Sol-Gel Preparation and Properties of Alumina Adsorbents for Gas Separation

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The sol-gel method is applied to prepare Cu^+ or Ag^+ containing alumina adsorbents which have potential application in purification or separation of carbon monoxide or olefins containing gases. Wet impregnation and sol-solution mixing methods are used to incorporate the active species into the sol-gel derived γ-alumina support. These alumina adsorbents have the characteristics of large specific surface area, high dispersion of active species on the grain surface, and mesopore size with a uniform pore size distribution. The gas chromatographic technique determines the carbon monoxide adsorption properties on these alumina adsorbents. Adsorption equilibrium constants, adsorption rate constants, axial dispersion coefficients, heat of adsorption, and adsorption activation energy are determined from GC response peaks by using the moment method. The alumina adsorbents prepared by the sol-gel method appear to be superior to the similar adsorbents prepared by other methods.

Introduction

Adsorption processes have become one of the key unit operation processes in chemical industry. The adsorbent is the most critical component in any adsorption process. From a commercial and technological point of view, a desirable adsorbent should possess: (1) high adsorption capacity guaranteed by the high surface area or micropore volume accessible to the adsorbate molecules; (2) high selectivity arising from the molecular sieve effect, adsorption equilibrium difference, and/or dynamic diffusivity difference; (3) low mass-transfer resistance; (4) good physical, chemical and mechanical stability. Traditional adsorbents used in industries include activated carbon, silica gel, activated alumina, zeolite molecular sieves and recently developed carbon molecular sieve adsorbents (Yang, 1987). These commercial adsorbents suffer from some shortcomings which prevent the adsorption technology from further development. For example, the hydrothermal instability of zeolite adsorbents is one of the serious problems encountered in the practical applications (Ruthven, 1984). Development of new adsorbents with superior properties or modification of existing adsorbents for property improvement become most effective in enhancing the efficiency of existing adsorption processes or extending the adsorption processes for other separation applications. Research in these areas has received considerable interest in chemical engineering and chemistry communities. The related recent studies include the synthesis of new adsorbents aimed at specific separation applications (Yang and Baksh, 1991; Chmel and Gajdůšková, 1991; Nayak, 1991; Urano and Tachikawa, 1991) and modification of adsorbents for property improvement (Baksh et al., 1989; Iovtchev et al., 1988; Moiseev et al., 1988; Davidson et al., 1990; Duistewinkel, 1991).

The sol-gel method is a novel material process technique recently employed extensively for synthesis of various types of advanced materials (Klein, 1988; Brinker and Scherer, 1990). Sol-gel processing refers to room temperature formation of solid inorganic materials from molecular precursors in liquid solution. Inorganic salts or metal organic compounds are dissolved in aqueous and/or organic solvents to form polymeric or particulate sols consisting of fine inorganic particles composed of metal-oxygen-metal bonds. These sols are then condensed to various types of gels, from which ceramic films, fibers, powders and bulk are formed. Ceramic thin films, sensors, nanoscale materials, multifunctional ceramic composites, optical fibers, ceramic membranes and many other products can be manufactured by the sol-gel process. Materials synthesized by the sol-gel method typically have large surface area,

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uniform pore-size distribution, controlled average pore size, and good mechanical strength, which are particularly important to the materials for separation applications.

Several studies have been reported on the preparation of metal oxide supported catalysts using the sol-gel technique (Pajonk, 1991; Fanelli et al., 1988; Lopez et al., 1991; Willey et al., 1991). Only limited studies have been published on the fabrication of adsorbents using the sol-gel method. A few studies on the preparation of adsorbents by the sol-gel method for the wastewater treatment in a nuclear power plant were conducted by Sharygin's research group in the former USSR. They reported briefly on the sol-gel derived adsorbents in the form of inorganic metal hydroxide, phosphate, ferrocyanide and/or composite from the salt of zirconium, titantium, tin, manganese, and niobium (Moiseev et al., 1988; Krylov et al., 1988; Perekhozheva et al., 1989; Galkin et al., 1989). Modified silica or diatomaceous earth oxides with impregnated active species have been applied as packings or supports in gas or liquid chromatography for many years (Grassini-Strazza et al., 1989; Kohli and Badaisha 1985). These materials generally have much lower surface area and were not studied for large-scale separation. Zirconia and titania, used either as supports or directly as adsorbents, were prepared recently by the sol-gel method (Trudinger et al., 1990; Rigney et al., 1989). Zirconia and titania were developed to replace silica as packing materials for high-pressure liquid chromatography (HPLC) (Werber et al., 1990; Blackwell and Carr, 1991). These adsorbents were used to separate structural isomers, amino acids and proteins by HPLC (Werber and Carr, 1990; Blackwell and Carr, 1992) and to separate peridines by ligand-exchange gas chromatography (GC) (Fujimara and Ando, 1977). Sol-gel prepared alumina adsorbents have also been employed as flue-gas cleaning adsorbents and proved to be superior to the conventional adsorbents with respect to their chemical and mechanical stability (Hakvoort et al., 1987; Duisterwinkel et al., 1989). To the best of our knowledge, no study was reported on the preparation of adsorbents for the separation of industrially important gases by the sol-gel method.

Carbon monoxide and ethylene are two very important basic materials in the chemical and petrochemical industries. The traditional method for producing carbon monoxide is steam reforming of methane at high temperature to form a synthesis gas of hydrogen, carbon monoxide and carbon dioxide. After removing carbon dioxide by chemical absorption, carbon monoxide is then separated from the gas mixture by cryogenic distillation. The ethylene is formed in the process of high temperature cracking of hydrocarbons and is also separated by cryogenic distillation. The combination of the high temperature reforming or cracking with the low temperature cryogenic distillation limits the efficiency of these processes. Several efforts have been reported to develop the adsorption system for the separation of carbon monoxide or ethylene based on adsorbents containing Cu^+ ions as the active site for selective adsorption. The adsorbents containing Cu^+ or Ag^+ can selectively adsorb carbon monoxide or olefin because of a reversible complexing reaction between the active species Cu^+ or Ag^+ and carbon monoxide or olefin through their π-bonds.

It was reported that the active species Cu^+ could be incorporated into zeolites by ion exchange (Huang, 1973; Cen, 1990). The wet-impregnation method was also used to coat Cu^+ on different supports such as alumina, silica, activated carbon, and polymer resin as described in the literature (Golden et al., 1992a; Matsuura, 1990; Hirai, 1987). Xie et al. (1990) prepared the adsorbents with high dispersion of Cu^+ by thermally mixing the support and cuprous salt at high temperature. Rabo (1977) showed that Ag^+ containing zeolite had a high degree of selectivity and affinity for carbon monoxide. The pressure swing adsorption (PSA) processes for the separation of carbon monoxide using activated alumina or activated carbon supported cuprous adsorbents were also reported recently (Kasuya and Tsuji, 1991; Zhu et al., 1991). The above studies concerning synthesis of Cu^+ or Ag^+ containing adsorbents represent interesting development in the area of synthesis or modification of adsorbents for industrial gas separation. Nevertheless, the properties of these Cu^+ or Ag^+ containing adsorbents are far from satisfactory. The copper or silver ion coated zeolite adsorbents suffer from some limitations such as high diffusion resistance arising from the too small pore size, limited amount of ion-exchange sites for active species determined by composition of zeolite materials, and low hydrothermal stability. The copper coated alumina adsorbents reported so far have a relatively low surface area which limits the loading amount of active species and, in turn, restrains the monolayer adsorption capacity of carbon monoxide or olefin on these adsorbents. Furthermore, no detailed information on the fundamental adsorption properties such as adsorption equilibrium, adsorption rates and their temperature dependency on these copper coated alumina adsorbents has been found reported. The fundamental study on the adsorption properties is essential to characterization, mechanism understanding and application of these adsorbents.

With many unique features of sol-gel derived materials, it was believed that adsorbents containing cuprous or silver ions prepared by the sol-gel method would have superior properties for carbon monoxide or olefin separation. Research has been conducted in this laboratory to develop synthesis method based on the sol-gel principle for preparation of copper or silver containing alumina adsorbents for carbon monoxide separation. Adsorption equilibrium and rate data on these adsorbents were measured to provide basic information on adsorption properties of this group of adsorbents, which are not available in the literature. The objective of this article is to report the synthesis and properties of these sol-gel derived alumina adsorbents.

Experimental Studies

Adsorbent synthesis

Stable 1M boehmite sol (γ-AlOOH) was prepared using the Yoldas process (Yoldas 1975a,b). The 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. One L of water was used per mole alkoxide. After heating at 90°C for one h, the resulting slurry with γ-AlOOH precipitates was peptized with HNO_3. Peptization, a very important step in the preparation of sols, requires a critical amount of certain acids to be introduced into the slurry. In this study, 0.07 mol of 1M HNO_3 was added into 1 mol of sol according to Yoldas (1975c). The peptized sol was refluxed at 90 ~ 100°C for 10 h, and a stable boehmite sol was obtained.

The pure γ-alumina adsorbents were prepared by drying a given amount of the boehmite sol in petri-dish under controlled conditions (air atmosphere, 40°C and 60% humidity). The dried boehmite xerogel was calcined at 450°C for 3 h with controlled heating and cooling rates (Leenaars et al., 1984; Lin et al., 1991). Boehmite transformed to γ-alumina during the calcination (Leenaars et al., 1984; Wilson, 1979a,b).

Two methods were used to coat copper or silver on the porous γ-alumina: wet-impregnation method and sol-solution mixing method. In the first method, a cuprous solution was synthesized by mixing cuprous chloride (CuCl) (Reagent ACS, Matheson Coleman & Bell Chemical Company), ammonia hydroxide (Reagent, ACS, Fisher Scientific), ammonia citrate (Reagent, Merck and Co. Inc.) and water with a given composition under controlled preparation conditions. Aqueous $AgNO_3$ solution was prepared by dissolving $AgNO_3$ (ACS grade, J&M) in water for coating silver into the alumina support. In coating the active species, the sol-gel derived γ-alumina supports following heat treatment at 200°C for several hours, were put into the cuprous or silver solution for more than 16 h. The weight ratio of the active species to the support, calculated from the weights of support, volume and concentration of the cuprous or silver solution, was about 5-10%. The impregnated samples were dried in a vacuum oven under the flow of nitrogen (normally for 2 h), and were then heated in the oven at 200°C under nitrogen atmosphere (normally for 20 h). Most of the samples were dried under the nitrogen flow rate of about 1,000 mL/min, but one copper coated sample (Copper-1) was dried at a much lower nitrogen flow rate (20 ~ 30 mL/min) at room temperature for 24 h, 120°C for 24 h and finally at 200°C for another 24 h.

The sol-solution mixing method was first reported by Lin et al. (1991a) to coat lanthanum on the grain surface of the γ-alumina support. In this method, a given amount of the cuprous or silver salt solution was mixed with the boehmite sol. Extreme care was taken to avoid destabilizing the boehmite sol after the mixing of sol with the salt solution. The doped sol was dried under the atmosphere of nitrogen, and the resulting gels were heated in the oven at 200°C under nitrogen atmosphere. This method has the advangage of being able to control precise amount of dopant.

A different copper coated alumina adsorbent was also prepared following the procedure reported by Golden et al. (1992a) in the patent literature for comparison purpose. In preparing this adsorbent, 10 grams of sol-gel derived γ-Al_2O_3 support was heat-treated in a furnace at 200°C for 16 h. The alumina was then impregnated with 10 mL of aqueous solution containing 3 grams of $CuCl_2 \cdot 2H_2O$ (crystal purified, Fisher Scientific) and 0.4 grams of ammonium citrate (reagent, Merck & Co. Inc.). The alumina was air dried at 120°C for 16 h and then activated at 200°C in nitrogen for another 16 h.

Characterization and carbon monoxide adsorption

BET surface area, pore volume, pore-size distribution and average pore size of the adsorbent samples were determined by nitrogen adsorption porosimeter (Micromeritics, ASAP 2000). The samples were first degassed at 150°C under vacuum for more than 2 h until the sample passed the degassing checkup test. The samples were then weighed and transferred to the testing port. 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, pore volume, and the desorption isotherm was used to calculate the pore-size distribution.

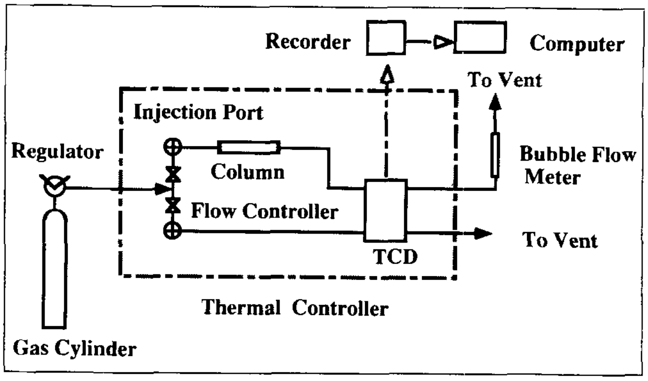


Figure 1. Dynamic flow system for CO adsorption measurements.

X-ray diffractometer (Siemens, CuKα1) was used to examine the phase structure of the adsorbent samples. The 2θ range used in the experiment was from 10° to 70° with a scanning speed of 3° per min. The chemical states of copper and silver ions on the surface of γ-alumina were examined by X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer, Model 5300). The base pressure in the spectrometer was 2.0×10^{-10} torr and the experimental pressure was about 1.0×10^{-9} torr. A achromatic Mg Kα1,2 anode (energy line 1,253.6 eV) powered at 15 kV and 20 mA was used for X-ray production. The binding energy scale of the spectrometer was calibrated by using the difference between Cu (2p) line (binding energy 932.66 eV) and Cu (3p) line (binding energy 75.02 eV). The binding energies were calculated with respect to the hydrocarbon peak in C (1s) photoelectron line set at 284.6 eV to correct for the charging of the samples. The intensities were estimated by integrating the area of each peak following background subtraction using Apollo software. The atomic concentration ratios were obtained by correcting the area ratios with theoretical sensitivity factors based on Scofield cross sections (Briggs and Seah, 1990).

Adsorption equilibrium and rate constants of carbon monoxide on these adsorbents were measured by the chromatographic technique. The dynamic flow system employed is shown in Figure 1. This included a constant temperature gas chromatography (GOW-MAC, Model 580) with flow controllers, injection ports, a thermal conductivity detector and a bubble flowmeter which was used to measure the flow rate of carrier gas. The ordinary chromatographic column was replaced by a short column which contained alumina adsorbent prepared in this work. The GC column is made of stainless steel tube with a diameter of 3.5 mm and a length of 40 mm. The adsorbents were ground into fine particles with an average particle size of about 10 μm determined by light microscopy (Olympus, type SZH).

Since carbon monoxide is a very toxic gas without color and odor, it must be handled very carefully in the laboratory. A carbon monoxide monitor (Sierra Monitor Corporation, Model 2006) was installed to monitor possible leakage of carbon monoxide. A special carbon monoxide gas sampling system was set up using a carefully designed sampling device, as shown in Figure 2. One end of the device was connected to the cylinder

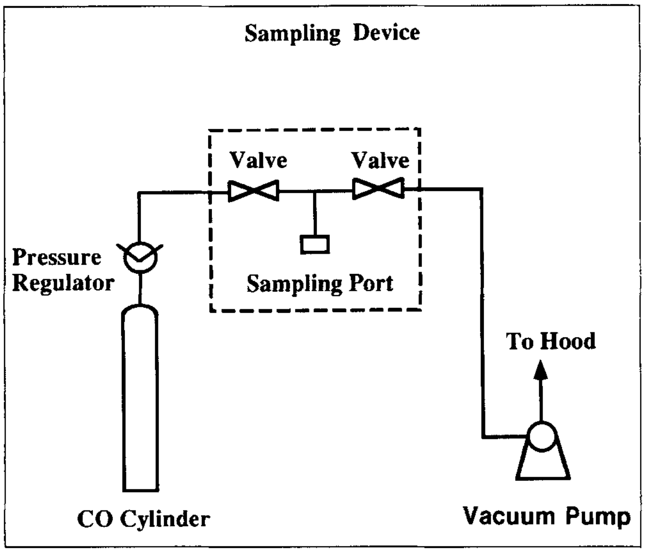


Figure 2. Carbon monoxide sampling system.

via the pressure regulator, the other end to a vacuum pump, and the sampling port was sealed by a silicone septum. Only a small amount (about 5 mL) of carbon monoxide was allowed to be stored in the sampling system when it was used. The sampling system was evacuated after sampling in order to eliminate the risk of carbon monoxide leakage. The carbon monoxide gas was sampled by a gastight syringe (Fisher Scientific, Hamilton Type 1800 series). The sampling amount of carbon monoxide was 0.01 to 0.1 mL each time. The carbon monoxide was injected into the injection port with the syringe, and was subsequently carried into the GC column by the carrier gas (helium). The response peaks were recorded at the outlet of the column by a GC integrator (Spectra-Physics) and were then input into personal computer for further calculation and analysis.

The selection of the GC method instead of the gravimetric method for carbon monoxide adsorption study was based on the following two considerations. First, the GC method provides a quick means for simultaneous determination of both adsorption equilibrium constant and adsorption rate constant. Secondly and more importantly, the GC method requires handling of only very small amount of carbon monoxide sample, as described above. In contrast, the gravimetric method would involve handling of considerable amount of carbon monoxide sample. With safety facilities available in a university laboratory, it is difficult to ensure the safe handling of carbon monoxide when performing the carbon monoxide experiments on a gravimetric apparatus (such as Cahn balance).

Table 1. Samples and Their Preparation Methods

Adsorbents	Color	Preparation Method
Pure Alumina	Translucent	Sol-Gel
Copper-1	Pale-Green	Sol-Gel/Wet-Impregnation
Copper-2	Pale-Green	Sol-Gel/Wet-Impregnation
Silver-1	Dark-Gray	Sol-Gel/Wet-Impregnation
Silver-2	Dark-Gray	Sol-Gel/Sol-Solution Mixing

Prior to the measurements of GC response peaks of carbon monoxide, adsorbent samples were activated at 150°C under the flow of helium in the GC column. GC response peaks of carbon monoxide were measured at temperatures of 26, 50 and 100°C, and at various carrier gas flow rates. Large carrier gas flow rates and lower injection sample amount were preferred to obtain small adsorbate concentration in the mobile phase so that the experiments could be performed in the linear adsorption isotherm region. As a result, the bridge current of the TCD was set at maximum (280 ~ 300 mA) in order to achieve the maximum sensitivity of the detector.

Results and Discussion

Characteristics of adsorbents

Five adsorbent samples prepared by the sol-gel methods are summarized in Table 1. The first sample is the pure γ-alumina without doping with active species. The second and third samples are γ-alumina coated with Cu^+ by the wet-impregnation method. The difference in these two samples is that the copper-1 sample was dried at a much slower drying rate than the copper-2 sample. These two samples were prepared primarily for the purpose of examining the effect of drying rate on the final properties of the adsorbent. The fourth and the fifth samples were coated with Ag^+ using the wet-impregnation method and the solution-sol mixing method, respectively. These samples were prepared to examine the effects of the different coating methods on the final results. The pure γ-alumina sample is translucent while the Cu^+ and Ag^+ coated samples are respectively pale green and dark gray. The typical color of cuprous chloride should be light gray. The fresh cuprous chloride used in this study is also pale green, same as that of the

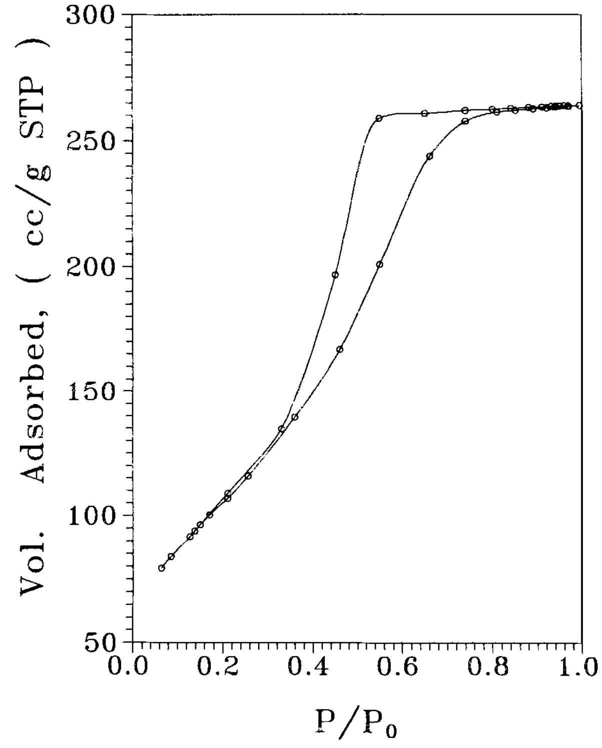
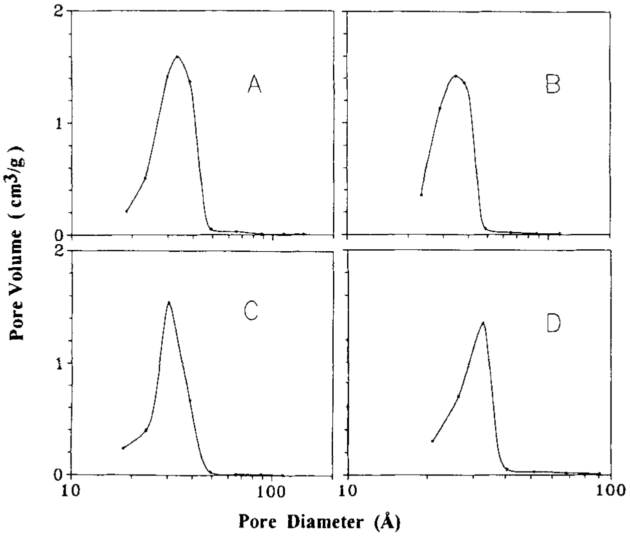


Figure 3. Nitrogen adsorption and desorption isotherms on adsorbent Copper-1.



A: Pure Alumina; B: Copper-2; C: Silver-1; D: Silver-2

Figure 4. Pore-size distribution of pure alumina and Cu^+ and Ag^+ doped alumina adsorbents.

cuprous adsorbents. This indicates that both the cuprous chloride purchased for this study and the final adsorbents prepared from it contain a mixture of Cu^+ and Cu^{2+} ions. This will be verified by XPS results presented next.

The nitrogen adsorption isotherms of all the five samples are of type IV (Gregg and Sing, 1982), as shown in Figure 3. The desorption hysteresis loop indicates that these adsorbents are mesoporous. Figure 4 shows the pore-size distributions (determined from nitrogen desorption isotherms) for the four adsorbents. The BET surface area, pore volume, average pore size and pore-size distribution range for these five adsorbents are summarized in Table 2. All adsorbent samples have a narrow pore-size distribution with an average pore diameter of around 3 nm. The surface area of these samples, especially that of the pure γ-alumina and Copper-1 samples, is large.

The uniform pore size and large surface area of these adsorbent samples are a result of the unique characteristics of the sol-gel processing. In synthesizing these adsorbents, boehmite particles were formed and grew via the hydrolysis and condensation of aluminum alkoxide in aqueous solution. The particles reached a final uniform nanoscale size due to the Ostwald ripening mechanism and proportional dependency of the repulsive force on the particle size (Ottewill, 1977; Overbeek, 1977; Brinker and Scherer, 1990). The sol contained the aggregates of primary 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). The nanoscale boehmite particles of about 5 nm size were connected to each other primarily by the van der Waals force after the drying process, as investigated in detail by Leenaars et al. (1984). Finally, the boehmite was transformed to γ-alumina and the particles were consolidated during the calcination step (at 450°C for 3 h) (Yoldas, 1975a,b,c; Wilson, 1979a,b; Leenaars et al., 1984; Brinker and Scherer, 1990). So the final adsorbent samples consisted of nanoscale primary particles of rather uniform size.

Table 2. Pore Structure of Alumina Adsorbents Prepared by Sol-Gel Method

Adsorbent Samples	BET Surface Area (m^2/g)	Avg. Pore Dia. (Å)	Pore Size (Å)	Pore Vol. (cm^3/g)
Pure Alumina	356.0	32.0	20~50	0.434
Copper-1	385.5	30.9	20~50	0.430
Copper-2*	283.0	32.8	20~50	0.294
Silver-1	298.9	29.5	20~50	0.293
Silver-2	206.7	26.9	20~50	0.286

*Dried at much lower drying rate (see Experimental section); other samples were dried under normal conditions.

The surface areas of the most Cu^+ or Ag^+ coated samples are smaller than that of the pure γ-Al_2O_3. Coating the active species also changes the average pore size and pore volume of the alumina adsorbents. However, the surface area of Cu^+ coated sample (Copper-1) is larger than that of Copper-2, and even larger than that of pure γ-alumina sample. These three samples were prepared in the same sol synthesis conditions and, for Copper-1 and Copper-2, the same impregnation conditions. But sample Copper-1 was dried at a very lower drying rate as compared to the other samples. Slow drying usually results in looser packing of the particles in the gel, yielding a microstructure with a large surface area after calcination. These results indicate that drying conditions are important in controlling the microstructure of these sol-gel derived adsorbents.

The surface area, average pore size and pore volume of the silver coated adsorbent prepared by the wet-impregnation method (Silver-1) are similar to that of the Cu^+ coated samples prepared by the same coating method (Copper-2). These suggest that the same sol synthesis and coating method will give same pore structure regardless of different active species. Comparing the two silver coated samples prepared by the different coating methods, the sol-solution mixing method yields an adsorbent with smaller surface area, pore volume and pore size. This is a result of the phenomenological difference between these two coating methods.

In the wet-impregnation coating method, the microstructure of the support (γ-alumina) has already been consolidated after the calcination step. Once the support is brought to contact with the impregnating solution, active species is adsorbed on the surface of the support and remains on the support surface after the solvent is removed during the drying step. Therefore, wet-impregnation does essentially not change the microstructure of the support. The sol-solution mixing method, developed initially for coating oxide layer on the grain surface of ceramic membranes for other property improvement (Lin et al., 1991, 1994), works in a very different fashion. In this method, stable boehmite sol is mixed with an active species containing salt solution. After mixing, the active species can be coated on the grain surface of the sols particles either during the sol aging step or drying step. However, mixing a salt solution into the boehmite sol may change the pH and ion (cation and anion) concentrations of the sol, which if not well controlled, may destabilize the sol resulting in the formation and precipitation of larger aggregates. In this work, mixing procedure and conditions were carefully controlled so that the boehmite sol remained stable after being doped with silver containing salt

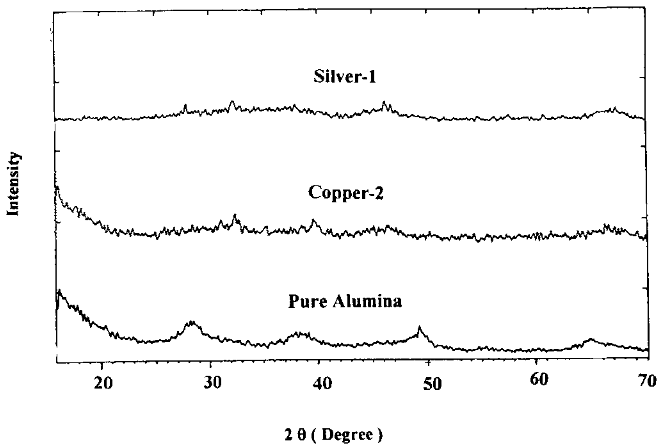


Figure 5. XRD patterns of pure alumina and Cu$^+$ and Ag$^+$ doped alumina adsorbents.

solution. Some other species could also be coated on the grain surface of the sol particles (Lin et al., 1994), but experiments performed in this laboratory showed that mixing cuprous salt solution with the boehmite sol destabilized the sol, yielding a final product with a small surface area (<90 m^2/g).

Although the silver salt doped boehmite sol remained stable, the slight change in the pH and ion concentrations after the doping still altered the size and shape of the primary particles. Thus, the difference in the microstructure of the two silver coated adsorbents is primarily due to the different primary particle size and shape, which together with the packing pattern and extent of consolidation, determine the pore structure of the final product. Despite the smaller surface area of the adsorbent prepared by the sol-solution mixing method, this method allows accurate control of the dopant concentration and eliminates the additional drying step required in the wet-impregnation coating method.

Figure 5 shows XRD patterns of the adsorbents of pure γ-alumina, Cu$^+$ doped alumina (Copper-2) and Ag$^+$ doped alumina (Silver-1). No sharp XRD reflection peaks are observed for all three samples. The sol-gel derived γ-alumina, although having a cubic crystalline structure, is known to have very weak X-ray reflection peaks (Wilson, 1979a,b; Wefers and Misra, 1987). From these XRD data, it is obvious that no other XRD detectable crystallites are present in these three samples. This suggests that the active species is more likely present in the form of two-dimensional (2-D) layer (possibly monolayer) on the grain surface of the γ-alumina support (Xie and Tang, 1990). This hypothesis will be substantiated by the carbon monoxide adsorption data presented next.

XPS measurements were performed on four samples (Copper-2, Silver-1, pure γ-alumina and fresh CuCl) to determine the surface composition and chemical state of Cu and Ag of these samples. The atomic fractions of various elements determined by XPS on the surface of these samples are listed in Table 3. The weight percentages of copper in Copper-2 and silver in Silver-1, calculated from the atomic fractions listed in Table 3, are about 7% and 16% respectively. XPS analysis also shows a considerable amount of carbon present in Copper-1 (12.61%), Silver-1 (6.10%) and CuCl (40.27%) samples, but with a negligible amount of carbon present in pure γ-alumina sample. These results suggest that Copper-2, Silver-1 and CuCl have a high affinity for carbon oxides.

Table 3. Atomic Fraction of Various Elements Determined by XPS

	Copper-2	Silver-1	γ-Al_2O_3	CuCl
Al 2p	50.37%	25.31%	28.40%	
O 1s	29.99%	64.31%	68.45%	23.79%
Cu 2p	2.61%			12.45%
Ag 3d		3.42%		
Cl 1s	4.41%			21.34%
C 1s	12.61%	6.10	2.96%	40.27%
N 1s		0.86%	0.18%	
Cr 2p				0.70%
Fe 2p				1.45%

XPS spectra which could indicate the state of Cu and Ag in these samples are given in Figure 6. Silver in Silver-1 sample is present in Ag$^+$ state, as shown in Figure 6A with the two Ag ($3d_{3/2}$) and Ag ($3d_{5/2}$) peaks at 368 ev and 374 eV respectively (Schön, 1973). The Cu ($2p_{1/2}$) and Cu ($2p_{3/2}$) XPS spectra of Copper-2 and fresh CuCl are roughly the same, as shown in Figure 6B and 6C. Both samples give two Cu^{2+} satellite peaks (peaks S at about 963 eV and 943 eV respectively), two Cu ($2p_{3/2}$) peaks at about 934 eV and 932.5 eV, and two Cu ($2p_{1/2}$) peaks at about 955 eV and 952.5 eV. The Cu ($2p_{3/2}$) peaks at 932.5 eV and Cu ($2p_{1/2}$) peaks at 952.5 eV in Figure

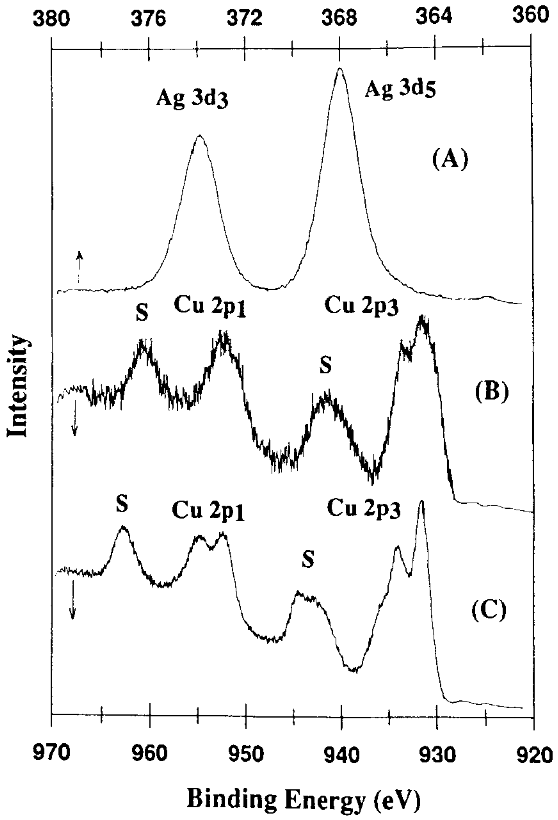


Figure 6. XPS spectra of Silver-1 (A); Copper-2 (B); fresh CuCl (C).

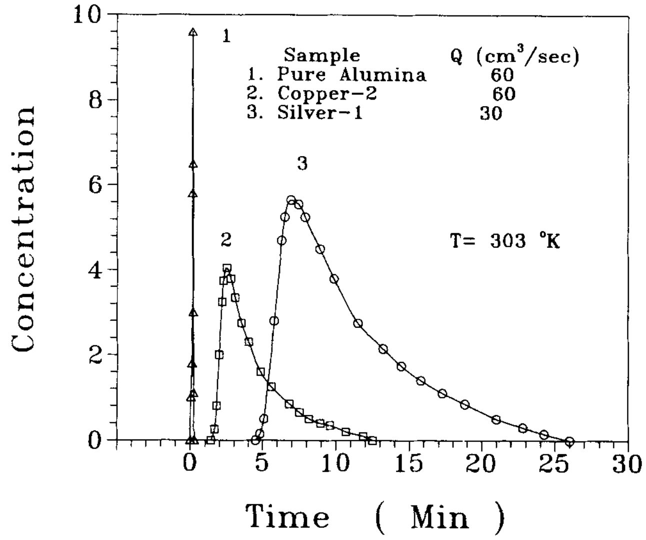


Figure 7. Typical chromatographic responses of CO from columns packed with pure γ-alumina, adsorbents Copper-2 and Silver-1.

6B and 6C indicates the presence of Cu^+ in both samples (Barr, 1978; Briggs and Seah, 1990). The approximate atomic ratios of Cu^+ to Cu^{2+} estimated from the peak area of Cu^+ to that of Cu^{2+} are about 1.5 in both Copper-2 and CuCl. This proves that the Cu^+ was not oxidized to Cu^{2+} during the synthesis of the copper coated adsorbents.

Carbon monoxide adsorption equilibrium and kinetics

The gas chromatographic moment method was employed to measure the equilibrium and rate constants for adsorption of carbon monoxide on these adsorbent samples. Figure 7 shows the response peaks of carbon monoxide from columns packed with the adsorbents of pure γ-alumina, Cu^+ coated alumina (Copper-2) and Ag^+ coated alumina (Silver-2). The retention time of the pure alumina is very short (essentially the same as the resident time through the column void space and dead volume). This indicates that the sol-gel derived γ-alumina adsorbent sample does not possess the adsorption capacity for carbon monoxide. In contrast, the carbon monoxide response peaks from the other two Cu^+ or Ag^+ coated adsorbents show the carbon monoxide adsorption capacity of these two adsorbents. Quantitative data of the adsorption equilibrium and rate constants were calculated using the model described next.

As mentioned earlier, the adsorbents prepared by the sol-gel method are composed of uniform dense nanoscale crystalline grains, of which the intergrain space is the pore space of the adsorbent. The column was packed with the adsorbent in powder form with an average particle size of around 10 μm. When carbon monoxide was carried by the carrier gas through the mobile phase of the column, the carbon monoxide molecules diffused through external mass-transfer film and the pore space of these adsorbent particles, and were adsorbed by the active species on the surface of the nanoscale grains. Adsorption of carbon monoxide on Cu^+ or Ag^+ is a reversible chemisorption process (Huang, 1973; Cen, 1990). The adsorption rate on the grain surface can be approximated by the linear driving force model as $q = k_{ads}(C\text{-}C_e)$, where k_{ads} is the adsorption rate constant. Thus, the carbon monoxide mass-transfer process in the column packed with the sol-gel derived adsorbent includes axial dispersion and convection in the mobile phase, external mass transfer, diffusion in the particle pores, and adsorption on the grain surface. With this model, differential equations were set up, from which the moment equations were derived using the well-known procedure (Carleton et al., 1978; Lin and Ma, 1989). The final results of the first and second moments are the same as reported by Schneider and Smith (1968):

$$\mu = \frac{\int_0^\infty Ct\,dt}{\int_0^\infty C\,dt} \tag{1}$$

$$\mu = \left(\frac{L}{V}\right) \cdot \left[1 + \beta \cdot \left(\frac{1-\alpha}{\alpha}\right) \cdot \left(1 + \frac{\rho_p}{\beta} K\right)\right] \tag{2}$$

$$\sigma^2 = \frac{\int_0^\infty (t-\mu)^2 C\,dt}{\int_0^\infty C\,dt} \tag{3}$$

$$\frac{\sigma^2}{2(L/V)} = \delta_a + \delta_i + \delta_e + \frac{D_L}{\alpha} \cdot (1+\delta_0)^2 \frac{1}{V^2} \tag{4}$$

$$\delta_0 = \left(\beta \cdot \frac{1-\alpha}{\alpha}\right) \cdot \left[1 + \left(\frac{\rho_p}{\beta}\right) \cdot K\right] \tag{5}$$

$$\delta_a = \left(\beta \cdot \frac{1-\alpha}{\alpha}\right) \cdot \left(\frac{\rho_p}{\beta}\right) \cdot \left(\frac{K^2}{k_{ads}}\right) \tag{6}$$

$$\delta_i = \delta_0 \frac{R^2 \beta}{15} \left(1 + \frac{\rho_p}{\beta} K\right) \frac{1}{D_c} \tag{7}$$

$$\delta_e = \delta_0 \frac{R^2 \beta}{15} \left(1 + \frac{\rho_p}{\beta} K\right) \frac{5}{k_f R} \tag{8}$$

The first and second moments of the chromatographic response peaks were calculated numerically from the experimental data according to Eqs. 1 and 3. As shown by Eq. 2, plots of the first moment (μ) with (L/V) or $(1/Q)$ should yield a straight line through the original of the coordinates. The experimental data of the first moment for adsorption of carbon monoxide on Copper-2 adsorbent at different temperatures are plotted vs. $(1/Q)$ in Figure 8. The experimental data can be correlated by straight lines. The adsorption equilibrium constants were calculated from the least-squared regressed slope of the μ vs. $(1/Q)$ straight lines, as suggested by Eq. 2. According to Eq. 4, the plots of $(\sigma^2/(2L/V)$ vs. $(1/V^2)$ or $(\sigma^2 x Q)$ vs. $(1/Q^2)$ should also give a straight line. These plots of the experimental data of carbon monoxide on another sample of the sol-gel prepared adsorbents (Silver-2) are shown in Figure 9. Least-squared regression of these straight lines gave intercepts and slopes, from which the summation of the mass-transfer resistances and axial dispersion term were calculated.

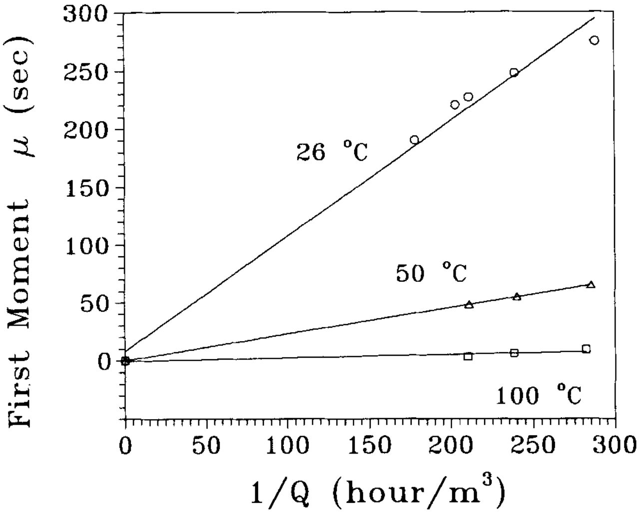


Figure 8. First moment plots for CO adsorption on adsorbent Copper-2 at different temperatures.

It should be pointed out that the moment method is strictly valid only for adsorption systems with a linear adsorption isotherm, which rarely exist in reality. Carbon monoxide adsorption isotherms on Cu^+ or Ag^+ containing adsorbents are nonlinear in the whole pressure range (Cen, 1990). When partial pressure of carbon monoxide in the mobile phase is low, the adsorption isotherm can be considered approximately linear although mathematically it is not. Under these conditions, the moment method applies. In this work, the moment data were measured with the CO injection amount of 0.01 mL (for data at 26°C) and 0.1 mL (for data at 100°C) in order to ensure that the measurements were performed in the approximately linear isotherm range. Figure 10 shows the dependence of the first moment on the CO injection amount at two different temperatures. At 100°C, the first moment is essentially independent of the CO injection amount in the range of 0.1 ~ 0.2 mL. At the lower temperature the first moment decreases slightly with increasing CO injection amount. Therefore, the lower temperature data were measured with a much smaller CO injection amount (0.01 mL) of which the lower limit was set by the sensitivity of the TCD detector. The fact that the first moment (μ) vs. $1/Q$ shown in Figure 8 can be correlated with straight lines supports that these moment data were obtained in the approximately linear isotherm range.

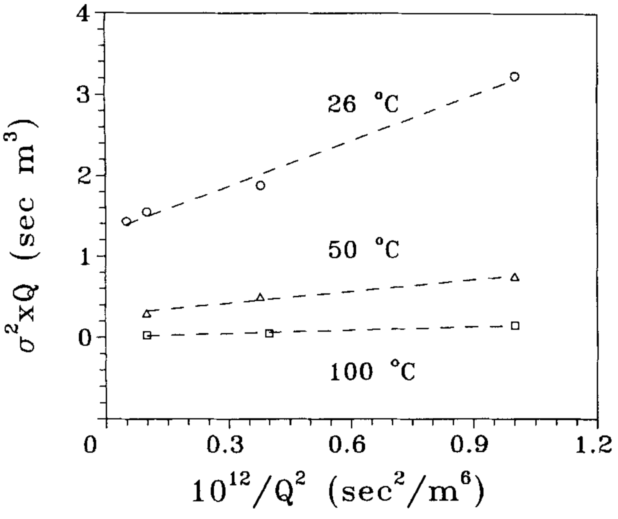


Figure 9. Second moment plots for CO adsorption on adsorbent Silver-2 at different temperatures.

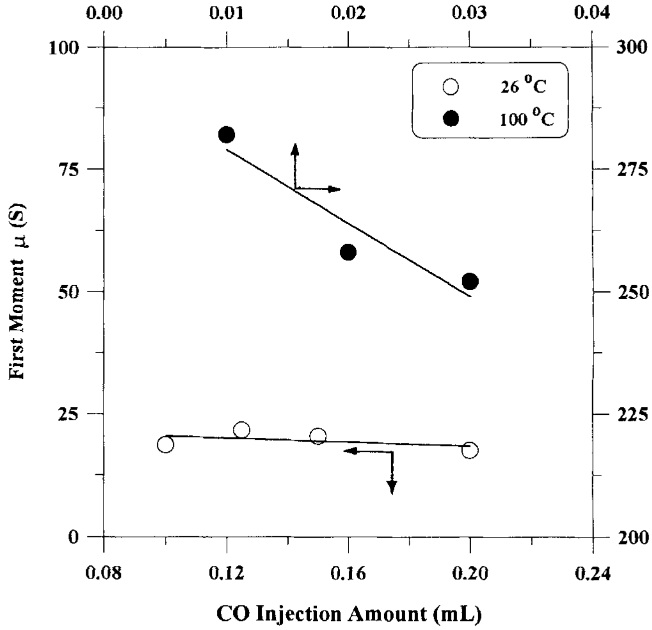


Figure 10. Effect of CO injection amount on the first moment.

To calculate the adsorption rate constants from the intercept of the second moment plots, contributions of other mass transport resistances should be estimated in advance. The external mass-transfer coefficient can be estimated from the following equation (Schneider and Smith, 1968):

$$N_{u,AB}=\frac{2Rk_f}{D_{AB}}=2, \quad \text{or} \quad k_fR=D_{AB} \tag{9}$$

As a result of small particles used in the experiments, the external mass-transfer resistance term (δ_e) predicted by Eqs. 8 and 9 for the present adsorption systems contributes less than 1% to the total mass-transfer resistance. Thus, the external mass-transfer resistance was neglected in the calculation. The intraparticle pore diffusion resistance was computed from Eq. 7, where the effective diffusion coefficient D_c was calculated by the following equation (Butt, 1980):

$$D_c=\frac{\beta}{\tau}D_K \tag{10}$$

in here D_K is the Knudsen diffusivity evaluated at $r_{avg}=16$ Å ($=1.6\times10^{-7}$ cm) using the following equation (Butt, 1980):

$$D_K=9{,}700\cdot r_{avg}\sqrt{\frac{T}{M}} \tag{11}$$

Table 4. Adsorption Equilibrium and Rate Constants for CO on Adsorbents

	26°C			50°C			100°C		
Adsorbents	K mmol·g·atm	k_{ads} mL/g·s	D_L cm^2/s	K mmol·g·atm	k_{ads} mL/g·s	D_L cm^2/s	K mmol·g·atm	k_{ads} mL/g·s	D_L cm^2/s
Copper-2	27.3	28.5	0.30	6.7	66.8	0.52	0.7	287.4	0.7
Silver-1	32.0	32.8	0.25	11.8	74.4	0.45	1.6	300.8	0.54
Silver-2	10.43	199.5	0.40	1.6	527.3	0.54	0.6	1,070.6	0.68

Diffusion in the pores of these adsorbents under the experimental conditions is in the Knudsen regime. The tortuosity factor ($\tau = 5.3$), and adsorbent particle porosity ($\beta = 53\%$) for the sol-gel derived γ-alumina were obtained from Leenaars et al. (1984).

Values of the adsorption equilibrium constants and adsorption rate constants for adsorption of carbon monoxide on the three doped alumina adsorbent samples and the corresponding axial dispersion coefficient of carbon monoxide in the column packed with these adsorbents are summarized in Table 4. The axial dispersion coefficients range from 0.2 to 0.7 cm^2/s and are essentially independent of the coated active species. The axial dispersion coefficient increases slightly with increasing temperature. These results are consistent with other findings reported on the axial dispersion of gases in the flow through packed bed (Butt, 1980; Wen and Fan, 1975). The temperature dependency of the adsorption equilibrium constants and adsorption rate constants can be described by the van't Hoff and Arrhenius equations, respectively, as shown in Figures 11. The heats of adsorption and activation energy for adsorption were calculated from the following van't Hoff and Arrhenius equations:

$$K = K_0 \mathrm{EXP}\left(-\frac{\Delta H}{R_g T}\right) \tag{12}$$

$$k_{ads} = k_{ads\,0} \mathrm{EXP}\left(-\frac{E}{R_g T}\right) \tag{13}$$

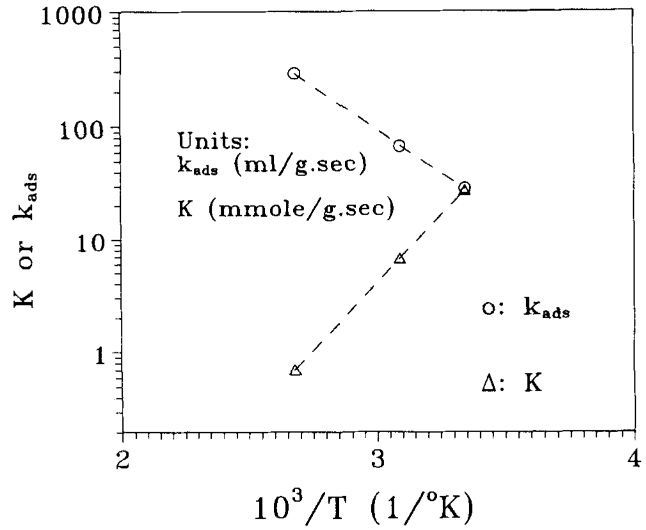


Figure 11. Temperature dependency of CO adsorption equilibrium constant and rate constant on adsorbent Silver-1.

The calculated parameters for these alumina adsorbents are tabulated in Table 5. To the best of our knowledge, no such comprehensive data of adsorption equilibrium and rate constants as well as heats of adsorption and activation energy for adsorption of carbon monoxide on Cu$^+$ and Ag$^+$ containing adsorbents were previously reported.

Comparing the two adsorbents containing different active species coated by the same wet-impregnation coating method (samples Copper-2 and Silver-1), the adsorption equilibrium constants are similar at low temperature. The adsorption rate constants are also very similar. Although these two samples contain different active species, they have the same surface area, which may be responsible for the similar values of adsorption equilibrium and rate constants. The heat of adsorption of the Cu$^+$ coated sample is about 30% larger than that of Ag$^+$ coated sample, reflecting the different Gibbs energy associated with the process of the reversible chemical adsorption of carbon monoxide on these two active species. The activation energy for carbon monoxide adsorption on these two samples is almost identical.

For both the Ag$^+$ containing adsorbents (Silver-1 and Silver-2), the adsorbent (Silver-2) prepared by the sol-solution mixing method gives smaller adsorption equilibrium constant but greater adsorption rate as compared to the adsorbent prepared by the wet-impregnation method. However, the heats of adsorption are the same for both Ag$^+$ containing adsorbents. The activation energy for adsorption on sample Silver-2 is about 15% larger than that on sample Silver-1. The smaller surface area of sample Silver-2 can explain partially the lower adsorption equilibrium constant. However, it is difficult to explain the larger adsorption rate and activation energy for this sample using the difference in the surface area. To fully understand this difference requires a more detailed study on the surface chemistry of the active species presented on the grain surface of γ-alumina.

Table 5. Adsorption Heat and Activation Energy for CO Adsorption on Adsorbents

Adsorbents	H (kJ/mol)	E (kJ/mol)
Copper-2	−48.8	28.5
Silver-1	−37.3	28.0
Silver-2	−36.1	32.6

Comparison with similar adsorbents prepared by other methods

Comparison of the present results with other similar adsorbents is difficult due to the fact that very scarce data on the synthesis and properties of Cu^+ containing adsorbents are available. The patents concerning Cu^+ containing adsorbents prepared by other methods (Golden et al., 1992a; Xie et al., 1990) described detailed procedures for syntheses of the adsorbents, but provided only limited data on the pore structure and carbon monoxide adsorption equilibrium properties. The carbon monoxide adsorption rate constant data on Cu^+ containing alumina adsorbents are not available.

The surface area of the copper coated alumina adsorbents prepared by Golden et al. (1992a) was not given in the patent. Commercial γ-alumina (LeRoche activated alumina) was used as support. Golden (1992b) reported on another occasion that their coating method reduced the surface area of the support from about 320 m^2/g to 230 m^2/g. To confirm these data, a copper coated alumina adsorbent sample was prepared following the Golden procedure (see Experimental section) with the sol-gel derived γ-alumina as support. This support has a larger surface area than the commercial support used by Golden et al. The surface area, pore volume and average pore size of this Cu^{2+} doped alumina adsorbent sample were 229.7 m^2/g, 0.34 cm^3/g, and 3.3 nm, respectively. The surface area of this sample is identical to what Golden reported although the supports used are different. This indicates that the surface area of the adsorbent prepared by the method of Golden et al. is determined by the coating method.

Henry constant for carbon monoxide adsorption on the adsorbent reported by Golden et al. (1992a) was 34.5 mmol/g·atm. The adsorption equilibrium constants on samples Copper-2 and Silver-1 (see Table 3) were 27.30 and 32.97 mmol/g·atm, slightly smaller than the value reported by Golden et al. It should be mentioned that the carbon monoxide adsorption equilibrium constants measured by the GC method at lower carbon monoxide concentration is usually smaller than the Henry constant (slope of adsorption isotherm at zero adsorbate concentration). Based on the fact that the surface area of these two samples prepared by the sol-gel method is about 25% larger than that of Golden et al., a larger Henry constant is expected for the sol-gel derived adsorbents. Furthermore, Xie et al. (1990) reported an equilibrium constant of 6.08 mmol/g·atm for carbon monoxide adsorption on the adsorbent they prepared. The equilibrium constants of carbon monoxide adsorption on the sol-gel derived adsorbents are larger than this value.

No heat of adsorption and adsorption rate constant data were reported for carbon monoxide adsorption on the alumina adsorbents prepared by Golden et al. (1992a) and Xie et al. (1990). The heats of adsorption of carbon monoxide on the sol-gel derived alumina adsorbents are in the same order of magnitude as that on Cu^+ coated zeolite type Y adsorbent (Huang, 1973). These values are however larger than the heat of physical adsorption of carbon monoxide on zeolilte and activated carbon adsorbents (Valenzuela and Myers, 1989). The adsorption rate constants determined in this study for adsorption of carbon monoxide on the sol-gel derived alumina adsorbents are smaller than that of hydrocarbon on silica adsorbent (Schneider and Smith, 1968). This is because the adsorption of carbon monoxide on Cu^+ or Ag^+ alumina adsorbents is a chemical complexing reaction process which is slow and involves large heat effects (Ruthven, 1984).

Conclusions

Cu^+ and Ag^+ coated alumina adsorbents were prepared by the sol-gel method for carbon monoxide separation. The sol-gel derived mesoporous adsorbents have a larger surface area and more uniform pore-size distribution, as compared with similar adsorbents prepared by other methods. The pore structure of the sol-gel derived adsorbents can be tailored by controlling the drying step of the sol-gel process.

Both wet-impregnation and sol-solution mixing methods were employed to coat the active species on the grain surface of the sol-derived γ-Al_2O_3 support. The active species were well dispersed on the grain surface of the support and most likely present in the form of monolayer covering the grain surface. The sol-solution mixing method gives adsorbent with a smaller surface area and pore volume as a result of the change in the shape and size of the sol particles after mixing. Nevertheless, the sol-solution mixing method allows precise control of the dopant amount and eliminates an additional drying step required in the wet-impregnation method.

Gas chromatography method was used to determine the carbon monoxide adsorption equilibrium and rate constants on these sol-gel derived adsorbents at three different temperatures. At room temperature, adsorption of carbon monoxide on the Cu^+ and Ag^+ coated alumina adsorbents prepared by the wet-impregnation method is characterized with an adsorption equilibrium constant of about 30 mmol/g·atm and adsorption rate constant of about 30 mL/g·s. The adsorption equilibrium constants on these sol-gel derived adsorbents appear to be larger than that on the similar adsorbents prepared by the other methods. The Ag^+ coated alumina adsorbent prepared by the sol-solution mixing method has a smaller adsorption equilibrium constant and a much larger adsorption rate constant.

The heat of adsorption of carbon monoxide on the Cu^+ coated alumina adsorbent is 48.8 kJ/mol, about 10 kJ/mol larger than that on Ag^+ coated alumina adsorbent. The activation energy for carbon monoxide adsorption on both the Cu^+ and Ag^+ coated alumina adsorbents is essentially the same (28 kJ/mol). The heat of adsorption of carbon monoxide on Cu^+ and Ag^+ coated alumina adsorbents is larger than heat of physical adsorption reported in literature.

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Notation

C = concentration of adsorbate in the mobile phase, mol/mL
C_e = concentration of adsorbate in the stationary phase, mol/mL
D_c = effective diffusion coefficient in the adsorbent pore defined by Eq. 10, cm^2/s
D_{AB} = binary molecular diffusivity, cm^2/s
D_K = Knudsen diffusivity, cm^2/s

D_L = effective axial dispersion coefficient, cm^2/s
E = activation energy for adsorption rate, kJ/mol
ΔH = heat of adsorption, kJ/mol
k_{ads} = adsorption rate constant, mL/g·s
k_{ads0} = pre-exponential coefficient defined by Eq. 13, mL/g·s
k_f = interparticle mass-transfer coefficient, cm/s
K = adsorption equilibrium constant, mmol/g·atm
K_0 = pre-exponential coefficient defined by Eq. 12, mmol/g·atm
L = length of the column, cm
M = molecular weight of adsorbate gas, g/mol
Nu_{AB} = Nusselt number for mass transfer, defined by Eq. 9
q = adsorption rate, mol/g·s
Q = volumetric flow rate of the carrier gas, mL/min
r_{avg} = average pore radius of the adsorbents, Å
R = particle size of the adsorbents, cm
R_g = gas constant
t = time, s
T = absolute temperature, °K
V = linear velocity of the carrier gas in the interparticle space, cm/s

Greek letters

α = interparticle void fraction in the column
β = intraparticle void fraction of the adsorbents
δ_0, δ_a, δ_i, δ_e = expressions defined by Eqs. 5–8
μ = first moment defined by Eq. 1
ρ_p = apparent particle density, g/mL
σ^2 = second moment defined by Eq. 3
τ = tortuosity factor for intraparticle diffusion, defined by Eq. 10

Literature Cited

Baksh, M. S. A., R. T. Yang, and D. D. L. Chung, "Composite Sorbents by Chemical Vapor Deposition on Activated Carbon," *Carbon*, **27**, 931 (1989).

Barr, T. L., "An ESCA Study of the Termination of the Passivation of Elemental Metals," *J. Phy. Chem.*, **82**, 1801 (1978).

Blackwell, J. A., and P. W. Carr, "Fluoride-Modified Zirconium Oxide as a Bicompatible Stationary Phase for High-Performance Liquid Chromatography," *J. Chromatog.*, **549**, 59 (1991).

Briggs, D., and M. P. Seah, *Practical Surface Analysis, Volume 1, Auger and X-ray Photoelectron Spectroscopy*, 2nd ed., Wiley, New York (1990).

Blackwell, J. A., and P. W. Carr, "Ligand Exchange Chromatography of Free Amino Acids and Proteins on Porous Microparticulate Zirconium Oxide," *J. Liquid Chromatog.*, **15**, 1487 (1992).

Brinker, C. J., and G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Acadmic Press, San Diego, CA (1990).

Butt, J. B., *Reaction Kinetics and Reaction Design*, Prentice-Hall, Englewood Cliffs, NJ (1980).

Carleton, F. B., L. B. Kershenbaum, and W. A. Wakehan, "Adsorption in Non-isobaric Fixed Bed," *Chem. Eng. Sci.*, **33**, 1239 (1978).

Cen, P. L., "Adsorption Uptake Curves of Ethylene on Cu(I)-NaY Zeolite," *AIChE J.*, **36**, 789 (1990).

Chmel, K., and V. Gajdùšková, "New Czechoslovak Sorbent, Eksorb," *J. Chromatog.*, **552**, 449 (1991).

Davidson, D. J., D. D. Ensor, J. L. Collins, and D. J. Pruett, "Preparation of Hydrous Titanium Oxides by Sol-Gel Process," *Abstract, Amer. Chem. Soc.*, **199**, 90 (1990).

Duisterwinkel, A. E., E. B. M. Doesburg, and G. Hakvoort, "Comparing Regenerative SO_2 Sorbents Using TG: The SRO Test," *Thermochim Acta*, **141**, 51 (1989).

Duisterwinkel, A. E., "Clean Coal Combustion with In Situ Impregnated Sol-Gel Sorbent," PhD Diss., Delft Univ. of Technology, The Netherlands (1991).

Fanelli, A. J., J. V. Burlew, and G. B. Marsh, "The Polymerization of Ethylene over $TiCl_4$ Supported on Alumina Aerogels: Low Pressure Results," *J. Cata.*, **116**, 318 (1988).

Freidman, R. M., and J. J. Freedman, "Characterization of Cu/Al_2O_3 Catalysts," *J. Cata.*, **55**, 10 (1978).

Fujimara, K., and T. Ando, "Ligand-Exchange Gas Chromatographic Separation of Pyridine Bases," *Anal. Chem.*, **49**, 1179 (1977).

Galkin, V. M., L. M. Sharygin, V. E. Moiseev, T. N. Perekhonzhevea, and E. V. Loguntesv, "Physicochemical Properties of Spherical Zirconium Phosphate Obtained by the Sol-Gel Method," *J. Appl. Phy. Chem. Russ.*, **62**, 2051 (1989).

Golden, T. C., Dept. of Chemical Engineering, Univ. of Cincinnati, seminar (Nov. 19, 1992b).

Golden, T. C., W. C. Karatz, and F. C. Wilbelm, "Highly Dispersed Cuprous Compositions," U.S. Patent 5126310 (1992b).

Grassini-Strazza, G., V. Carunchio, and A. M. Girelli, "Flat-Bed Chromatography on Impregnated Layers," *J. Chromatog*, **466**, 1 (1989).

Gregg, S. J., and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, 2nd ed., Academic Press, London (1982).

Hakvoort, G., C. M. Van Den Bleek, J. C. Schouten, and P. J. M. Valkenburg, "TG Study of Sorbent Materials for Desulfurization of Combustion Gases at High Temperature," *Thermochim Acta*, **114**, 103 (1987).

Hirai, H., "Solid Adsorbents for Carbon Monoxide and Process for Separation from Gas Mixture," U.S. Patent No. 4696682 (1987).

Huang, Yun-Yang, "Selective Adsorption of Carbon Monoxide and Complex Formation of Cuprous-Amines in Cu(I)Y Zeolites," *J. Cata.*, **30**, 187 (1973).

Iovtchev, K., L. Nikolov, and D. Elenkov, "Experimental Study of New Mechanically Resistant Adsorbent," *Can. J. Chem. Eng.*, **66**, 1013 (1988).

Kartheuser, B., B. K. Hodett, A. Riva, M. Ruwet, P. Grange, and N. Passarini, "Temperature-Programmed Reduction and X-ray Photoelectron Spectroscopy of Copper Oxide on Alumina following Exposure to Sulfure Dioxide and Oxygen," *Ind. Eng. Chem. Res.*, **30**, 2105 (1991).

Kasuya, F., and T. Tsuji, "High Purity CO Separation by Pressure Swing Adsorption," *Gas Sep. Purification*, **5**, 242 (1991).

Klein, L. C., *Sol-Gel Technology for Thin Film, Fibers, Performs, Electronics and Specialty Shapes*, Noyes Publications, Park Ridge, NJ (1988).

Kohli, J. C., and K. K. Badaisha, "Improved Procedures for the Thin-Layer Chromatography of Terpenoids on Silver Ion-Silica Gel," *J. Chromatog*, **320**, 455 (1985).

Krylov, V. N., S. M. Borisov, and A. G. Burov, "Sorption of Radionuclides by Ferrocyanide Sorbents: I. Titanium Ferrocyanide as Inorganic Sorbent," *Sov. Radiochem.*, **30**, 615 (1988).

Leenaars, A. F. M., K. Keizer, and A. J. Burggraaf, "The Preparation and Characterization of Alumina Membrane with Ultrafine Pores," *J. Mater. Sci.*, **19**, 1077 (1984).

Lin, Y. S., and Y. H. Ma, "Comparative Chromatography Study of Liquid Adsorption and Diffusion in Microporous and Macroporous Adsorbents," *Ind. Eng. Chem. Res.*, **28**, 622 (1989).

Lin, Y. S., K. J. de Veries, and A. J. Burggraaf, "Thermal Stability and Its Improvement of the Alumina Membrane Top-Layers Prepared by Sol-Gel Methods," *J. Mat. Sci.*, **26**, 715 (1991).

Lin, Y. S., C.-H. Chang, and R. Gopalan, "Improvement of Thermal Stability of Porous Nano-Structured Ceramic Membranes," *Ind. Eng. Chem. Res.*, **33**, 860 (1994).

Lopez, T., I. Gracia-Cruz, and R. Gomez, "Synthesis of Magnesium Oxide by the Sol-Gel Method: Effect of the pH on the Surface Hydroxylation," *J. Cata.*, **127**, 75 (1991).

Matsuura, Jun-Ichi, "Carbon Monoxide Carriers Prepared from Copper(II) Salts/ Benzoin/*N*-Methlimidazole and Copper(II) Salts/Ascorbic Acid-Methlimidazole," *Gas Separation Technology*, E. F. Vansant and R. Dewolfs, eds., Elsevier Science Publishers, Amsterdam, Netherlands, p. 549 (1990).

Moiseev, V. E., L. M. Sharygin, V. P. Pyshkin, R. V. Kuzmina, T. G. Malykh, and V. M. Galkin, "Synthesis of Titanium Phosphate by the Sol-Gel Method and Reproducibility of the Composition and Properties of the Sorbent," *J. Appl. Chem. Russ.*, **61**, 891 (1988).

Nayak, V. S., "New Solid Adsorbents for the Separation of Low Hydrocarbons and Permanent Gases: II. Ammonium Molybdophosphate," *J. Chromatog.*, **556**, 425 (1991).

Ottewill, R. H., "Stability and Instability in Disperse System," *J. Colloid Interf. Sci.*, **58**, 357 (1977).

Overbeek, J. Th. G., "Recent Developments in the Understanding of Colloid Stability," *J. Colloid Interf. Sci.*, **58**, 408 (1977).

Pajonk, G. M., "Aerogel Catalysts," *Appl. Cata.*, **72**, 217 (1991).

Perekhozeva, T. N., L. M. Sharygin, and G. P. Albantova, "Kinetic Characteristic of the Ion-Exchange Process on Zirconium Phosphate Prepared by the Sol-Gel Method," *Inorg. Mat.*, **25**, 1295 (1989).

Rabo, J. A., "Adsorption of Carbon Monoxide Using Silver Zeolites," U.S. Patent No. 4019880 (1977).

Rigney, M. P., T. P. Werber, and P. W. Carr, "Preparation and Evaluation of a Polymer-Coated Zirconia Reversed-Phase Chromatographic Support," *J. Chromatog.*, **484**, 273 (1989).

Ruthven, D. M., *Adsorption Principle and Adsorption Processes*, Wiley, New York (1984).

Schneider, P., and J. M. Smith, "Adsorption Rate Constants from Chromatography," *AIChE J.*, **14**, 762 (1968).

Schön, G., "ESCA Studies of Ag, Ag_2O and AgO," *Acta Chemica Scandinavica*, **27**, 2623 (1973).

Trüdinger, U., G. Müller, and K. K. Unger, "Porous Zirconia and Titania as Packing Materials for High-Performance Liquid Chromatography," *J. Chromatog.*, **535**, 111 (1990).

Urano, K., and H. Tachikawa, "Process-Development for Removal and Recovery of Phosphorus from Waste-Water by a New Adsorbent: 1. Preparation Method and Adsorption Capability of a New Adsorbent," *Ind. Eng. Chem. Res.*, **30**, 1893 (1991).

Valenzuela, D. P., and A. L. Myers, *Adsorption Equilibrium Data Handbook*, Prentice Hall, Englewood Cliffs, NJ (1989).

Wen, C. Y., and F. T. Fan, *Models for Flow Systems and Chemical Reaction*, Marcel Dekker, New York (1975).

Werber, T. P., P. W. Carr, and E. F. Funkenbusch, "Evaluation of a Zirconia-Based Carbon-Polymer Composite Reversed-Phase Chromatographic Support," *J. Chromatogr.*, **519**, 31 (1990).

Weber, T. P., and P. W. Carr, "Composition of Isomer Separation on Carbon-Clay Microporous Zirconia and Conventional Reversed-Phase High-Performance Liquid Chromatography Support," *Anal. Chem.*, **62**, 2620 (1990).

Wefers, K., and C. Misra, "Oxides and Hydroxides of Alumina," *Alcoa Technical Paper*, rev., **19**, Alcoa Center, PA (1987).

Willey, R. J., H. Lai, and J. B. Peri, "Investigation of Iron Oxide-Chromia-Alumina Aerogels for the Selective Catalytic Reduction of Nitric Oxide by Ammonia," *J. Cata.*, **130**, 319 (1991).

Wilson, S. J., "Phase Transformation and Development of Microstructure in Boehmite-Derived Transition Aluminas," *Proc. British Ceramic Soc.*, **28**, 281 (1979a).

Wilson, S. J., "The Dehydration of Boehmite, γ-AlOOH, to γ-Al_2O_3," *J. Solid State Chem.*, **30**, 247 (1979b).

Xie, Youchang, N. Bu, J. Liu, G. Yang, J. Qiu, N. Yang, and Y. Tang, "Adsorbents for Use in the Separation of Carbon Monoxide and/or Unsaturated Hydrocarbons from Mixed Gases," U.S. Patent No. 4917711 (1990).

Xie, You-Chang, and You-Qi Tang, "Spontaneous Monolayer Dispersion of Oxides and Salts onto Surface of Supports: Applications to Heterogeneous Catalysis," *Adv. Cata.*, **37**, 1 (1990).

Yang, R. T., and M. S. A. Baksh, "Pillared Clays as a New Class of Adsorbents for Gas Separation," *AIChE J.*, **37**, 679 (1991).

Yang, R. T., *Gas Separation by Adsorption Processes*, Butterworth, Boston (1987).

Yoldas, B. E., "Transparent Porous Alumina," *Amer. Ceram. Soc. Bull.*, **54**, 286 (1975a).

Yoldas, B. E., "Alumina Sol Prepared from Alkoxides," *Amer. Ceram. Soc. Bull.*, **54**, 289 (1975b).

Yoldas, B. E., "Alumina Gels that form Porous Transparent Al_2O_3," *J. Mater. Sci.*, **10**, 1856 (1975c).

Zhu, Li-qun, Jin-ling Tu, and Ya-jun Shi, "Separation of CO-CO_2-N_2 Gas Mixture for High-Purity CO by Pressure Swing Adsorption," *Gas Sep. Purif.*, **5**, 173 (1991).

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