Engineering
Telephone: (513)-556-2769
and
S. G. Deng
Department of Chemical Engineering
University of Cincinnati
Cincinnati, OH 45221-0171

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Executive Summary

In the past year (1994-1995), our research supported by OCDO was focused on (1) synthesis of sol-gel derived alumina supported CuO sorbents in the practical granule form; (2) study of mechanical, sulfation and regeneration properties of the alumina supported CuO sorbents; and (3) preparation of DAY zeolite supported CuO sorbents. The research was aimed at developing novel sorbents possessing better sulfation properties and improved attrition resistance for use in the dry-regenerative flue gas desulfurization (FGD) process for efficient removal of SO_2.

A sol-gel granulation method was developed to prepare spherical γ-alumina granular supports and supported CuO granular sorbents for flue gas desulfurization. The size of the granules ranges from 1 mm to 5 mm. The prepared spherical γ-alumina granular supports were found to have: (1) desirable pore texture including large surface area (380 m^2/g), large pore volume (0.5 cm^3/g), narrow pore size distribution (20-60 Å) and controllable average pore size (35 Å) and (2) excellent mechanical properties including high crushing strength (> 100 N per granule) and attrition resistance (0.033 wt.%/h. These mechanical properties are far better than the commercially available alumina granules or zeolite pellets.

In comparison with the sol-gel derived sorbents in powder form or other similar sorbents reported in literature, the spherical γ-alumina supported CuO granular sorbents prepared in this work have: (1) higher loading (30-40 wt.%) of CuO dispersed in the monolayer or sub-monolayer form and (2) larger SO_2 sorption capacity (>20 wt.%) and faster sorption rate. It also shows that CO_2 has negligible effects on the desulfurization properties of these sorbents. Theses favorable desulfurization results and the desirable pore texture and mechanical properties make the γ-alumina supported CuO granular sorbents prepared in this work very attractive for use as sorbents for flue gas desulfurization.

Research efforts were also made to prepare DAY zeolite supported sorbents with various CuO contents by the microwave and conventional thermal dispersion methods at different conditions. Monolayer or sub-monolayer coating of $Cu(NO_3)_2$ or CuO was achieved on several DAY supported sorbents by the microwave heating method but not by the conventional thermal dispersion method. The DAY zeolite supported CuO sorbents prepared by the microwave heating method can adsorb up to 15 wt.% of SO_2. The results obtained have demonstrated the feasibility of effective preparation of zeolite supported sorbents by the microwave heating method.

The sulfation kinetic study shows that for sorbents with more than 20 wt. % CuO the sulfation process can be described by a reaction kinetics of second order with respect to the concentration of CuO coated on the support. For sorbents containing 20 wt% or less CuO the interaction of support γ-Al_2O_3 with SO_2 plays an important role in influencing the sulfation process. The kinetic study suggests that increasing the monolayer coating amount of CuO on the support not only increases the sorption capacity but also improves the sulfation rate. Modeling of the regeneration process shows that the regeneration kinetics for the sol-gel derived γ-alumina supported CuO sorbents with methane or hydrogen as the reducing gas can be partly described by the zero or first order reaction model.

Introduction

Dry regenerative sorption processes have recently attracted increasing attention in flue gas desulfurization (FGD) because of their several advantages over the conventional wet-scrubbing processes. Dry sorbents are usually made by coating a transition or alkaline earth metal precursor on the surface of a porous support. Major disadvantages of these sorbents prepared by the conventional methods include relatively poor attrition resistance and low SO_2 sorption capacity. The physical and especially chemical attrition (associated with the sulfation-oxidation-reduction cycles in the process) deteriorates the performance of the sorbents. The low SO_2 sorption capacity is primarily due to the small surface area of the support. Materials with a high surface area are not used as the supports for FGD sorbents because these materials usually are not thermally stable at high temperatures.

A research program focusing on synthesis and properties of sol-gel derived alumina and zeolite sorbents with improved properties for FGD was initiated in 1993 in our laboratory. The sol-gel derived alumina was expected to have large surface area, mesopore size and excellent mechanical strength. Some alumina-free zeolites not only posses the basic properties required as a sorbent for FGD (hydrophobicity, thermal and chemical stability, mechanical strength) but also have extremely large surface area and selective surface chemistry. The major objectives of this research program are to synthesize the sol-gel derived sorbents and to explore use of zeolites either directly as adsorbents or as sorbent support for FGD. Study on SO_2 sorption equilibrium, kinetic, mechanical and attrition properties of these sorbents is also a major component of this research program.

In year four (1993-1994) of this project a sol-gel method was developed in our laboratory to prepare γ-alumina supported copper oxide sorbents in powder form as described in our previous OCDO report (Lin and Deng, 1994). These sorbents have been shown to have desirable pore texture, high monolayer loading of active species (CuO), large SO_2 sorption capacity and good thermal and chemical stability (Deng and Lin, 1996, 1995a). These results clearly demonstrate that the sol-gel derived γ-alumina supported copper oxide sorbents prepared in our laboratory are promising for use in FGD process.

Since these sorbents are in powder form which are difficult for direct use in the commercial FGD processes, preparation of practically applicable granular sorbents is needed.

The dealuminated Y (DAY) zeolite, a hydrophobic zeolite sorbent recently commercialized by Degussa AG, was also studied in year four (Lin and Deng, 1994) for its SO_2 adsorption and diffusion properties, and thermal, hydrothermal and chemical stability. The results obtained in our laboratory (Deng and Lin, 1995b) have demonstrated that the DAY zeolite have a much larger surface area (712 m^2/g) than that of γ-Al_2O_3 supports (350 m^2/g). Moreover, the DAY zeolite has a good hydrophobicity, and exceptional thermal, hydrothermal and chemical stability. These unique properties make the DAY zeolites very attractive as sorbent or catalyst support for FGD or other environmental or chemical processes where severe operating conditions are involved. Since the physical adsorption capacities of SO_2 in the DAY zeolite are small at 100 °C, the DAY zeolite is not effective when it is directly used as sorbent in flue gas desulfurization processes operated at temperatures higher than 100 °C. Appropriate modifications on the DAY zeolite are needed to make it more reactive to SO_2 at the regular temperature of flue gas in the flue gas clean-up processes.

The specific objectives of the research proposed for year five (1994-1995) were:

(1) fabrication of granular CuO/γ-Al_2O_3 sorbents

(2) measurements of mechanical and attrition properties of the synthesized sorbents

(3) study of SO_2 sorption and regeneration on the supported CuO sorbents and

(4) synthesis and characterization of CuO/DAY zeolite sorbents.

The results obtained in year five are presented next.

Technical Discussion

Granular Alumina Supports and Supported CuO Sorbents

Sorbent Synthesis

The sol-gel fabrication of the γ-alumina spheres started with an aqueous sol of pseudo-boehmite (gelatinous boehmite). The first step was to prepare 2M boehmite sol (γ-ALOOH) using the Yoldas's process (Yoldas, 1975). The 2M boehmite sol was synthesized by dissolving alumina-tri-secondary butoxide (97%, Janssen) in the deionized water at an initial temperature of 75 °C, and stirred vigorously. After heating at 90 °C for 1 h, the resulting slurry with γ-ALOOH precipitates was peptized with 1M HNO_3. The peptized sol was refluxed at 90~100 °C for 10 h to yield a stable boehmite sol. The pseudo-boehmite sol was prepared by adding nitric acid or nitric acid mixed with urea into the 2M 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 pseudo-boehmite 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 experiments of granulation, an water soluble organic monomer (acrylic acid) was also added into the pseudo-boehmite sol as a polymerization initiator before dropping the sol into oil layer.

A flow diagram of the formation of spherical supports and adsorbents by the sol-gel granulation method is shown in Fig. 1. This process consists of droplet generation, shaping and partially gelating the droplets into spherical wet-gel granules, and gelating and aging the wet-gel granules into solid get granule. The oil layer was about 1.0 m high and filled with a paraffin oil (white, density: 0.7864 g/cm^3, kinetic viscosity: 34.5 centistokes at 40 °C, Fisher Scientific) which was heated at 90-100 °C during the granulation experiments. The ammonia solution layer (15% NH_3) was about 0.15 m high and was kept at room temperature.

The starting pseudo-boehmite sol was dispersed into droplets by a dropper, the droplets were than suspended in the immicible paraffin oil layer to form a spherical droplet due to the surface tension. Partial gelation of the droplets occurred in the oil-layer to make the droplet integral wet-gel granule. Some surfactant was added into the oil layer to facilitate the formation of a thin oil film around the wet-gel granule to protect its integrity when the droplets fell further into the aqueous solution of ammonia. The oil film remained in place for a few seconds, after which it broke up and rose to the oil layer. The ammonia would penetrate through the oil film to neutralize the acid in the sol. Therefore, the wet gel granules were further gelated, aged and became solid granules in the ammonia layer. The wet-gel solid granules formed from the above process were then withdrawn from the forming reactor, 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 the controlled conditions for alumina calcination (Chang, 1993). The boehmite was converted into the γ-alumina during the calcination step. Different size of droppers were used to control the particle size of the final spheres.

Experiments showed difficulty to form unbroken γ-alumina wet gel granules with relatively large size (1-5 mm) by the sol-gel granulation method directly from 1M boehmite sol commonly used to synthesize γ-alumina powder supports and membranes (Lin et al., 1994). This is primarily because the particulate concentration (6 wt.% of AlOOH) of the starting boehmite sol (1M) was too small compared with 20-40 wt.% of AlOOH in the starting sol as reported in the literature for the fabrication of γ-alumina granules by the "oil-drop" process (Meyer and Noweck, 1982; Shepeleva et al., 1991). So 2M boehmite sol was synthesized and used to form the starting pseudo-boehmite sol in this work. In order to determine the solid concentration of AlOOH in the pseudo-boehmite sol prepared in this work, 5 g of pseudo-boehmite sol was dried and calcined under the standard conditions for preparing γ-Al_2O_3 (Chang, 1993), about 0.735 g of γ-Al_2O_3 was obtained. From this experimental result the solid concentration of AlOOH in the pseudo-boehmite sol prepared in this work was estimated to be 17.3 wt.%.

The major difference between the sol-gel granulation method developed in this work and other established "oil-drop" methods for preparation of alumina supports is that the pseudo-boehmite sol used in this work was prepared from 2M boehmite sol and pseudo-boehmite sol prepared by dispersion of pseudo-boehmite powder in acid solution were used in all other reported methods (Cahen et al. 1979; Myer and Noweck 1982; Shepeleva et al. 1991; Svoboda et al. 1994). It is expected that the pseudo-boehmite sol used in this work will have high purity, more uniform primary particle size and therefore more desirable pore structure and mechanical properties. Since the properties of the starting pseudo-boehmite sol used in this work can be tailored to meet various applications, the sol-gel granulation process developed is more flexible and versatile.

Several different spherical γ-alumina samples (AL-S-1 to AL-S-6) were prepared by the sol-gel granulation method using the pseudo-boehmite sol derived from 2M boehmite sol under various experimental conditions summarized in Table 1. As shown in Table 1, the optimal pH range of the pseudo-boehmite sol to obtain integral wet gel granules was found to be 1.55~1.75. The samples AL-S-2 and AL-S-3 prepared from the pseudo-boehmite sol with a pH of 1.65 were found to be the best in terms of the integrity and sphericity of granules. The difference between these two samples was that sample AL-S-3 was prepared from the pseudo-boehmite sol added with 0.5 wt.% of 0.5 wt.% acrylic acid. It is believed that the introduction of organic monomer as a polymerization initiator could promote the forming of rigid bonds within the spheres (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 could be 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 into the starting pseudo-boehmite 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 pseudo-boehmite 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. The same conclusion can be found in the literature on the preparation of spherical alumina supports using the "oil-drop" method from different pseudo-boehmite sols. Although the addition of urea to the pseudo-boehmite 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 decomposition of urea, the residual urea in the wet gel granules was difficult to remove and would have detrimental effect on the integrity of the granules formed. The γ-alumina granules (Sample AL-S-5) made from the pseudo-boehmite sol added with urea were found to have poor mechanical strength.

After aged in the ammonia solution and separated from the liquid media the wet gel of the alumina granules became rigid enough to be transported, washed and dried. 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 is very important and necessary to obtain perfect alumina spheres with desirable pore structure and mechanical properties. The standard drying and calcining conditions for preparation of γ-alumina supports and membranes have been extensively studied and established (Lin et al., 1994). All the spherical γ-alumina granules were dried and calcined under these standard conditions. The wet gel of the alumina granules shrank about 2 times in diameter after drying and calcination. By changing the size of dropper, spherical γ-alumina granules with different diameter ranging from 1 to 3 mm were prepared. Among these samples the spherical γ-alumina granules with diameter around 1.75 mm were prepared in large quantity and used to prepare the γ-alumina supported copper oxide granular sorbents.

Wet-impregnation method was used to prepare the γ-alumina supported copper oxide sorbents as described elsewhere (Deng and Lin, 1996). As precursor solution for active species CuO, an aqueous salt solution containing copper 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-treated at 200°C for several hours, were put into the solution containing 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 the active species 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 the Cu^{2+} in the solution used in the wet-impregnation step. Doping amount of copper oxide on the γ-alumina granular supports ranging from 20-40 wt.% was used in order to obtain high loading of CuO on the γ-alumina support. It was reported that uniform dispersion of CaO could be achieved on the surface of γ-alumina by *in situ* impregnation during gelation of γ-alumina in an aqueous solution (Duisterwinkel, 1991; Duisterwinkel and Frens, 1995). Since stability of the sol would be disturbed if aqueous cupric chloride solution was mixed with boehmite sol as observed in our previous study (Lin and Deng, 1994), it was difficult to coat CuO on the γ-alumina using cupric chloride as copper source by this *in situ* impregnation method.

Characteristics of Sorbents

The appearance, calibration, sphericity and diameter of the spherical γ-alumina supports and sorbents prepared were examined by a 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 at liquid nitrogen temperature (78 °K) automatically. The adsorption isotherm was used to calculate the BET surface area, and the desorption isotherm was used to calculate the pore size distribution. 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). These experiments were carried out to examine if the sol-gel derived γ-alumina granular supports and sorbents have the similar pore structure, phase structure as those of the γ-alumina supports and sorbents in powder form obtained in our previous works.

A microscopic view of a single granule and multiple granules prepared under the same experimental conditions is shown in Fig. 2. A close look of a single granule as shown in Fig. 2(A) clearly demonstrates that the γ-alumina granule (diameter: 1.75 mm) obtained is a spherical granule with smooth surface which does not have any cracks or protrusions, and particle fragments. Fig. 2(B) shows that the multiple granules prepared under the same experimental conditions are non-aggregated spherical particles without lumps. The particle sizes of these granules are uniform. This smooth spherical shape and narrow particle size distribution provided the necessary homogeneity of γ-alumina support for catalyst or adsorbents used in either 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 size can be used and the generation of sol droplets can be performed by spraying the starting sol into the oil layer.

Nitrogen adsorption isotherms of all the samples are of type IV, as shown in Fig. 3(A) for sample AL-S-2. The desorption hysteresis loop indicates that these sorbents have a mesoporous pore size distribution as shown in Fig. 3(B) for sample AL-S-2. The BET surface area, pore volume, average pore size and pore size distribution range for these sorbents are summarized 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 prepared from 1M boehmite sol in our previous studies (Deng and Lin, 1996).

As shown in Table 2, 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 small amount of organic monomer to the starting pseudo-boehmite 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 pseudo-boehmite 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 BET surface area (200~300 m^2/g) of other alumina spheres fabricated by other sol-gel methods from different starting sols (Cahen et al. 1979; Myer and Noweck 1982; Shepeleva et al. 1991; Svoboda et al. 1994). The large BET surface area, pore volume and uniform pore size distribution make the γ-alumina granules prepared in this work very unique supports for adsorbents and catalysts. The improvement of the pore structure of the γ-alumina granules obtained in this work is primarily because the starting pseudo-boehmite sol used in this work has more uniform primary particles which was obtained from 2M boehmite sol synthesized in this work under the controlled conditions.

Sample AL-P-0 was prepared by directly drying, followed with calcining, the starting pseudo-boehmite sol under the standard drying and calcining conditions for preparation of γ-alumina from boehmite sol (Lin et al., 1994). As compared with the γ-alumina granules obtained by the sol-gel granulation method shown in Table 2, sample AL-P-0 has a smaller BET surface area and pore volume. This is because the preparation method of the γ-alumina granules developed in this work was very unique. Several stages involved in the forming of the granules might contribute to the improvement of the pore structure of the γ-alumina granules. The interfacial energy of the gel particles would be reduced and less shrinkage was expected when the pseudo-boehmite sol droplets were gelated in the hot paraffin oil layer. The aging of 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. The extraction of oil and water with alcohol during the washing stage might also reduce the interfacial energy during the drying process of the alumina particles due to the replacement of water with ethanol which can be removed much more easily and faster than water.

According to the monolayer dispersion theory (Xie and Tang, 1990), about 40 wt.% of the CuO can be coated on the surface of γ-Al_2O_3 support with a BET surface area of 350 m^2/g. In the preparation of adsorbents 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 thus to enhance the adsorption capacity of SO_2 of the sorbents. Sorbents containing about 20 wt.%, 30 wt.% and 40 wt.% of CuO were prepared to explore the monolayer coating amount on this specific γ-alumina support. As shown in the XRD patterns of these three CuO sorbents in Fig. 4, no sharp response peak was detected in all these samples. Based on the results shown in this figure it is reasonable to conclude that 40 wt.% or less of CuO can be coated as a monolayer or sub-monolayer on the surface of the spherical γ-alumina granular supports. According to our previous studies (Deng and Lin, 1996), about 20 wt.% of CuO could be coated on the surface of a sol-gel derived γ-alumina powder support in a monolayer form, and the CuO sorbent containing 20 wt.% of CuO gave the best desulfurization performance. The higher monolayer loading of CuO achieved on these granular sorbents is primarily because the specific surface area of the granular support (380-400 m^2/g) is about 15% larger than that of the powder support. About 5 g of the γ-alumina supported CuO granular sorbents containing 30 wt.% of CuO were prepared for the study of desulfurization properties of these γ-alumina supported CuO granular sorbents on microbalance.

Mechanical Properties of Granular Alumina Supported CuO Sorbents.

The crushing strength of individual granular γ-alumina supports and sorbents of different size prepared in this work and other commercial supports and adsorbents were experimentally determined by an universal testing instrument (Instron 4465). During this experiments, an 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 loading frame of the instrument and the other flat plate attached to a crosshead moving towards the granule at a controlled speed of 2 mm/min. A compression load cell (force sensor, 0-400 1b) 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 test, the granule crushes or collapses 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 crushing strength.

Several attrition tests are available to measure the attrition tendency of fluidized solids or moving solids in a drum (Danner and Unger, 1987; Doolin, 1993; Lee et al., 1993; Spek and van Beem, 1982). Many of these tests assign a number to 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 these established attrition test methods, the Peter Spence method is a simple and practical one. As shown in Fig. 5, a Peter Spence attrition apparatus (Spek and van Beem, 1982) consisting of a motor, a motor controller and an attrition testing tube was set up to measure the attrition rate of the alumina supports and sorbents prepared in this work. The attrition tube which comprises a stainless steel tube of internal length 315 mm and internal diameter 16 mm was 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 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) were used as attrition index and calculated by the following equation:

$$\text{Attrition Index} = (\text{Initial Weight} - \text{Remaining Weight}) / \text{Initial Weight} / \text{Time} \times 100\% \qquad (1)$$

Several supports and adsorbents including the sol-gel derived spherical γ-alumina granules prepared in this work, a commercial γ-alumina support (D-135, in spherical form, made by Alcoa), and two commercial zeolite adsorbents (DAY zeolite made by Degussa AG, and silicalite by Union Carbide Co., cylindrical) were tested for their crushing strength. Fig. 6 shows the typical load-displacement curves obtained in the crushing strength test for the sol-gel derived spherical γ-alumina supports. As shown in Fig. 6, the alumina particles are elastic and the maximum displacements before crushed are about 40~75% of the diameter of the spheres. All the spherical γ-alumina granules of different diameters have the same type of load-displacement curve, initial part of all the load-displacement curves (at low load) following the same trajectory. The side crushing strength is the maximum load to crush a particle. The side crushing strength seems to be proportional to the diameter of the granules tested in this work.

The experimental results of the side crushing strength (maximum load to break a single particle) of samples prepared in this work and commercial samples are summarized in Table 3. As summarized in Table 3, the largest crushing strength obtained on the γ-alumina granular supports (diameter = 2.6-2.8 mm) prepared in this work is 190 N, about 4.5 times as large as that of a commercial alumina granular support (LD-350, diameter = 4-4.6 mm) made by Alcoa. The crushing strengths of the two commercial zeolite adsorbents (extrudates) are less than 40 N, much less than that of the γ-alumina granular supports (diameter > 1.5) prepared in this work. The values of crushing strength of the γ-alumina granular supports prepared in this work are in the same range of the γ-alumina granular supports made by other sol-gel methods from different starting boehmite sols (Cahen et al. 1979; Myer and Noweck 1982; Shepeleva et al. 1991; Svoboda et al. 1994). The large crushing strength of these sol-gel derived alumina granules is the unique property of sol-gel derived ceramic materials.

In attrition experiments, each granule sample after attrition run was examined for its breakage and formation of particle fragments and fine powder. No breakage and particle fragments were found in all samples except in silicalite adsorbent. Most of the silicalite extrudates were found broken into small particles and certain amount of fine powder was generated after the attrition test. This may indicate that the attrition of silicalite followed both particle fracture and abrasion mechanisms, and attrition of other granules follows the abrasion mechanism only. The attrition index of the sol-gel derived spherical γ-alumina granules along with other commercial supports and adsorbents determined by the Peter Spence method are summarized in Table 3. As compared with other commercial supports and adsorbents, the sol-gel derived spherical γ-alumina granules prepared in this work have the smallest physical attrition index: 0.033 wt.%/h, about 1/5 of that of a commercial alumina granule (LD-350 of Alcoa). This clearly demonstrates that the sol-gel derived spherical γ-alumina granules have exceptional attrition resistance.

As listed in Table 3, the attrition weight loss for the spherical γ-alumina granules prepared in this work is 0.785 wt.% after 24 h attrition test, which is comparable with the reported value of 0.61 wt.% for a γ-alumina support prepared by the "oil-drop" method after 6 h attrition test (Doolins et al., 1993). Because the attrition index of particles is associated with the experimental method, it is difficult to quantitatively compare the attrition index obtained in this work with those reported values for sol-gel derived alumina adsorbents and other commercial adsorbents. It was also reported by Doolins et al., (1993) that the attrition of the γ-alumina support prepared by the "oil-drop" method follows the "fracture" mechanism, while the attrition of γ-alumina prepared by the "snow-ball" method follows the "abrasion" mechanism. This may be used to explain why the sol-gel derived spherical γ-alumina granules prepared in this work have a much better attrition resistance than other granular supports and adsorbents listed in Table 3. Since the attrition of the γ-alumina support prepared by the "oil-drop" method follows the "fracture" mechanism, the attrition of this type of support would be very small if mechanical stress is not large enough to break the particles in the attrition test. This is probably the situation occurred in the attrition test in this work.

The high mechanical strength, high attrition resistance as well as the desirable pore structure of the spherical γ-alumina granules prepared in this work are the unique properties of sol-gel derived ceramic materials. In synthesizing these adsorbents, particles. These aggregates were broken apart into the primary boehmite particles during the drying step as a result of large capillary force involved (Leenaars et al., 1984). Finally the boehmite was transformed to γ-alumina and the particles were consolidated during the calcination step. So the final adsorbent samples consisted of nanoscale primary particles of rather uniform size. These uniform particles are strongly bounded together during the calcination step and the adsorbent granules become mechanically very strong.

Sulfation Properties of Alumina Supported CuO Sorbents

Sulfation Properties of Granular Alumina Suported CuO Sorbents

A microelectronic recording balance system (Cahn C-1000) as shown in Fig. 7 was employed to determine the desulfurization properties of the γ-alumina supported copper oxide granular sorbents. The sulfation, regeneration and oxidation curves on the γ-alumina supported pellets were measured under controlled conditions as listed in Table 4. About 100 mg of sorbent particles were put in the sample basket made of stainless steel sheet. Gas flows from certified gas cylinders were controlled by the mass flow controllers and blended to generate desired sulfation, regeneration and oxidation gas mixture. The temperature of the reactor tube (2"-inside diameter quartz tube) was maintained isothermally with a furnace and was measured by a thermocouple placed on the outer surface of the reactor tube. The temperature differences between the inside and outside of the reactor tube were calibrated in advance under a wide range of operation conditions. The weight change of the sorbent, temperature, pressure were recorded by a personal computer with a data acquisition software (QuickLog).

The sulfation runs at a given condition were performed to examine the sulfation properties of the prepared sorbents. Sulfation curves at 500 °C with air stream containing 0.8 % SO_2 at a total flow rate of 600 ml/min were measured on a γ-alumina supported copper oxide granular sorbent with 30 wt.% of CuO. Sulfated sorbents were regenerated at 500 °C with 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. Sulfation on the same sorbent copper oxide granular sorbent with 30 wt.% of CuO. Sulfated sorbents were regenerated at 500 °C with 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. Sulfation on the same sorbent at different temperatures of 300, 400 and 500 °C were also carried out to examine the temperature effect on the sulfation properties. The interaction between CO_2 and the supported copper oxide sorbents during the sulfation reaction and its effects on the sulfation properties of the sorbents were also studied in this work. A gas stream containing 15% CO_2 in air (about 13% of CO_2 in the flue gas) or a gas stream containing 15% CO_2, and 0.8% SO_2 in air was introduced to the reactor tube at the normal experimental conditions to observe the weight change of the supported copper oxide sorbents.

Sulfation, regeneration and oxidation properties on the sol-gel derived alumina powder supported CuO sorbents were systematically investigated in our previous works and presented in previous report (Lin and Deng, 1994) and publications (Deng and Lin, 1996, 1995a). This section will only present the major results obtained on the CuO sorbent granules and compare them with the results on powder sorbents. All the desulfurization experiments reported here are carried out on the CuO granular sorbent containing 30 wt.% of CuO. The experimental results on the sulfation, regeneration and oxidation of the γ-alumina supported CuO granular sorbents at 500 °C are given in Fig. 8. The specific conditions for each experimental step (A to E) shown in Fig. 8 are listed in Table 4. As shown in Fig. 8, similar sulfation, regeneration and oxidation curves are observed on the granular sorbents as those on the powder sorbents (Deng and Lin, 1996). The SO_2 sorption capacity on the CuO sorbent increases with the increasing of temperatures in the temperature range of 350-500 °C as shown in Fig. 9. This trend of variation of sulfation uptake with temperatures is also similar to that on the powder sorbents. But the granular sorbents have a larger SO_2 sorption capacity and faster sulfation rate as compared with the powder sorbents studied in our previous work (Deng and Lin, 1995a). This is because the granular sorbent tested in this work has a higher

CuO loading and larger BET surface area than those of the powder sorbents studied in our previous work and described in our previous report (Lin and Deng, 1994).

Fig. 10 presents a comparison of the sulfation uptake curves of the sol-gel derived granule, powder supported CuO sorbents and a similar alumina supported CuO sorbent reported in the literature (Centi et al., 1990). Some of the detailed sulfation results on these CuO sorbents are listed in Table 5. The granular CuO sorbent tested in this work has the largest loading of CuO (30 wt.%) and therefore the largest adsorption capacity of SO_2 (25 wt.% in 75 minutes at 500 °C) as compared with other CuO sorbents listed in Table 5. The absolute sulfation rate on the granular CuO sorbent tested in this work is also the largest among these CuO sorbents compared in Table 5. These results clearly demonstrate that the γ-alumina supported CuO granular sorbent has at least the same sulfation properties as compared with other alumina supported CuO sorbents. The regeneration and oxidation curves shown in Fig. 8 are similar to those on the powder CuO sorbents, which indicates that the granular CuO sorbent has the similar regeneration and oxidation properties as those of the powder sorbents.

The effects of CO_2 on the supported CuO sorbent and its sulfation properties is experimentally determined by introducing 15% of CO_2 into the sulfation gas stream at 500 °C. The results of CO_2 effects on the sulfation properties are shown in steps D and E in Figs. 8 and 11. Fig. 11 is a close look at steps D and E in Fig. 8. As shown in Fig. 11, the weight change of the CuO sorbent due to carbonation reaction between CO_2 and CuO (step D) was very small as compared with the sulfation uptake on the same CuO sorbent when the CuO sorbent was exposed to a gas stream containing of 15% CO_2 in air after the oxidation step. The second sulfation uptake curve (step E) in Fig. 8 is basically the same as the first sulfation curve (step A) in Fig. 8. It is reasonable to draw the conclusion that CO_2 has negligible effect on the CuO sorbents during the sulfation stage.

Sulfation and Regeneration Kinetics on CuO Sorbents

In the sulfation step of the sol-gel derived alumina supported CuO sorbents, it is believed that CuO catalyses the oxidation of SO_2 to SO_3 which in turn reacts with CuO to form $CuSO_4$. The aim of this kinetic study is to analyze the mechanism of SO_2

adsorption-oxidation to form sulfate species on the above sorbent. The data for the analysis was taken from the experiments conducted in our previous work (Deng and Lin, 1996). The data was on five sorbents with CuO loading ranging from 10 wt. % to 50 wt. % at 500 °C and 1 vol.% concentration of SO_2 in the gas phase, as plotted in Fig. 12.

It has been reported that approximately 20 wt. % CuO corresponds to complete monolayer coverage of the γ-Al_2O_3 support. For our sorbents with more than 20 wt. % CuO, the S/[CuO]$_0$ ratio is less than one. Hence, if the γ-Al_2O_3 support does not come in contact with the gas phase SO_2, it can be said that only CuO sites are the active species in the reaction with SO_2. In this case the overall reaction for the sulfation on the alumina supported CuO sorbent can be expressed as:

$$CuO\,(s) + SO_2\,(g) + 1/2\ O_2\,(g) \Rightarrow CuSO_4 \qquad (2)$$

In the reactions carried out, the partial pressures of SO_2 and O_2 were held constant, and the weight gain of the sorbent due to sulfation was studied as a function of time. Thus the reaction rate is a function only of the free available CuO sites on the surface. We assumed that the sulfation reactions involve the following steps:

adsorption of SO_2:

$$SO_2(g) + I <-> \{SO_2\} \qquad (3)$$

where I is the active site for adsorption. CuO catalyzes the oxidation of SO_2 to SO_3 as:

$$CuO + \{SO_2\} <-> \{CuSO_3\}^* \qquad (4)$$

Finally, the sulfation reaction occurs:

$$CuO + \{CuSO_3\}^* -> CuSO_4 + Cu \qquad (5)$$

Assuming that reactions (3) and (4) are in equilibrium, and reaction (5) is the rate-limiting step, we can derive the following rate equation:

$$-r_{CuO} = [CuO]^2k'P_{SO2}/(1 + bP_{SO2}) \tag{6}$$

For constant P_{SO2}, we denote

$$K= k'P_{SO2}/(1 + bP_{SO2}) \tag{7}$$

So the above equation becomes:

$$d[CuO]/dt = -K[CuO]^2 \tag{8}$$

This indicates a mechanism of second order with respect to the concentration of CuO on the support surface. Following the definition of the conversion of CuO during the sulfation reaction as:

$$X = (\text{wt\% gain})/M_{SO3}/(\text{wt\% of CuO coated})/M_{CuO} \tag{9}$$

where M_{SO3} and M_{CuO} are molecular weight of SO_3 and CuO (80.0 and 79.5 respectively), we integrated eq.(8) with proper initial conditions to give:

$$X = [CuO]_oKt/(1+[CuO]_oKt) \tag{10a}$$

or

$$X/(1-X) = [CuO]_oKt \tag{10b}$$

Thus, X [or X/(1-X)] can be plotted vs time (t) to test for the second order dependence.

The correlation results for the model are summarized in Table 6 where K is the constant shown in Eq.(7). Fig.13 shows graphical comparison between the calculation and experimental results for sulfation on three sorbents containing 20 wt.%, 30 wt.% and 40 wt.% CuO. For sorbents with more than 20 wt. % CuO, the second order model compares very well with the experimental data. For the 20 wt % sorbent, the present model does not fit with the experimental data due to the effects of sulfation on the alumina support.

Also we see that the uptake for 30 wt. % sorbent is lower than that for 20 wt.% sorbent It is possible that although the loading is 30 wt %, the additional CuO might be blocking the pores, and thus some active species do not come in contact with SO_2. The above observed agreement between the model and experimental data is also reflected numerically by the regression coefficient R^2, which is also summarized in Table 6. The closer to one of the value of R^2, the better the model fits the experimental data.

Centi et al. (1992) have performed a kinetic analysis for 4.8 wt. % CuO sorbent at various SO_2 partial pressures (0.2 - 1.05 vol. %) and at temperatures ranging from 250 °C to 350 °C. Since they had very low CuO loading, they reported that the γ-Al_2O_3 support also played a role in the sulfation reactions. They reported maximum molar ratio of $S/[CuO]_0$ is 1.8, which is higher than 1 for the case when only CuO took part in the reactions. Centi et al. (1992) also reported that the sulfation kinetics on CuO can be best described by the second order reaction model. In our experiments we also observed molar ratio of $S/[CuO]_0 = 1.4$ on 10 wt. % CuO sorbent. Our results are consistent with those reported by Centi et al.

Only a few studies on regeneration of sulfated copper oxide sorbents have been reported in the literature (Markussen et al. 1994). Since the material and energy consumption in the regeneration stage is the major economic concern of the flue gas desulfurization process, the selection of appropriate regeneration conditions will be very crucial to the success of the commercialization of the copper oxide process.

It is known that both regeneration reactions with CH_4 or H_2 are thermodynamically favorable at temperatures higher than room temperature (Deng and Lin, 1995). With increasing temperature, the equilibrium constant and reaction rate constant for both regeneration reactions increase. This suggests that high temperature is always preferred in the regeneration stage. The regeneration curves of sulfated copper oxide sorbent (20 wt.% CuO) at 400, 450 and 500°C with methane containing gas are plotted in Fig. 14. The regeneration experiment was performed first at 400 C for 60 minutes, then at 450 °C for 15 minutes, and finally at 500 °C for 15 minutes.

The regeneration curves at 400 and 450 °C can be well described by a reaction model of zero order with respect to both reactants ($CuSO_4$ or CH_4). The regeneration curve at 500 °C can be correlated by a reaction model of first order with respect to $CuSO_4$. Kinetic constants determined for the regeneration curves plotted in Fig. 14 are given in Table 7. The zero order regeneration rate constant at 500 °C obtained in this work (3.67×10^{-3} s^{-1}) is in the same order of magnitude as the value for a similar sorbent reported by Markussen et al. (1994) (4×10^{-3} s^{-1}). The activation energy of the zero order reaction obtained in this work is 141.9 KJ/mol, larger than that of the reported value on a similar sorbent prepared by the conventional method (111.7 KJ/mol). Markussen et al. (1994) also found that the first order reaction model could only fit a part of the regeneration curve (for $X_A<0.7$). This indicates that the regeneration of the sulfated sorbent involves several different reaction mechanisms. One simple reaction model is not sufficient to describe the regeneration kinetics.

The regeneration curve on sulfated sorbent with 20 wt.% of CuO (sorption amount of SO_2 is 5.66 mmol/g) at 500 °C with gas containing hydrogen is shown in Fig. 15. Obviously the regeneration rate in this case is much faster than that shown in Fig. 14. As shown by the data given in Table 7, the ratio of the first order reaction rate constants for regeneration by H_2 to that by CH_4 is about 2. Although the regeneration reaction using hydrogen as reducing agent is thermodynamically and kinetically more advantageous, economically it is undesirable to use hydrogen as the reducing agent.

SO_2 Removal from Gas Stream by Alumina/CuO Packed Adsorber

The performance of our sorbents in packed-bed adsorber for removal of trace amount of SO_2 from gas stream is directly related to the adsorption capacity and sulfation rate of the CuO/Al_2O_3 sorbent. We have performed some preliminary computational work to simulate the breakthrough curves from an adsorber packed with one of our sorbents (containing 30 wt.% CuO). With the sulfation kinetic and capacity data given in Fig.9 and Fig.12, we have calculated SO_2 breakthrough curves for a laboratory scale adsorber of 20 cm in length and 1 cm in diameter. The calculated breakthrough curves for feed streams containing 3000, 5000 and 10000 ppm SO_2 are shown in Fig.16.

As shown in Fig.16, before the breakthrough time the SO_2 removal efficiency is 100%. The breakthrough time increases with decreasing SO_2 concentration in the feed stream. For 3000 ppm stream, the breakthrough time is 80000 sec (22.2 h) at interstitial flow velocity of 20 cm/s. Considering the length of reactor and flow velocity, the result suggests that the effluent stream from the adsorber contains no SO_2 until the SO_2 containing stream in the amount 80,000 times the volume of the fixed-bed reactor has passed through the adsorber. The adsorber is ready for regeneration after the breakthrough time.

Synthesis and Properties of Zeolite Supported CuO Sorbents

Synthesis by Conventional Thermal Dispersion Method

The conventional thermal dispersion method, as proposed originally, was first applied to prepare supported CuO sorbents using CuO or $Cu(NO_3)_2$ as copper precursor and the DAY zeolite powder as support. The CuO or $Cu(NO_3)_2$ was first milled to fine powders with agate pestle and mortar, and then mechanically mixed with the DAY zeolite powder, milled with agate pestle and mortar for about 10 minutes. The mixed powder were heated in a Muffle furnace instead of in the microwave oven. The heat-treatments were carried out at 850 °C for 36 h with heating and cooling rate of 100 °C/h.

The X-ray diffraction (XRD) patterns for all the prepared sorbents were measured to examine their crystalline structure and the dispersion of the active species on the surface of support. The pore texture data for selected sorbents were determined by the nitrogen adsorption/desorption porosimeter (Micromeritics, ASAP 2000). Detailed information on XRD experiment and pore structure characterization were given in the previous report (Deng and Lin, 1996).

Selected DAY zeolite supported CuO sorbents were tested for their desulfurization properties in a Cahn balance system as shown in Fig. 7. The SO_2 adsorption uptake curves the supported CuO sorbents were measured at 500 °C with air stream containing 0.8% SO_2 at a flow rate of 600 ml/min. Regeneration of the sulfated sorbent was carried out at a higher temperature (600 °C) with a nitrogen stream containing 10% of methane at a flow rate of 500 ml/min. Oxidation was carried out at 500 °C under flow of air stream at flow rate of 500 ml/min.

Five DAY zeolite supported CuO sorbents (DAY5 to DAY4) were prepared by the conventional thermal dispersion method using $Cu(NO_3)_2$ or CuO as precursor. Table 8 lists the content of CuO, pore texture data and strength of characteristic peaks of CuO in XRD patterns for each sorbent sample. Sample DAY0 was obtained by heating pure DAY zeolite powder under the conditions shown in Table 8. Samples DAY1 and DAY2 were prepared with CuO as precursor, and sample DAY4 and DAY5 with $Cu(NO_3)_2$ as precursor. The pore structure data given in Table 8 show that the average pore size for all the samples are 6.6 Å, which is the same as that of pure DAY zeolite before heat treatment (Deng and Lin, 1995b). The corrected BET surface area for all the samples are of the same order. These results suggest that the pore structure of the DAY zeolite is basically the same after thermal dispersion of CuO.

X-ray diffraction experiment was used as the major tool to evaluate and assess the dispersion of active species on the surface of supports. Xie and Tang (1990) and several others (Friedman et al., 1978; Sivaraj and Kantarao, 1988) have demonstrated that the active species will not be XRD detectable if they are dispersed on the surface of support in a monolayer or sub-monolayer form. The XRD patterns for samples DAY0 to DAY4 along with pure CuO were plotted in Fig. 17. As shown in Fig. 17, the two characteristic XRD peaks of CuO as marked in the figure (at 2θ of 35.6° and 38.7°, for CuO (tenorite, monoclinic), JCAPC file No. 5-661) were detected in all the DAY zeolite supported sorbents (DAY1 to DAY4), indicating monolayer coating was not achieved by the conventional heating method when CuO or $Cu(NO_3)_2$ was used as precursor. This is probably because CuO has a very high melting point (1026 °C), and is relatively difficult to be thermally dispersed on the internal surface of the DAY zeolite by the conventional thermal dispersion method. Although $Cu(NO_3)_2$ has a much lower melting point (114.5 °C), upon heating at 850 °C, $Cu(NO_3)_2$ was converted to CuO before it was uniformly dispersed on the surface of the support because copper nitrate is very easy to decompose.

Sulfation experiments on DAY1 and DAY3 showed that very small adsorption amount and slow adsorption rate of SO_2 on these two sorbents were observed. About 1.0 wt.% of weight gain was measured on DAY1 after sulfation at 500 °C for 30 minutes, which is about two times the sulfation amount on the pure unsupported CuO powder

(Centi et al., 1990). It is not surprising that the sorbents DAY1 and DAY3 prepared by the conventional thermal dispersion method under the studied conditions were not very reactive to SO_2 since the XRD results, as discussed above, have already shown that the CuO was not coated on the internal surface of DAY zeolite in a monolayer or sub-monolayer form. These demonstrate the difficulty to disperse CuO on the internal surface of the DAY zeolite by the conventional thermal dispersion method.

Microwave Heating Synthesis

In microwave heating synthesis, two copper precursors (CuO or $Cu(NO_3)_2$) were used to prepare the DAY zeolite supported CuO sorbents. The copper precursors were first milled to fine powder with agate mortar and pestle, and then mechanically mixed with the DAY zeolite powder in the same way for about 10 minutes, followed by microwave heat treatment for a period of time of up to 60 minutes. The ending temperature of the sample was measured right after the power was switched off. Different doping amounts of CuO or $Cu(NO_3)_2$) were used to examine the effects of coating amount on the properties of the prepared sorbents. The phase structure, pore structure and sulfation and regeneration properties were studied by the same methods and procedures as described in the preceding subsection.

For efficient dispersion of a precursors on the surface of the support as a monolayer or sub-monolayer by microwave heating method, the precursors used should have a low melting point or fast microwave heating rate. This is the reason that $Cu(NO_3)_2$ and CuO were chosen as the precursors for preparation of the DAY zeolite supported CuO sorbents by the microwave heating method. 12 sorbents (M-DAY0 to M-DAY6 and M-AL1 to M-AL5) were prepared by the microwave heating method with loose packing mode under the full microwave power output. The ending temperatures of these samples were measured right after the switching off of the power. These samples and their preparation conditions are listed in Table 9.

As shown in Table 9, sample M-DAY0 was prepared to study the effect of microwave heating on the properties of pure DAY zeolite. Samples M-DAY1 to M-DAY4 prepared with DAY zeolite as support and different contents of $Cu(NO_3)_2$ as precursor were designed to explore the monolayer coating of CuO on the DAY zeolite. Samples M-DAY5 and M-DAY6 were prepared with DAY zeolite as support and CuO as precursor. These two sample were used to examine if CuO can be thermally dispersed on the DAY zeolite by the microwave heating method. Sample M-AL1 to M-AL4 were prepared with γ-Al_2O_3 as support and Cu(NO3)2 as precursor, while M-AL5 and M-AL6 were prepared with γ-Al_2O_3 as support and CuO as precursors.

The pore structure data of samples M-DAY0, M-DAY1, M-DAY2 and M-DAY4 are listed in Table 10. As shown in Table 10, the pore sizes are basically the same for all the samples, including the uncoated fresh DAY zeolite. The corrected BET surface area are between 935 to 1009 m^2/g, about 30-40% larger than that of the fresh DAY zeolite (712 m^2/g). The same changes of BET surface area was also observed when the DAY zeolite was at 850 °C in a conventional furnace. The change of the BET surface area indicates that the pore texture of the DAY zeolite may have changed during the microwave heating. It is interesting to point out that ending temperatures (145-158 °C) of these samples listed in Table 9 are much lower than 850 °C, but the changes in BET surface area are similar to those obtained by conventional heating at 850 °C. This directly shows that microwave heating is more powerful and can achieve the same results at a much lower temperature as compared with conventional heating method.

The ending temperatures for samples M-DAY1 to M-DAY4 and M-AL1 to M-AL3 are higher than 114.5 °C, the melting points of $Cu(NO_3)_2$, so dispersion of $Cu(NO_3)_2$ on the surface of the DAY zeolite in a uniform layer are expected. For the same reason, CuO was not expected to be dispersed on the DAY zeolite in the monolayer form in sorbents M-DAY5, M-DAY6 and M-AL4 because the ending temperatures of these samples (185-220 °C) were much lower than the melting point of CuO.

XRD patterns of the DAY zeolite supported sorbents listed in Table 9 are given in Fig. 18. As shown in the figure, the XRD pattern of sample M-DAY0 is the same as that of the fresh DAY zeolite, indicating that the microwave heating of the DAY zeolite has not changed its crystalline structure. Monolayer coating of $Cu(NO_3)_2$ was achieved in sorbents M-DAY1 and M-DAY2 since no detectable XRD characteristic peak of

$Cu(NO_3)_2$ as marked in Fig. 18 (at 2θ of 12.5°, $Cu(NO_3)_2$, JCAPC file No.1-164) was found in these two samples. The monolayer coating amounts of $Cu(NO_3)_2$ on the DAY zeolite, based on the results discussed above, is about 10 wt % (or 0.037 g CuO/g) in terms of CuO content in the sorbent. With the monolayer dispersion of $Cu(NO_3)_2$ on the surface of the DAY zeolite in samples M-DAY1 and M-DAY2, it is possible to form monolayer dispersion of CuO on the DAY zeolite by decomposing $Cu(NO_3)_2$ to given CuO at temperatures of 550 °C or higher.

As shown in Fig. 18, XRD peaks of $Cu(NO_3)_2$ were detected in sample M-DAY3 and M-DAY4, indicating that monolayer dispersion of on the DAY zeolite was not achieved in these two samples. This is probably because the monolayer coating amount of $Cu(NO_3)_2$ is less than 30 wt.%, or the heating time was not longer enough to achieve a uniform dispersion of $Cu(NO_3)_2$ in samples M-DAY3 and M-DAY4. Monolayer dispersion of CuO on the DAY zeolite was not achieved in samples M-DAY5 and M-DAY6 as found in the experiments. This is basically because the ending temperatures attained in the preparation of these two sorbents were much lower than 2/3 of the melting point of CuO.

Sulfation, regeneration and oxidation experiments on sample M-DAY4 (40% CuO) were performed to examine its flue gas desulfurization properties. As shown in Fig. 7-8, about 15 wt.% weight uptake of SO_2 is observed in the first sulfation stage. The first regeneration stage was carried out at 500 °C with a gas stream containing 10% CH_4 and 90% nitrogen. It was found that the regeneration rate is too slow at 500 °C as shown in Fig. 19. The temperature was then increased to 600°C. The regeneration stage can be divided into two steps: the decomposition of $CuSO_4$ to CuO and the reduction of CuO to Cu. Oxidation of Cu to CuO is very fast at 500 °C under the flow of air. The CuO amount in the sample estimated from the oxidation curve is about 40 wt.%. The second and the third cycles of sulfation, regeneration and oxidation are essentially the same. But the sulfation weight gain is about 7%, half of the first sulfation weight uptake. It should be noted that sample M-DAY4 exhibited much better desulfurization properties than those obtained on samples DAY1 and DAY3 which were prepared by the conventional thermal dispersion method. This indicates the effectiveness of the microwave heating method for sorbent synthesis. It is believed that sorbents with better properties could be synthesized once the microwave heating synthesis process is optimized.

Conclusions

A sol-gel granulation method was developed to prepare spherical γ-alumina granular supports and supported CuO granular sorbents for flue gas desulfurization. The prepared γ-alumina supported CuO sorbents exhibit desirable pore structure and excellent mechanical properties. The sorbents contain higher loading (30-40 wt.%) of CuO dispersed in the monolayer or sub-monolayer form, giving rise to a larger SO_2 sorption capacity (>20 wt.%) and a faster sorption rate as compared to similar sorbents reported in the literature. With these excellent sulfation and mechanical properties, the sol-gel derived γ-alumina supported CuO granular sorbents offer great potential for use in the dry, regenerative flue gas desulfurization process.

Research efforts were also made to prepare DAY zeolite supported sorbents with various CuO contents by the microwave and conventional thermal dispersion methods at different conditions. Monolayer or sub-monolayer coating of $Cu(NO_3)_2$ or CuO was achieved on several DAY supported sorbents by the microwave heating method but not by the conventional thermal dispersion method. The DAY zeolite supported CuO sorbents prepared by the microwave heating method can adsorb up to 15 wt.% of SO_2. The results obtained have demonstrated the feasibility of effective preparation of zeolite supported CuO sorbents by the microwave heating method.

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Appendices

1. Figures Presented in This Report

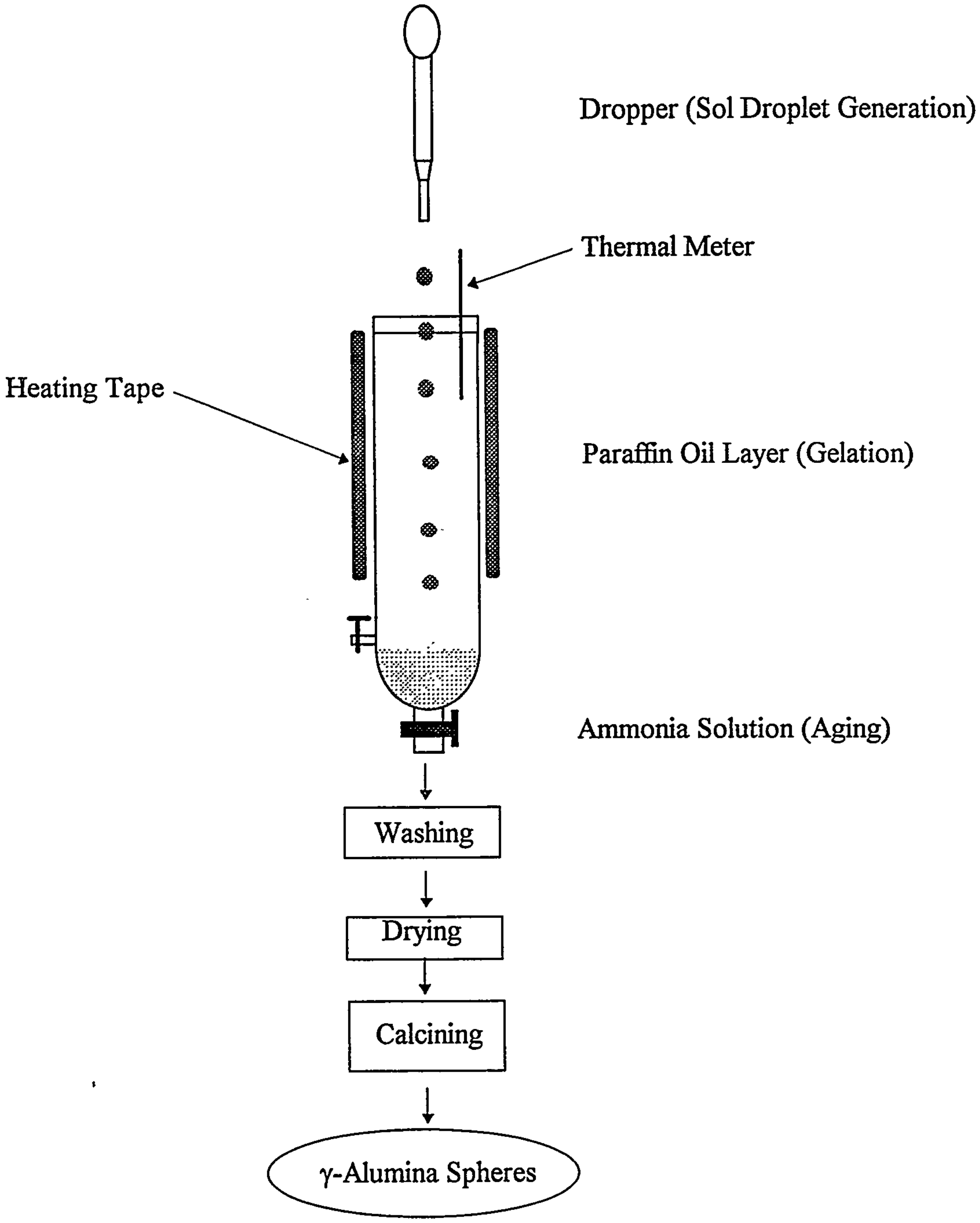

Fig. 1. Schematic diagram of the sol-gel granulation process.

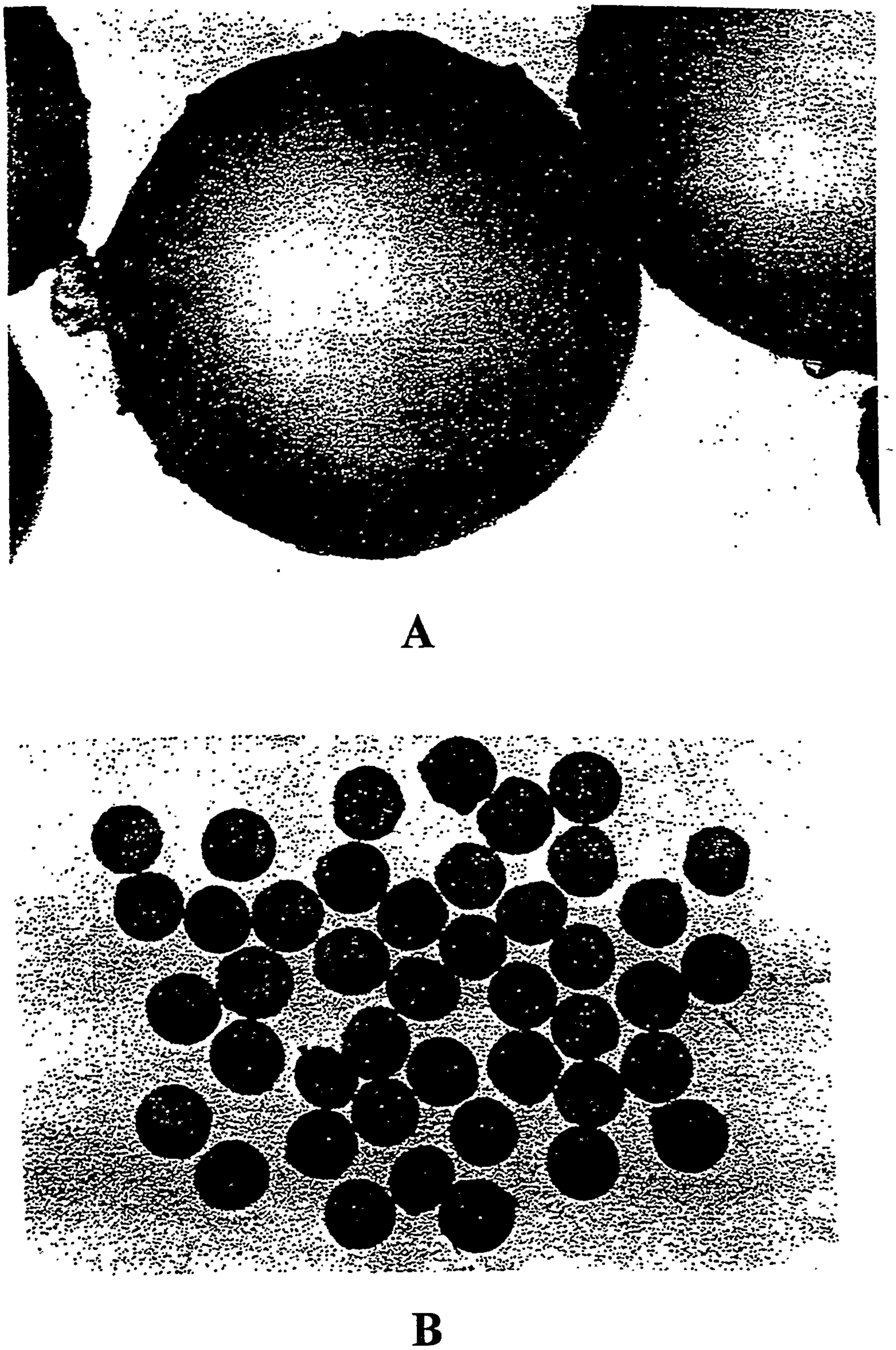

Fig. 2. Microscopic view of spherical γ-alumina granules (A: Single granule; B: Mutiple granules).

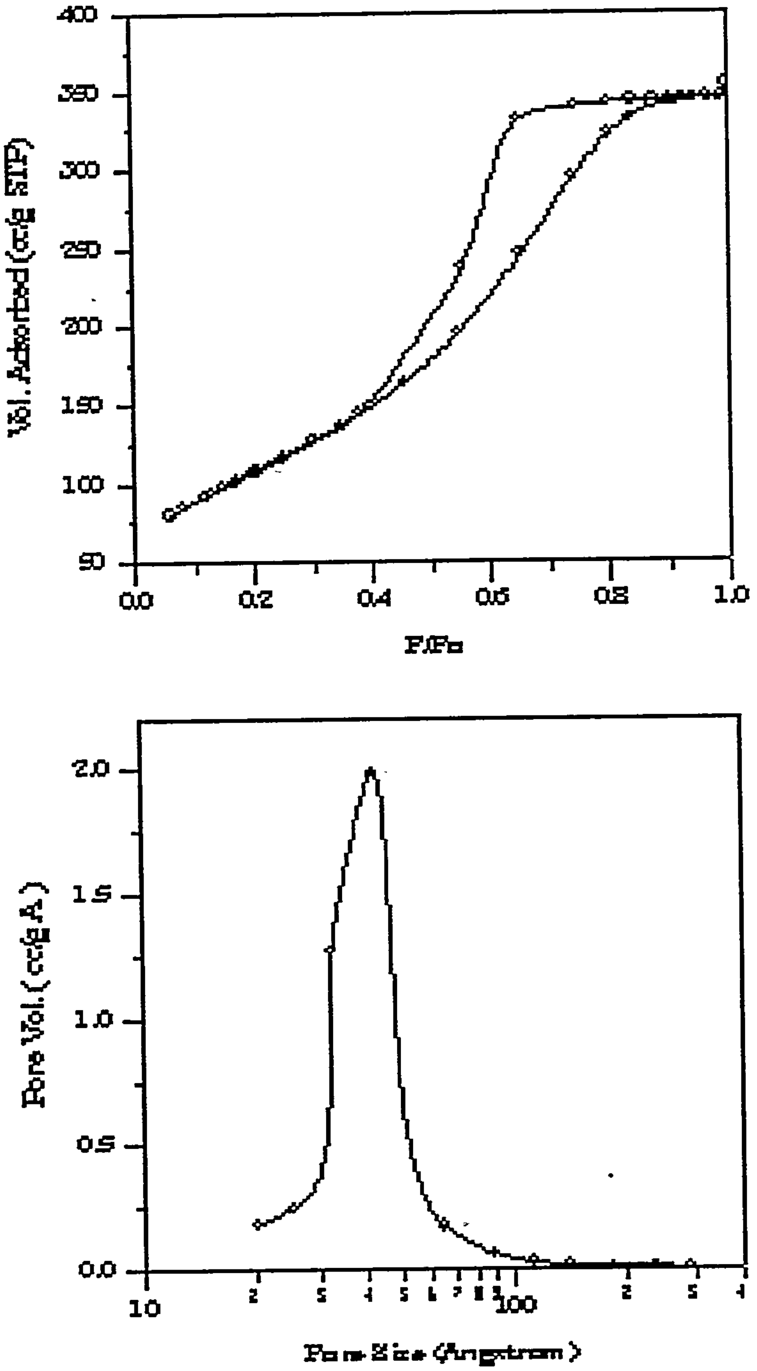

Fig. 3. Nitrogen adsorption isotherm on spherical alumina granule sample AL-S-2 (A) and its corresponding pore size distribution (B).

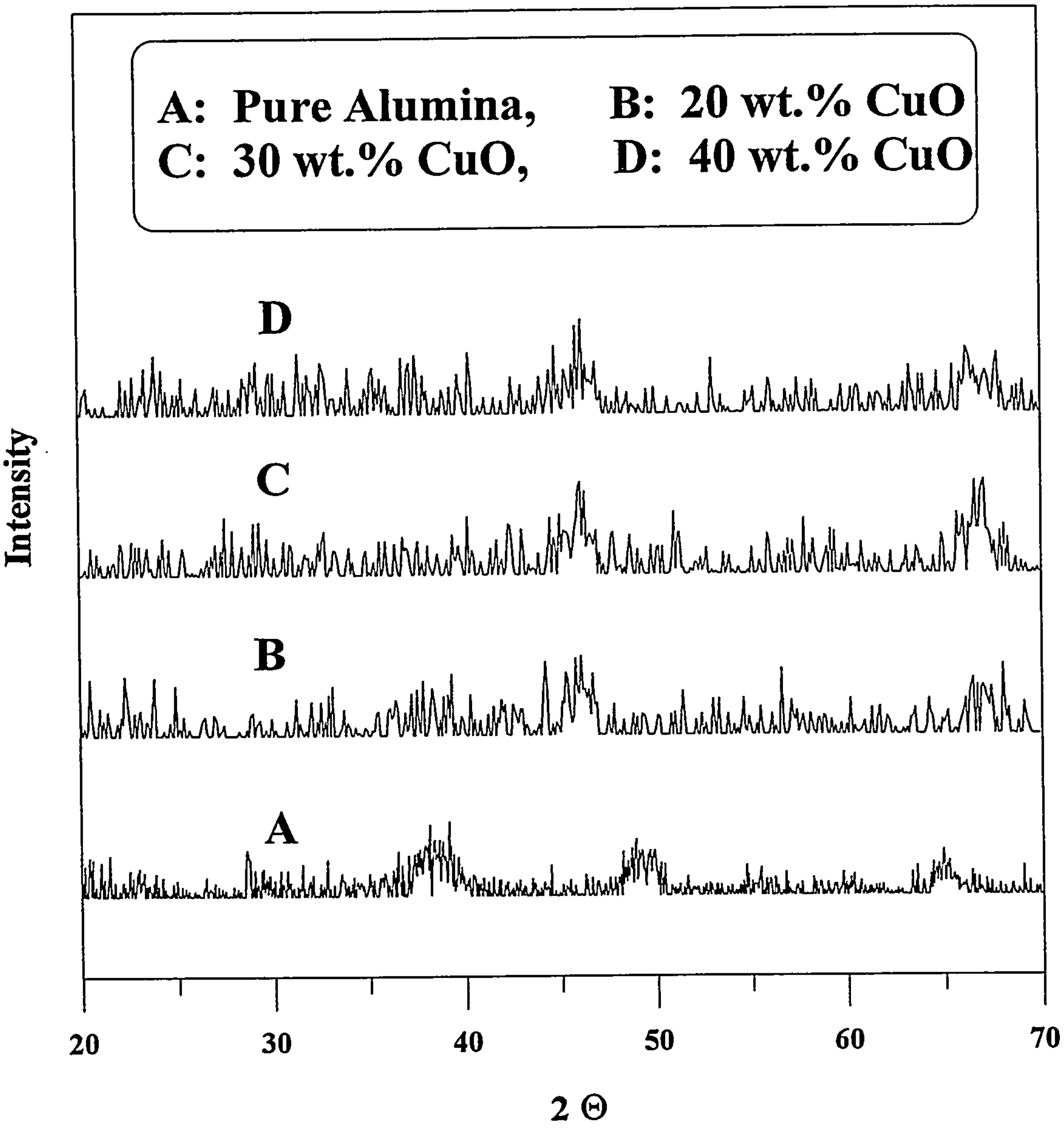

Fig. 4. X-ray diffraction patterns for alumina granular supports and supported CuO granular sorbents

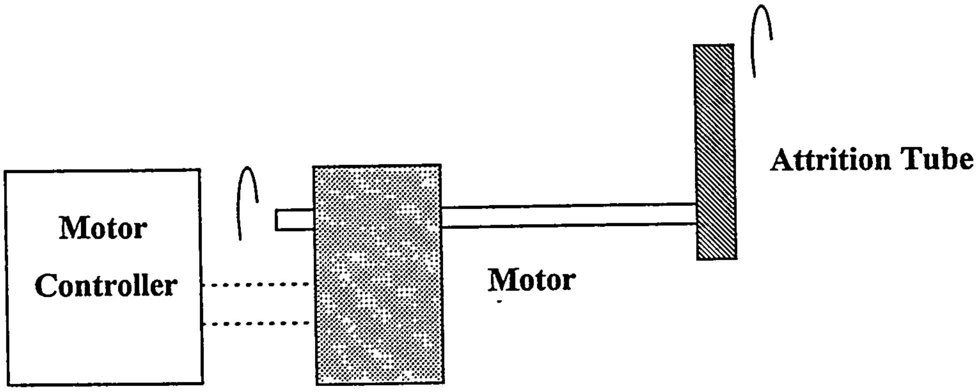

Fig. 5. Schematic diagram of Peter Spence attrition apparatus.

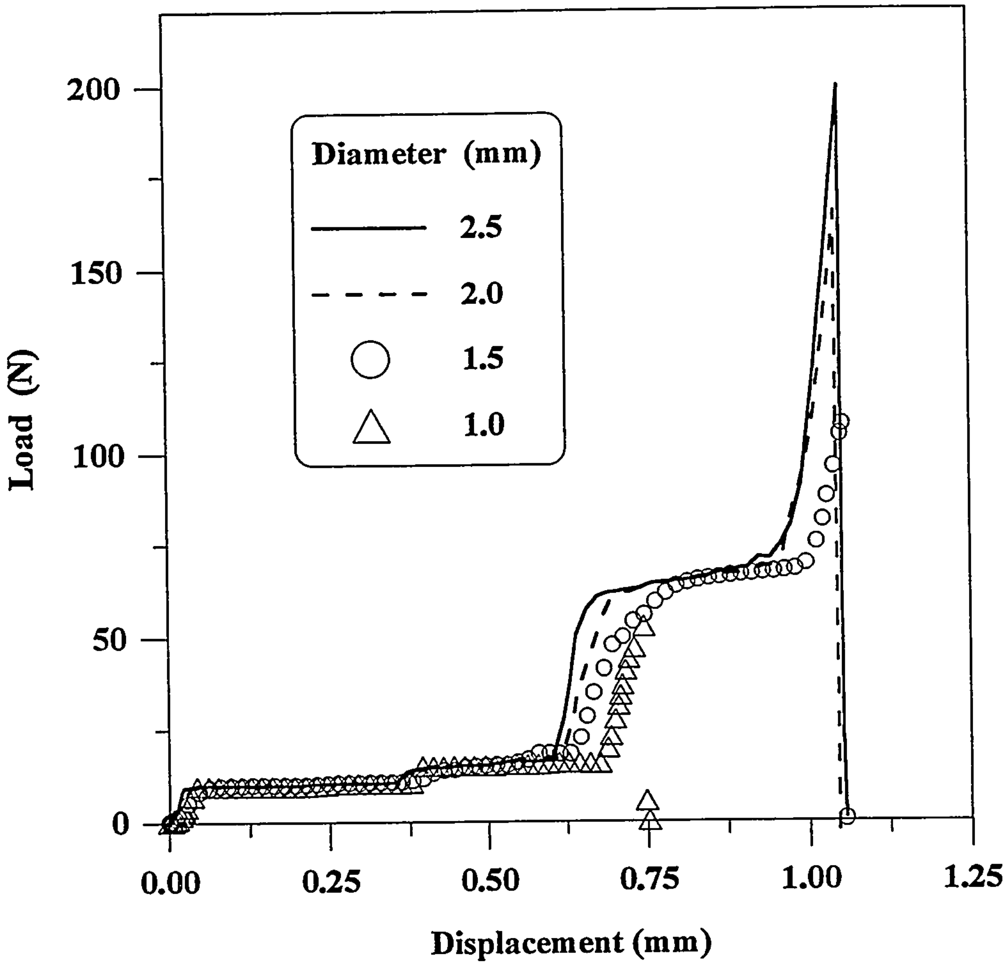

Fig. 6. Load-displacement behavior curve of γ-alumina granules.

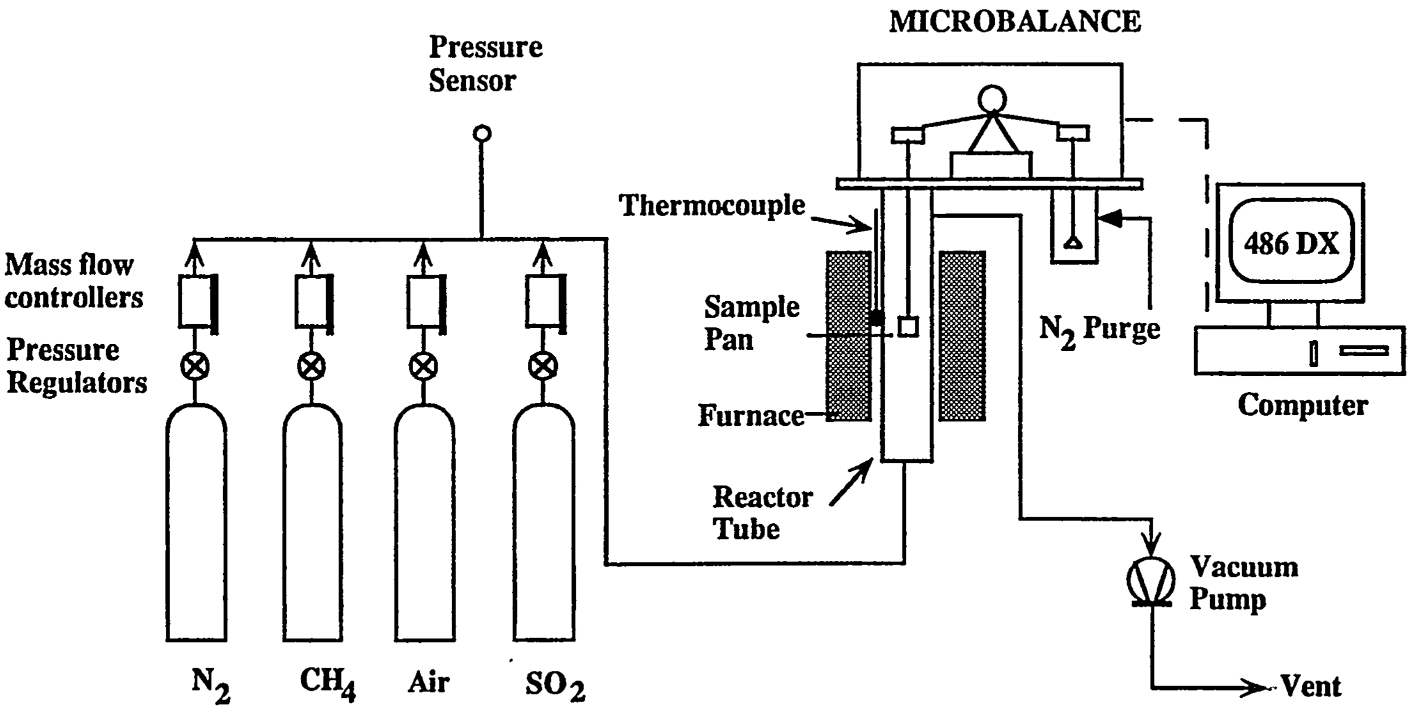

Fig. 7 Schematic Diagram of Cahn Electronic Microbalance System for Sulfation Experiments

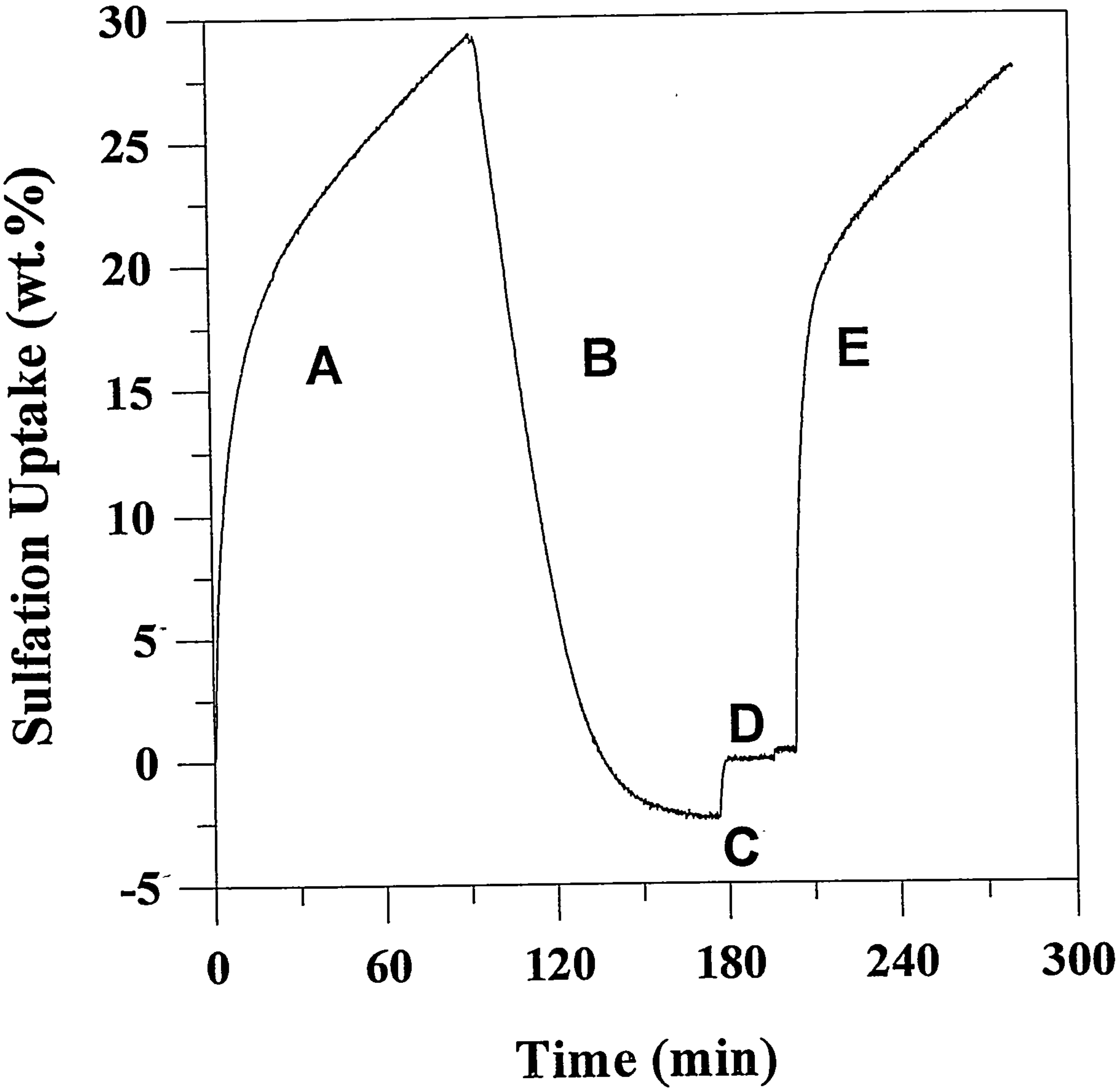

Fig. 8. Sulfation, regeneration and oxidation uptakes on granular sorbents at 500 °C.

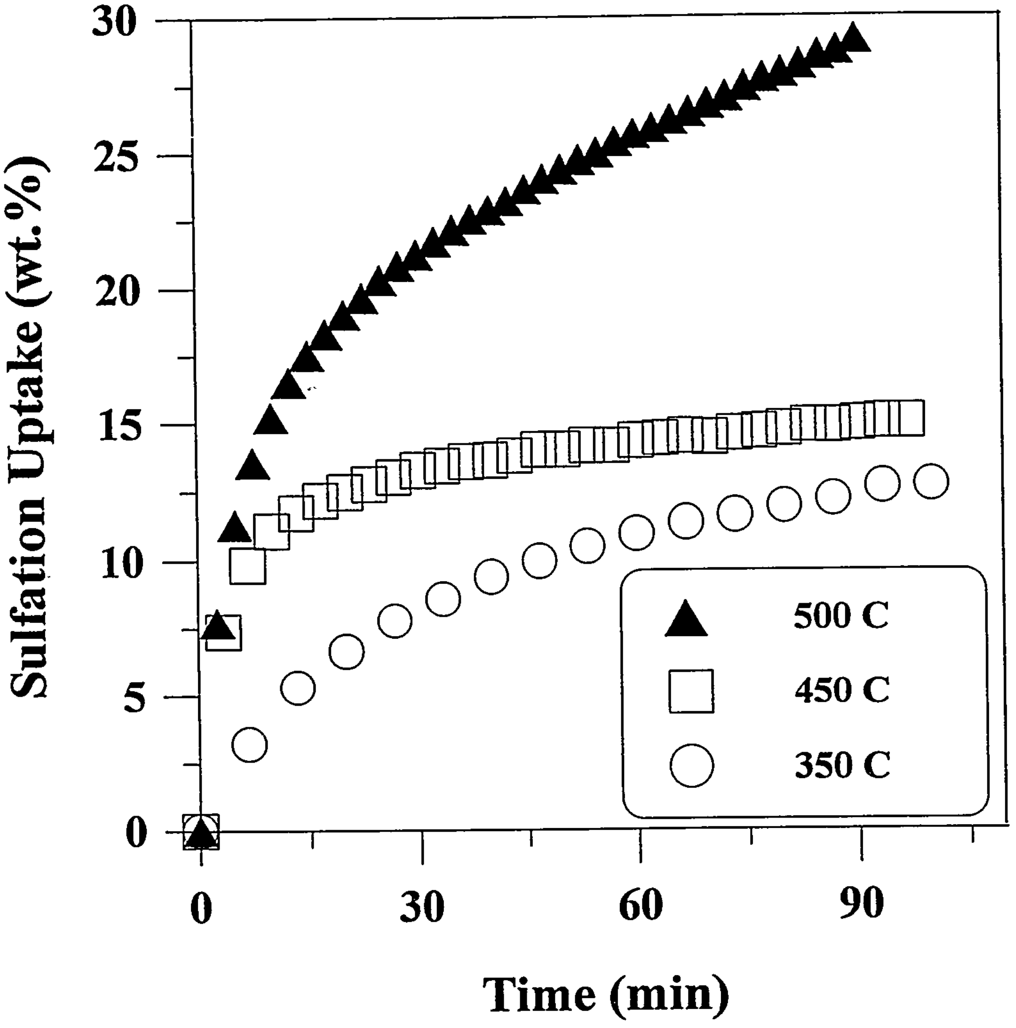

Fig. 9. Sulfation uptakes on γ-alumina supported copper oxide granular sorbents. (Flow rate: 600 ml/min, 0.8% SO_2, 99.2% air).

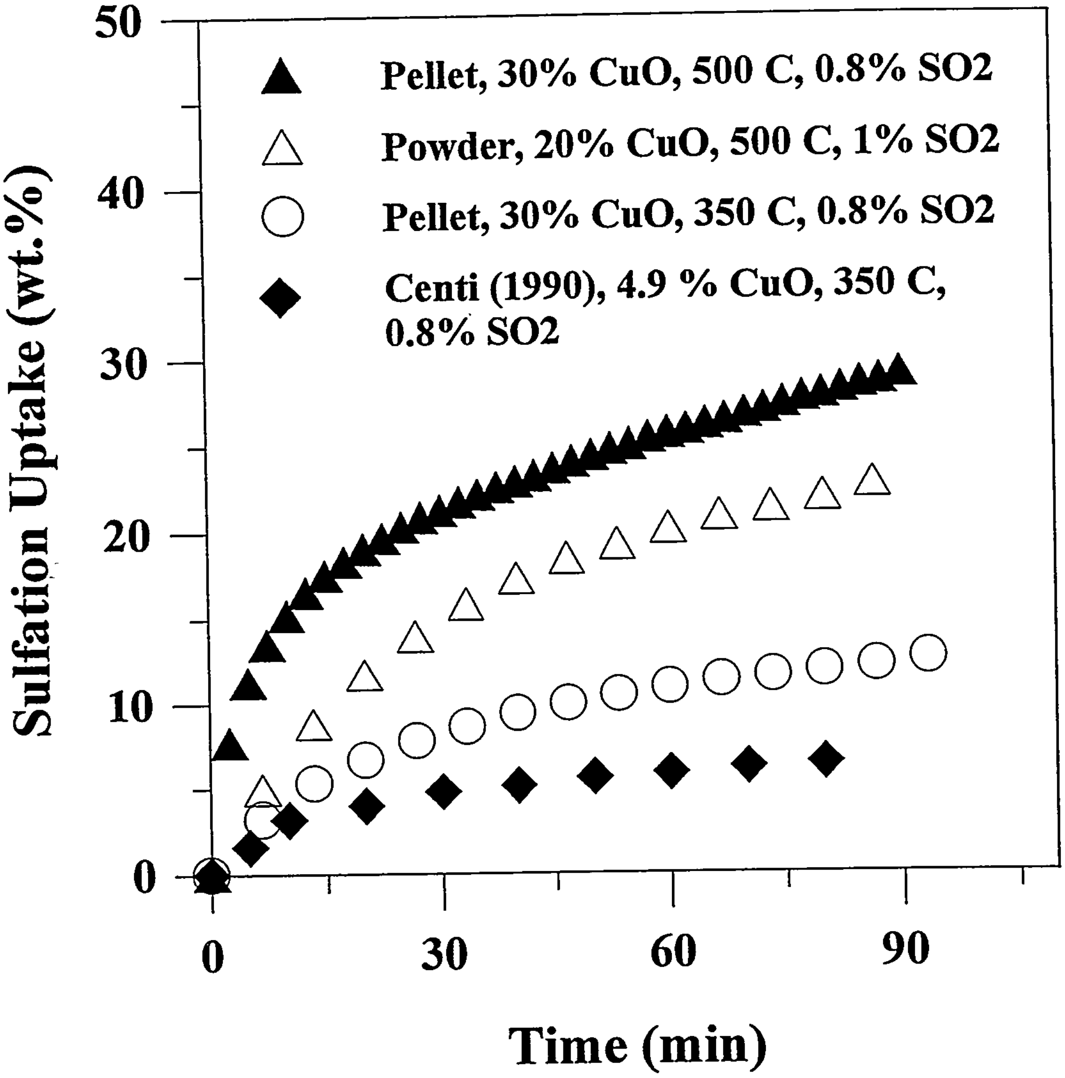

Fig. 10. Comparison of sulfation uptakes on different supported copper oxide sorbents.

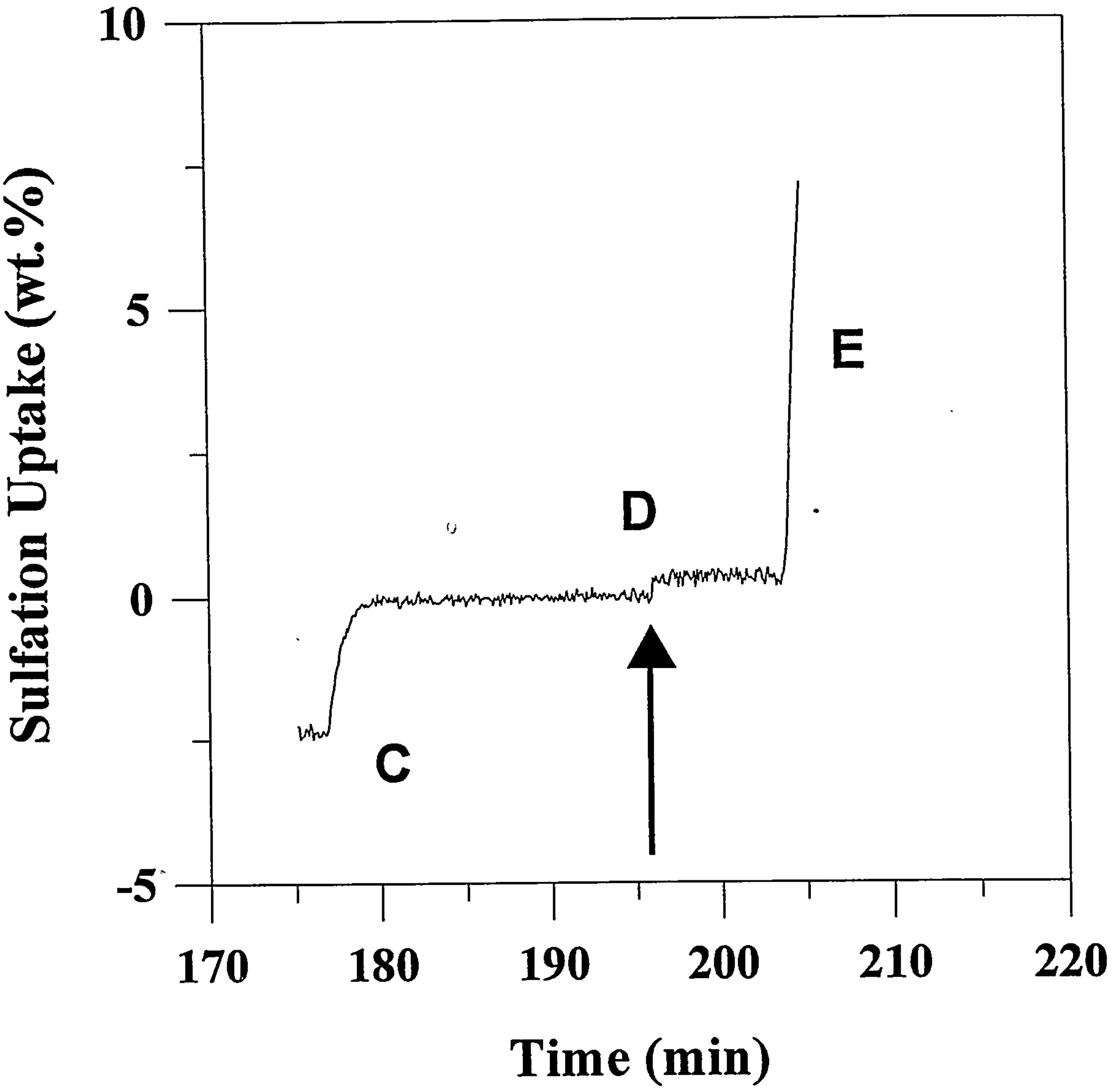

Fig. 11. Effects of Carbon dioxide on sulfation properties of γ-alumina supported copper oxide granular sorbents at 500 °C.

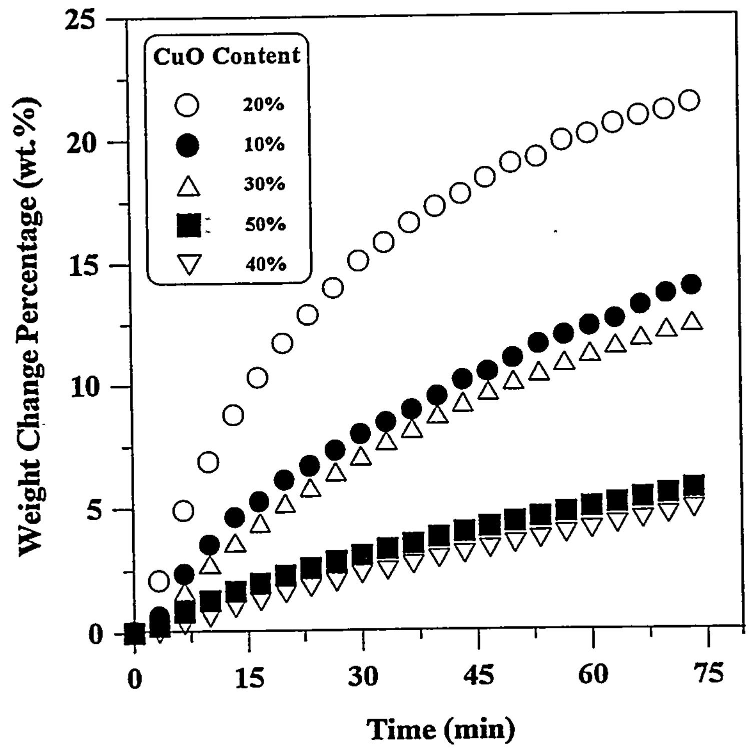

Fig. 12. Sulfation curves on alumina supported CuO sorbents
(500 °C, 1% SO_2, flow rate: 600 ml/min)

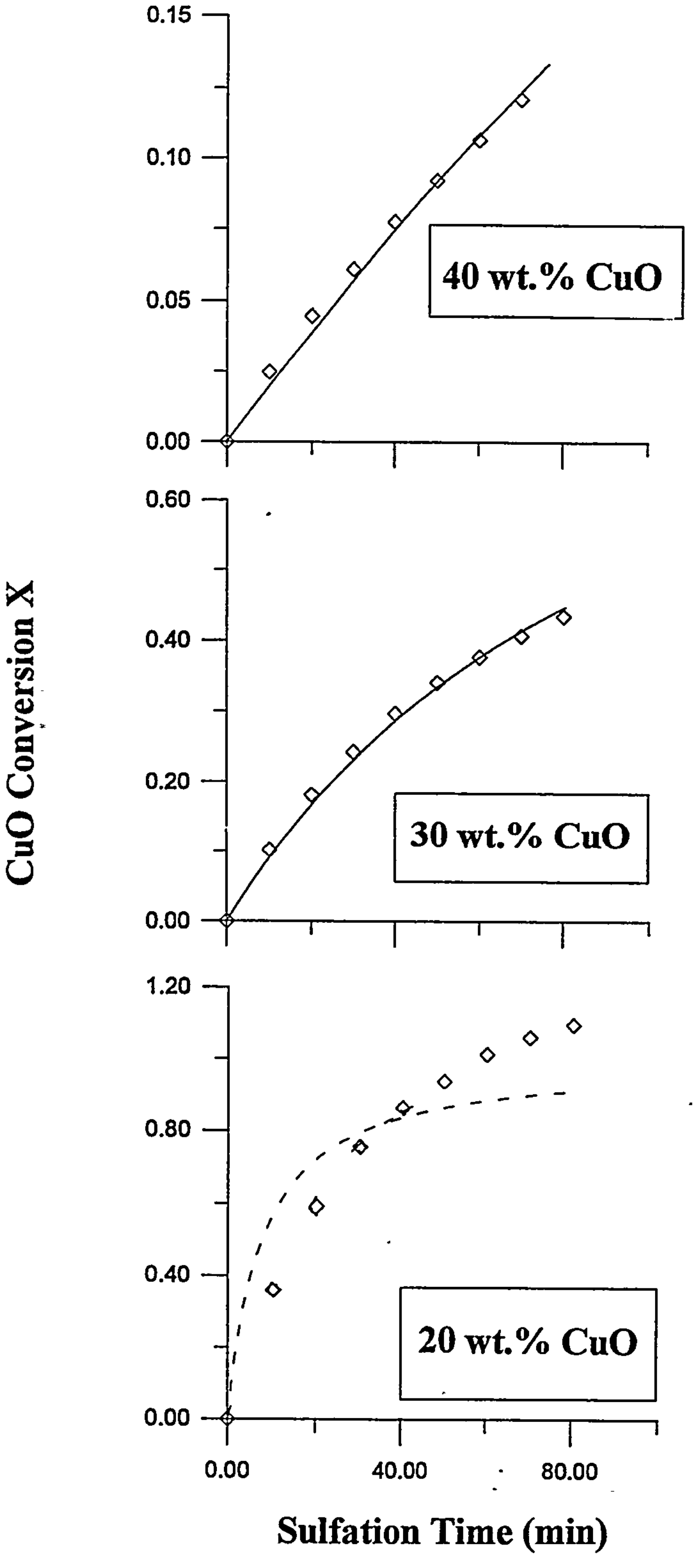

Fig. 13. Comparison of experimental sulfation results (points) with theoretical results based on the second order sulfation kinetics (solid curves) for three sorbents with different CuO content

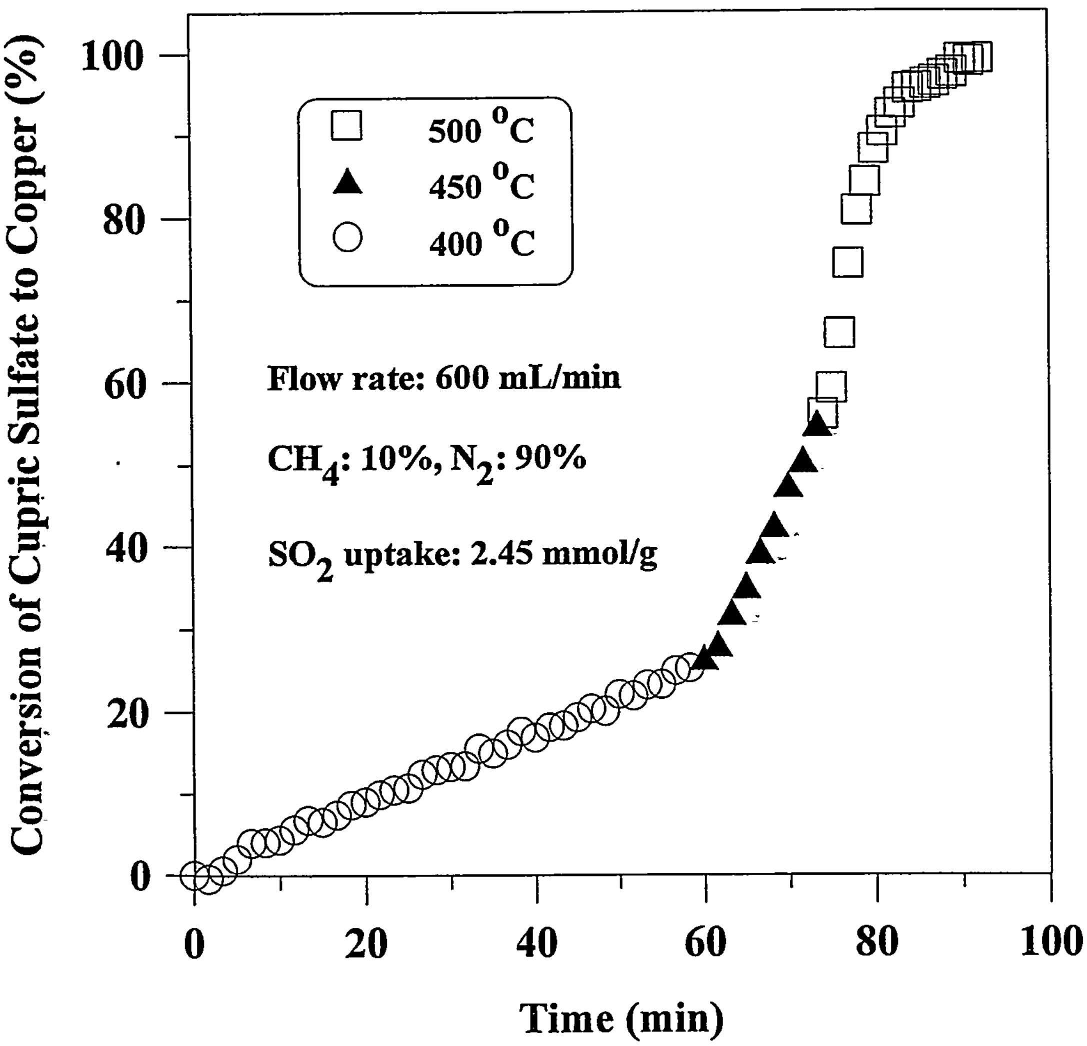

Fig. 14. Regeneratino curves on sulfated sorbent at different temperatures with CH_4 as the reducing gas

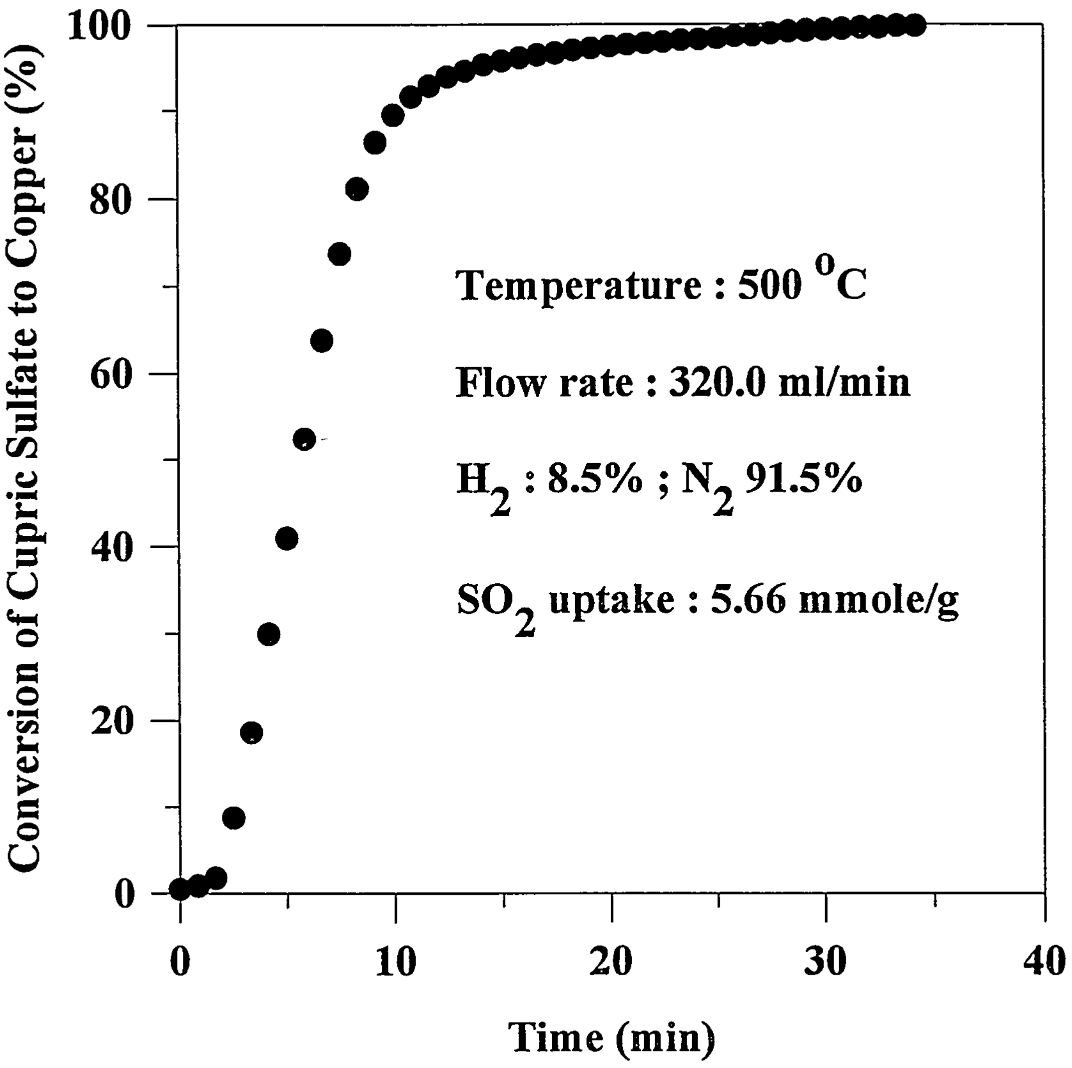

Fig. 15. Regeneratino curves on sulfated sorbent with H_2 as the reducing gas

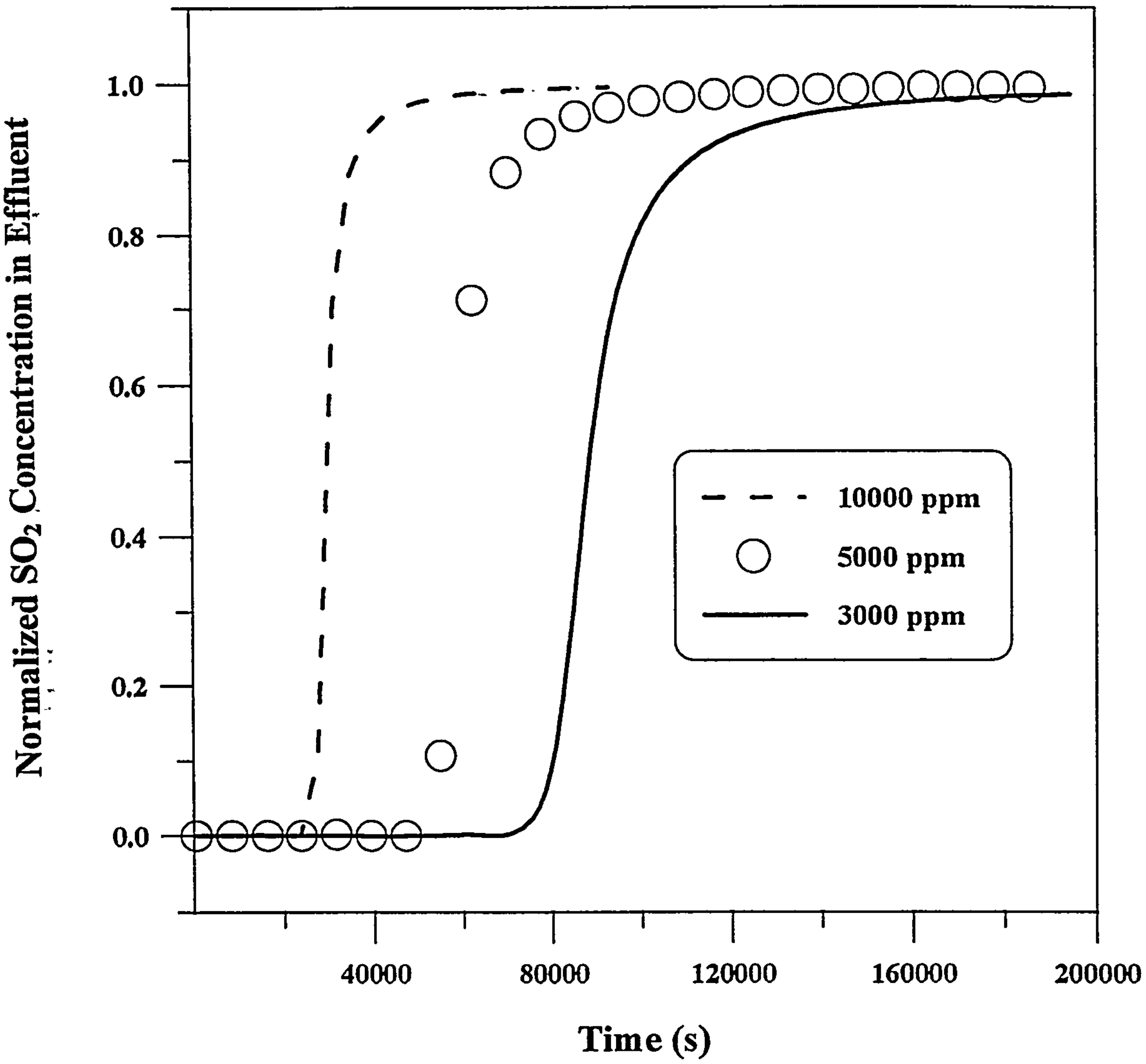

Fig. 16. Calculated SO_2 breakthrough curves of three feed streams containing different SO_2 concentration from adsorber packed with CuO/Al_2O_3 sorbent (sulfation temperature: 400°C, adsorber length: 20 cm, interstitial velocity: 20 cm/s)

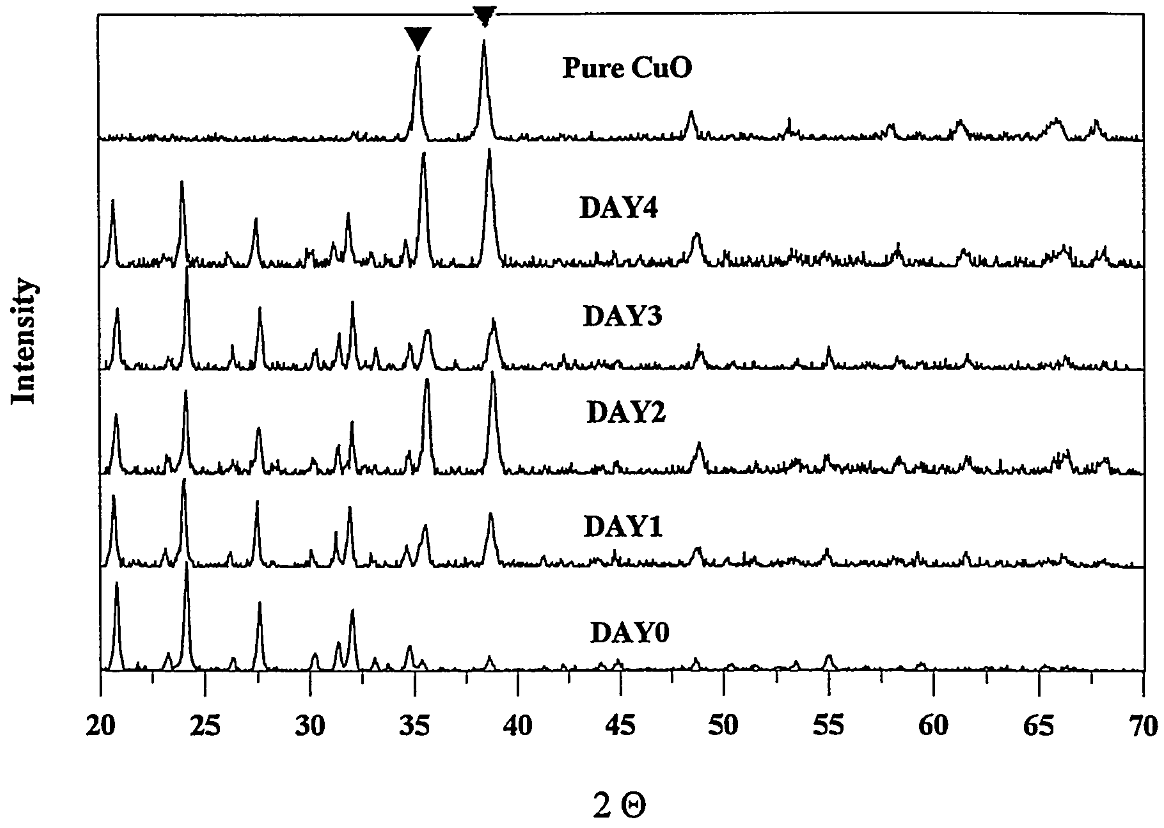

Fig. 17. X-ray diffraction patterns for DAY zeolite supported CuO sorbents prepared by the conventional heating method

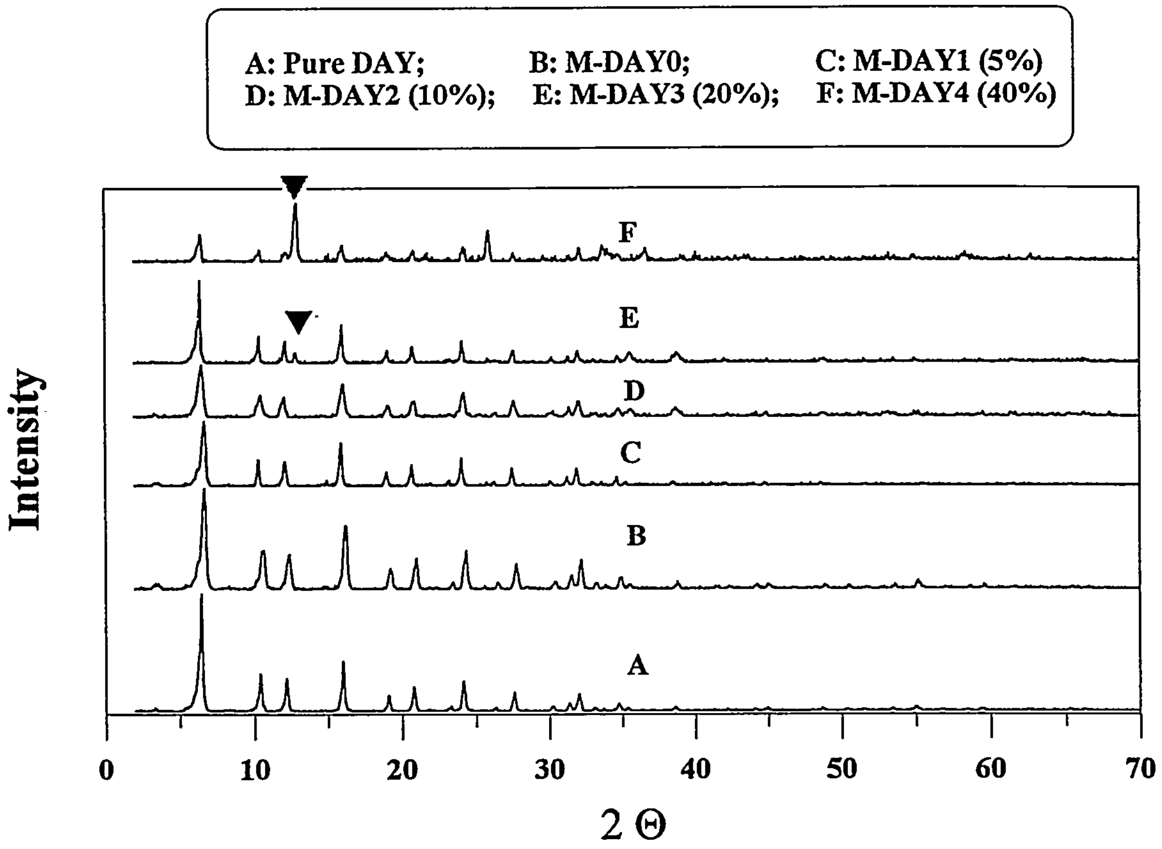

Fig. 18. X-ray diffraction patterns for DAY zeolite supported CuO sorbents prepared by the microwave heating method

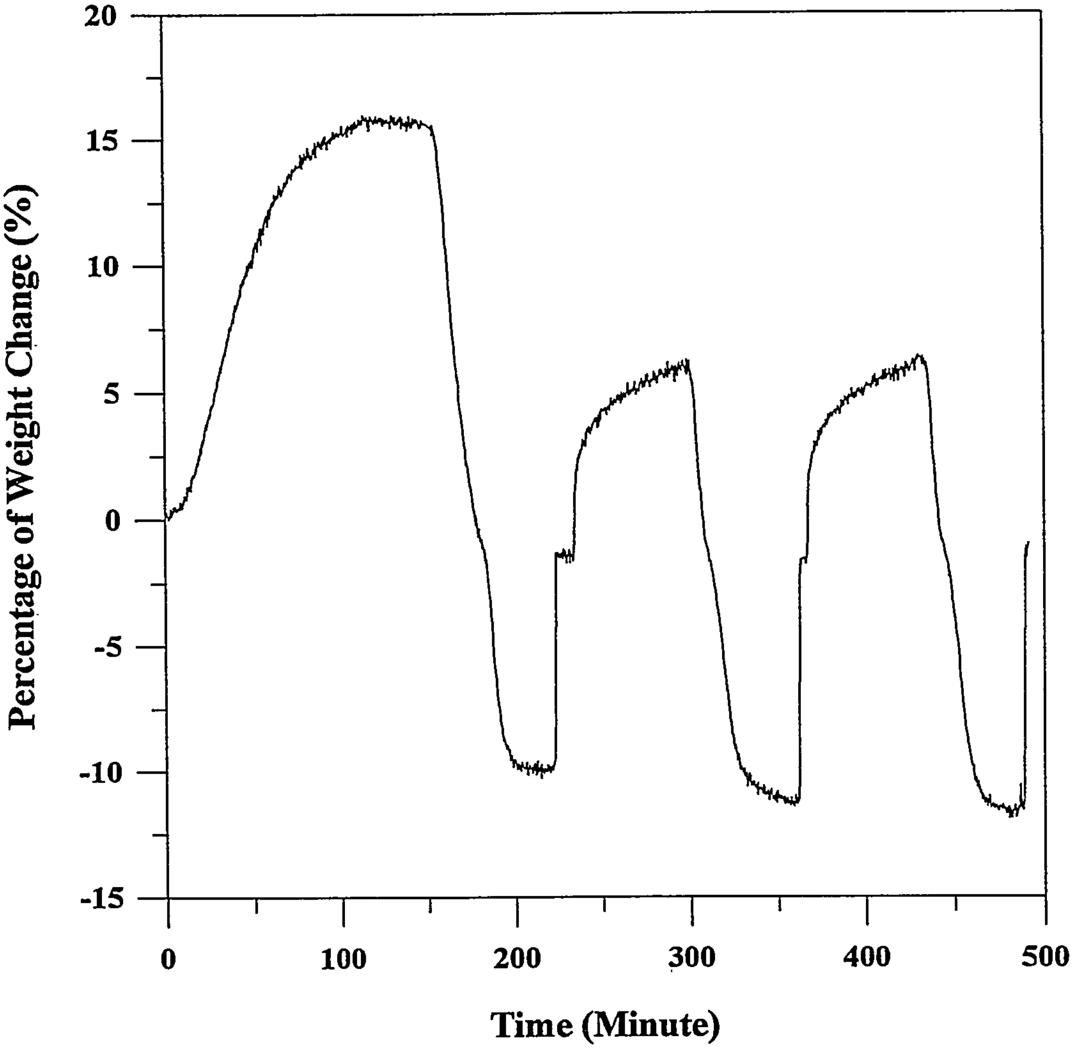

Fig. 19. Sulfation, regeneration and oxidation uptakes on sorbent M-DAY4 at 500 °C.

2. Tables Presented in This Report

Table 1. Preparation Conditions of γ-Alumina Spheres

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	Fair Good	Fair Good
AL-S-5	2.10	5.0 wt.% urea	Fair Good	Broken
AL-S-6	9.55	None	No large spheres	N/A

Table 2. Pore Texture Data of the Sol-Gel Derived γ-Alumina Supports

Samples	BET (m^2/g)	Pore Vol. (cm^3/g)	Pore Size (Å)	Median Pore (Å)	Method
AL-S-2	388.9	0.50	20-60	35.3	Oil-drop
AL-S-3	384.8	0.48	20-60	34.0	Oil-drop
AL-P-0	351.3	0.40	20-50	31.3	Sol-gel

Table 3. Side Crushing Strength and Attrition Index of Spherical γ-Alumina Granules and Some Commercial Adsorbents

Samples	Rang of Diameter (mm)	Average Diameter (mm)	Rang of Load (N)	Average Load (N)	Attrition Index (wt.%/h)	Attrition Weight 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

* These two zeolites are cylindrical, not spherical.

Table 4. Experimental Conditions for Sulfation, Regeneration and Oxidation Stages Shown in Fig. 8

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

Table 5. Comparison of Sulfation Results on Different Sorbents

	Granule Sorbents	Granule Sorbents	Powder Sorbent (Deng and Lin, 1996)	Centi et al. (1990)
BET Area (m^2/g)	228	228	214	102
CuO Loading	30%	30%	20 %	4.9 %
Temperature (°C)	500	350	500	350
SO_2 % in Gas Stream	0.8 %	0.8 %	1 %	0.8 %
Flow Rate (ml/min)	600	600	600	100
Uptake after 60 min (wt.%)	25.6%	10.9%	20.2 %	5.8 %
Molar Ratio of S/Cu after 60 min	0.85	0.36	1.01	1.18
Time for 5 % Uptake (min)	1.5	12	7	40

Table 6. Modeling results of sulfation kinetics on sorbents with variable CuO loading.

CuO loading (wt. %)	Reaction time (min.)	CuO conversion $X=S/[CuO]_0$	Total uptake after 70 min. (wt. % SO_3/100 g)	Model constant K#	R^2
20	84.0	1.10	21.33	0.683*	0.874
30	80.3	0.43	12.27	0.027	0.994
40	76.0	0.13	4.67	0.004	0.990
50	81.0	0.12	5.56	0.003	0.987

* - Data correlated only upto 90 % conversion. (As final $S/[CuO]_0$ ratio is >1)

- Units for K (100 g sorbent/mol(CuO).min)

Table 7. Summary of regeneration kinetic data

Temperature (°C)	Rate equation
	CH_4 used as the reducing agent
400	$X_A = 8.33\times10^{-5}\, t$
450	$X_A = 5.0\times10^{-4}\, t$
500	$-\ln(1 - X_A) = 3.67\times10^{-3}\, t$
	H_2 used as the reducing agent
500	$X_A = 3.3\times10^{-3}\, t$ (for $X_A < 0.9$)
500	$-\ln(1 - X_A) = 7.0\times10^{-3}\, t$ (overall)

X_A: conversion of $CuSO_4$ to Cu in regeneration stage;

t; time of regeneration (in second)

Table 8. Properties of DAY Zeolite Supported CuO Sorbents
Prepared by the Conventional Thermal Dispersion Method
(850 °C, 36 h, 100 °C/h heating and cooling rate)

Sample	Copper Precursor	CuO Cont. (wt. %)	BET (m^2/g sorbent)	BET (m^2/g zeolite)	Average Pore Size (Å)	CuO XRD Peaks
DAY0	N/A	0	830.8	830.8	6.6	N/A
DAY1	CuO	16.7	583.8	700.8	6.6	weak
DAY2	CuO	33.3	632.5	948.3	6.6	strong
DAY3	$Cu(NO_3)_2$	16.7	594.1	713.2	6.6	weak
DAY4	$Cu(NO_3)_2$	33.3	566.1	848.7	6.6	strong

Table 9. Preparation Conditions of Supported Sorbents by Microwave Heating Method

(Sample weight = 1.0g, loose packing)

Sample	Precursor	CuO wt%	Heating Time (min)	Ending Temp. (°C)
M-DAY0	N/A	0	30	145
M-DAY1	$Cu(NO_3)_2$	5	30	146
M-DAY2	$Cu(NO_3)_2$	10	30	150
M-DAY3	$Cu(NO_3)_2$	20	30	153
M-DAY4	$Cu(NO_3)_2$	40	30	158
M-DAY5	CuO	5	60	185
M-DAY6	CuO	10	60	210

Table 10. Pore Structure Data of the DAY Zeolite Supported CuO Sorbents

Sample	BET (m^2/g sorbent)	Corrected BET (m^2/g zeolite)	Pore Size (Å)	Pore Vol. (cm^3/g)
M-DAY0	935	935	6.6	0.384
M-DAY1	891	938	6.7	0.357
M-DAY2	908	1009	6.6	0.326
M-DAY4	594	990	6.6	0.235