Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Adsorption of Carbon Dioxide on Chemically Modified Carbon Adsorbents

Hyun-K Song; Kun-Hing Lee

To cite this Article Song, Hyun-K and Lee, Kun-Hing(1998) 'Adsorption of Carbon Dioxide on Chemically Modified Carbon Adsorbents', Separation Science and Technology, 33: 13, 2039 — 2057

To link to this Article: DOI: 10.1080/01496399808545045

URL: http://dx.doi.org/10.1080/01496399808545045

SEPARATION SCIENCE AND TECHNOLOGY, 33(13), pp. 2039–2057, 1998

Adsorption of Carbon Dioxide on Chemically Modified Carbon Adsorbents

HYUN-KON SONG and KUN-HONG LEE*
DEPARTMENT OF CHEMICAL ENGINEERING
POHANG UNIVERSITY OF SCIENCE AND TECHNOLOGY
SAN 31, HYOJA-DONG, NAM-KU, POHANG, KYUNGBUK, 790-784, SOUTH KOREA

ABSTRACT

Carbon adsorbents were chemically modified to have base sites on their surfaces, and the adsorption characteristics of carbon dioxide on them were investigated. Three kinds of carbon materials were used as support materials: two activated carbons and a carbon black. Base sites were introduced by impregnating the support materials with calcium acetate solution, followed by calcination at 700°C for 2 hours in an inert gas flow. Chemical modification reduced the surface areas of adsorbents due to the blocking of micropores. Irreversible adsorption of carbon dioxide occurs up to 300°C due to chemisorption. However, reversible adsorption was possible by pretreating adsorbents with carbon dioxide. Strong interaction between carbon dioxide and base sites enhanced adsorption of carbon dioxide at higher temperatures up to 250°C.

INTRODUCTION

Use of fossil fuels produces carbon dioxide, resulting in global warming. The report of Working Group 1 of IPCC concluded that there is a discernible human influence on global climate (1). Increases in the concentration of carbon dioxide in the atmosphere contributes over half of the greenhouse effect (2). Worldwide acceptance of a carbon tax is expected in the future, so the reduction of carbon dioxide production is a high priority. Separation of carbon

---

* To whom correspondence should be addressed.

dioxide from effluent gas streams is an existing technology, and there is no need for modification of existing processes.

Various technologies can be used to separate carbon dioxide from effluent gas streams. The large-scale separation of carbon dioxide by absorption is a commercial operation used throughout the world (3). Other techniques, such as membrane separation and adsorption, focus on smaller-scale separations. Although they are still in the development stage, much interest has been given to these small-scale techniques due to their lower energy requirements and cleaner operations.

Active research efforts have been placed on the separation of carbon dioxide by adsorption, and several plants are now in operation as a result. The key component of adsorption technology is the adsorbent. Introduction of better adsorbents greatly improves the overall performance of the separation process. Adsorbents with large surface areas such as activated carbons or zeolites have been widely investigated as the adsorbents for carbon dioxide separation. Activated carbon fibers recently emerged as promising materials (4).

The amount of adsorption on an adsorbent depends on the available surface area and the affinity for the adsorbate gas (5). An adsorbent used for gas separation should have an affinity based on physical interaction between the surface of the adsorbent and the adsorbate molecules since the process should be reversible. Stronger physical affinity leads to enhancement of adsorption capacity.

Effluent gas streams mainly consist of nitrogen and carbon dioxide. Since carbon dioxide is a quadrupole and has a polarizability greater than that of nitrogen (6), modification of the electrostatic field on the surface of an adsorbent results in enhancement of the physical affinity for carbon dioxide, and thus the adsorption capacity of a given adsorbents to a greater extent than for nitrogen.

Introduction of alkali metals or alkaline earth metals on the surface of an adsorbent gives base sites which have a strong affinity for molecules of acidic gases like carbon dioxide. The basicity of a metal oxide decreases with the ratio of electric charges to the radius of the metal ion. Since calcium oxide and magnesium oxide have low values of this ratio, they can provide strong base sites on the surface of an adsorbent (7). This idea was also tested with inorganic membranes. Magnesium oxide (8) or calcium oxide (9) was impregnated to enhance the adsorption of carbon dioxide and thus the surface diffusion effect. Natural sepiolite, which mainly consists of magnesium oxide and silica, shows a large capacity for carbon dioxide adsorption and can separate carbon dioxide from nitrogen at 500 to 600°C (10). A perovskite compound also adsorbs a large amount of carbon dioxide per unit surface area at high temperature although the total surface area is small (11).

In the present study, carbon adsorbents were designed so that the base sites on their surfaces provide high affinity for carbon dioxide. Surfaces of three carbon materials were chemically modified by impregnation with calcium acetate solution. Calcination of these adsorbents results in a homogeneous distribution of calcium oxide on the surfaces. The effects of introducing base sites were investigated by measuring the amount of carbon dioxide adsorbed at various temperatures.

EXPERIMENTAL

Calcium Oxide

Calcium acetate monohydrate (Sanyo Pure Chemicals, minimum purity of 98%) was used as a precursor of calcium oxide. Thermogravimetric analysis and differential thermal analysis were simultaneously carried out using TG/DTA (Seiko, TG/DTA 300). Calcium acetate monohydrate (10 mg) loaded in a platinum pan was heated at a rate of 10°C/min up to 900°C with nitrogen flowing at 100 mL/min.

The interaction between calcium oxide and carbon dioxide was studied using a differential scanning calorimeter (TA Instruments, DSC 3000) and an x-ray diffraction technique [Rigaku, DMAS-B (CuKa)]. Calcium oxide with an extended surface area was prepared by calcining calcium acetate monohydrate at 700°C for 2 hours.

Two samples of calcium oxide were analyzed by using DSC. One sample was heated at a rate of 20°C/min up to 500°C with carbon dioxide flowing at 50 mL/min. The other sample underwent a heating–evacuation–cooling cycle three times, up to 330°C for the first cycle and to 600°C for the second and third cycles. Evacuation operations were performed at each holding temperature for 2 hours.

X-ray diffraction patterns of three calcium oxide samples were investigated over diffraction angles ranging from 20 to 60°. One sample was the calcium oxide with an extended surface area. Other samples were prepared from the reaction of this calcium oxide with carbon dioxide in a tube furnace (Lindberg, 55000) at 330 or 600°C.

The adsorption of carbon dioxide on the calcium oxide was carried out using the static volumetric method (Micromeritics, Accusorb 2100E). Calcium oxide powders (0.05–0.10 g) were used in each measurement. The surface areas of samples were calculated using the BET equation and nitrogen adsorption data at 77 K. The sample volumes were measured using He at the adsorption temperatures of carbon dioxide. Adsorption isotherms of carbon dioxide were obtained at 25, 100, and 250°C. At least three identical runs were repeated to guarantee the reproducibility of the isotherms.

Carbon Adsorbents

Three kinds of carbon adsorbents were used as support materials: two activated carbons [designated as AC1 (Kansai Coke and Chemicals, Maxsorb) and AC2 (Aldrich, 27,809-2)] and carbon black [designated as CB (Cabot, Vulcan XC 72 GP-3211)]. Calcium acetate monohydrate (10 g) was dissolved in 20 mL of deionized water for 5 hours with agitation. A saturated solution was obtained by removing undissolved salt by vacuum filtration. One gram of each support material was impregnated with this solution for 1 hour at 25°C. Vacuum filtration and vacuum drying for 10 hours at 120°C followed. Finally, the impregnated support materials were calcined at 700°C for 2 hours in nitrogen flowing at 1 L/min. The chemically modified carbon adsorbents were designated AC1(Ca), AC2(Ca), and CB(Ca).

The microstructures of these adsorbents were analyzed from the nitrogen adsorption isotherms at 77 K. Surface areas and pore size distributions were calculated from the BET equation and the MP method, respectively. Experimental values of the statistical thickness by Lippens et al. (12) were used in the MP method.

The surface morphologies of carbon adsorbents before and after chemical modification were observed using a scanning electron microscope (Phillips, SEM515). The distributions of calcium atoms on the surface of the carbon adsorbents were also shown in an x-ray map obtained by electron probe microanalysis (Jeol, JXA-8600L).

RESULTS AND DISCUSSION

Interaction between Calcium Oxide and Carbon Dioxide

Calcination of various calcium salts gives calcium oxides with high specific surface areas and large pore volumes (13). Calcium acetate monohydrate was chosen in this study because of its solubility in water and large pore volume after calcination.

Figure 1 shows the thermogram of calcium acetate monohydrate obtained from TGA and DTA experiments. It could be suggested from this figure and other literature (14) that the calcium acetate monohydrate was converted into calcium oxide through the following pathway during calcination:

$$Ca(OAc)_2{\cdot}H_2O \rightarrow Ca(OAc)_2 \rightarrow CaCO_3 \rightarrow CaO$$

Based on this knowledge, calcium oxide was prepared in our experiments by calcining calcium acetate monohydrate at 700°C for 2 hours to guarantee complete conversion to calcium oxide.

Interaction between calcium oxide and carbon dioxide was investigated using DSC and an x-ray diffractometer. Figure 2 shows DSC thermograms

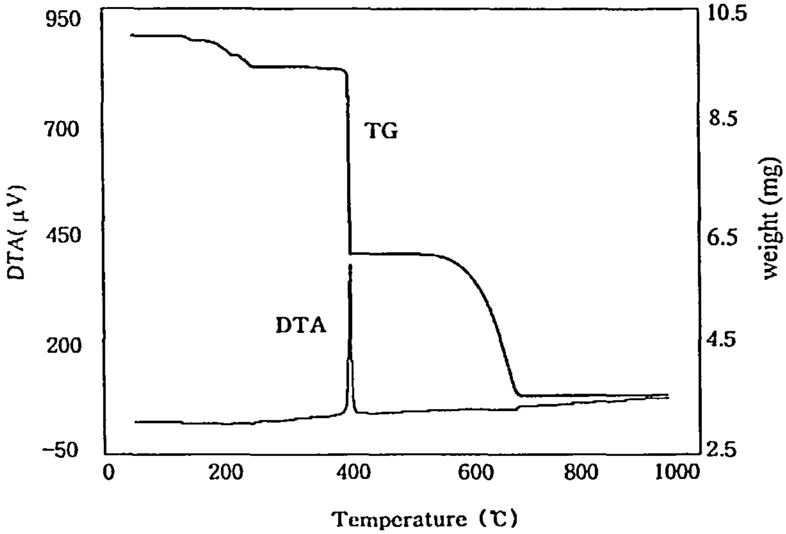


FIG. 1 Thermogram of calcium acetate monohydrate. Heating rate 10°C/min up to 900°C and nitrogen flow rate 100 mL/min.

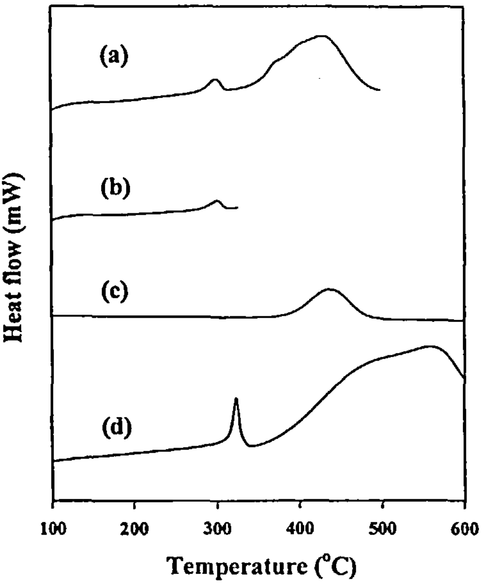


FIG. 2 DSC thermograms of calcium oxide in carbon dioxide atmosphere: (a) reference data, (b) first run with a fresh sample, (c) second run after evacuation at 330°C for 2 hours, (d) third run after evacuation at 600°C for 2 hours. Heating rate 20°C/min.

of calcium oxide obtained from calcium acetate monohydrate in a carbon dioxide atmosphere. Thermogram (a) was obtained by heating calcium oxide up to 500°C. Two exothermic peaks were observed near 300 and 450°C. A similar thermogram can be seen with commercial calcium oxide. Thermograms (b) through (d) were obtained through repeated heating and cooling of an identical sample. A sample of calcium oxide was first heated up to 330°C (b), followed by 2 hours of evacuation at 330°C, and cooled to room temperature. Heating was repeated up to 600°C to obtain (c). The exothermic peak near 300°C disappeared in (c) while the second exothermic peak around 430°C remained. This proves the irreversible chemisorption of carbon dioxide on the surface of the calcium oxide. Finally, (d) was obtained by evacuating the same sample at 600°C for 2 hours, followed by the cooling and reheating cycle. Here, both exothermic peaks were recovered due to the regeneration of active sites.

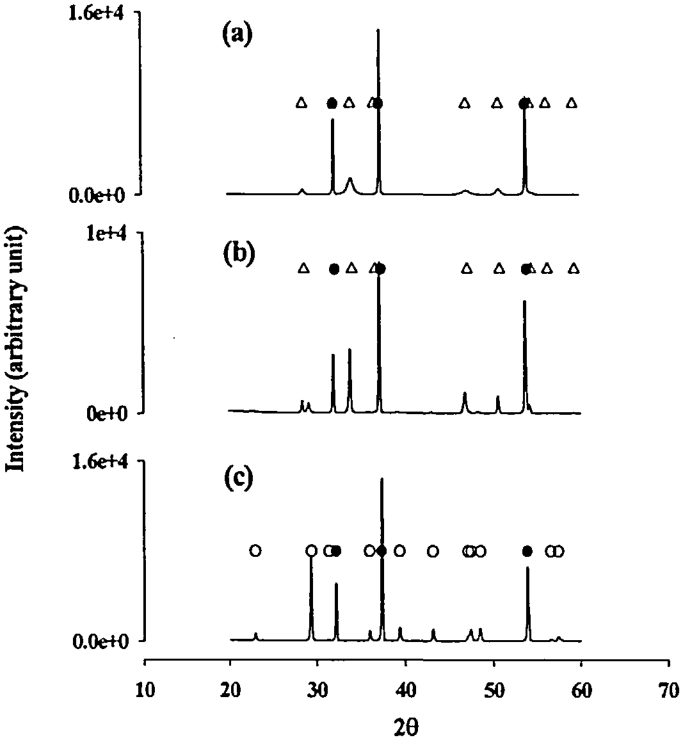


FIG. 3 X-ray diffraction patterns of calcium oxide: (a) calcium oxide obtained from calcium acetate monohydrate, (b) same sample after reaction with carbon dioxide at 330°C, (c) same sample after reaction with carbon dioxide at 600°C. The following symbols are used in the figure: (●) CaO, (Δ) $Ca(OH)_2$, (O) $CaCO_3$.

Figure 3 shows the x-ray diffraction patterns of calcium oxide samples reacted with carbon dioxide at different temperatures. Calcium oxide as a starting material showed some calcium hydroxide peaks as well as main peaks of calcium oxide as shown in Fig. 3(a). The calcium hydroxide peaks result from absorption of water from air. The pattern of calcium oxide reacted with carbon dioxide at 330°C (Fig. 3b) is similar to that of calcium oxide as a starting material, except that small peaks of calcium carbonate are shown in Fig. 3(b). The appearance of calcium carbonate peaks can be understood by the fact that calcium hydroxide readily absorbs carbon dioxide, forming calcium carbonate. Differently from Fig. 3(b), calcium oxide which reacted with carbon dioxide at 600°C showed intensive calcium carbonate peaks due to bulk carbonation of calcium oxide.

It can be concluded from the above observations that the main interaction between carbon dioxide and calcium oxide can be divided into two temperature domains; irreversible chemisorption up to ca. 300°C and bulk carbonation near 400°C and above. Similar results were reported previously (15).

The amount of carbon dioxide adsorption on the surface of calcium oxide was investigated in the chemisorption temperature region, as shown in Fig. 4. The amount of adsorbed carbon dioxide in the first runs increased with increasing temperature. There were large differences in the amount of ad-

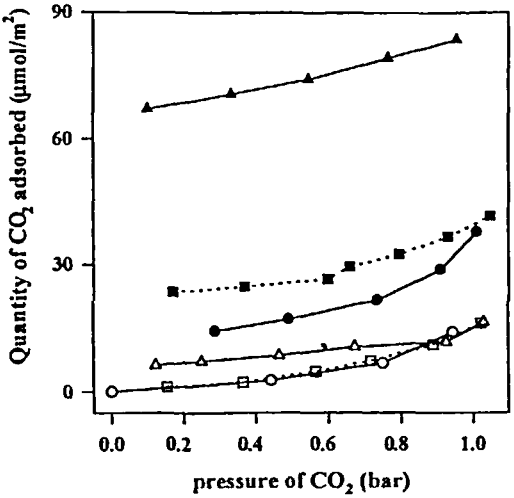


FIG. 4 Adsorption of carbon dioxide on calcium oxide. Thorough evacuations were carried out between the first runs and second runs. The following symbols are used in the figure: (●) 1st run at 25°C, (○) 2nd run at 25°C, (■) 1st run at 100°C, (□) 2nd run at 100°C, (▲) 1st run at 250°C, (△) 2nd run at 250°C.

sorbed carbon dioxide between the first runs and the second runs. However, such differences were not observed between runs after the second (they are not shown here). A plausible explanation of these observations is that the chemisorption sites are completely consumed by the first run, and only physical adsorption is possible thereafter. Reversible physisorption is of interest since a separation technique based on adsorption requires reversibility. One thing to be added here is that the data denoted by open symbols in Fig. 4 are less accurate since samples with a small surface area are prone to generate data with less credibility. Nevertheless, it was revealed in our preliminary study that the amount of reversible adsorption per unit surface area of calcium oxide is greater than that of porous carbon and silica materials at 100 and 250°C. This means that the surface of calcium oxide with chemisorbed carbon dioxide has a stronger affinity for carbon dioxide than the surface of pure carbon adsorbents.

Adsorption of carbon dioxide on the surface of CaO-doped adsorbents is depicted in Fig. 5. The pure calcium oxide surface has a strong affinity for carbon dioxide, resulting in irreversible chemisorption. On the other hand, the base sites (calcium oxide with chemisorbed carbon dioxide) has an intermediate affinity for carbon dioxide. The affinity is too weak to induce chemisorption, but stronger than that of pure carbon surface. Therefore, enhancement of adsorption at elevated temperatures can be achieved by the addition of base sites on the surface of porous carbons.

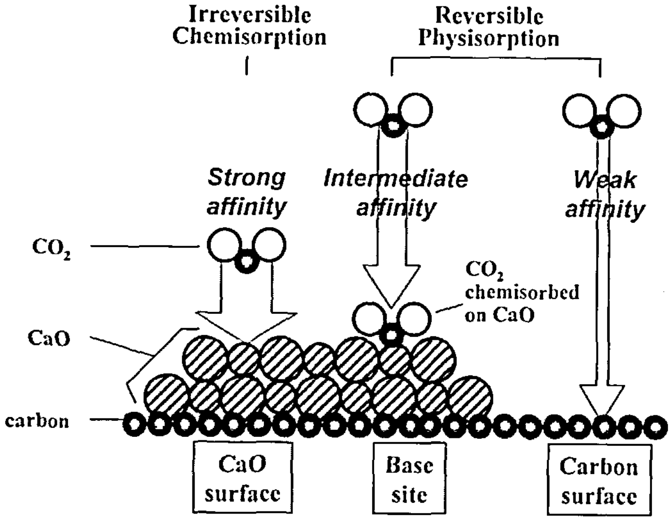


FIG. 5 Adsorption of carbon dioxide on the surface of calcium-oxide-doped adsorbents.

Morphology of Adsorbents

Microstructures of the pure and modified carbon adsorbents were examined through nitrogen adsorption. Carbon adsorbents which experienced only thermal treatment at 700°C for 2 hours in the inert atmosphere gave the same morphological characteristics as unmodified adsorbents which were not treated thermally. That is, thermal treatment alone does not make a considerable change in the microstructures of carbon adsorbents. Therefore, the morphology of carbon adsorbents is changed mainly by chemical modification with salts.

The effects of the chemical modification on morphology can be investigated by comparing modified adsorbents with unmodified ones. Isotherms of the carbon adsorbents appear in Fig. 6. Type I isotherms with no hysteresis were obtained with AC1 and AC1(Ca), indicating microporous materials. AC2 and AC2(Ca) gave isotherms associated with materials having both micropores and mesopores. The isotherms for CB and CB(Ca) indicate that they are nonporous materials or include bigger pores than activated carbons.

Surface areas and pore size distributions were calculated from these isotherms. Table 1 summarizes the morphological characteristics of the adsor-

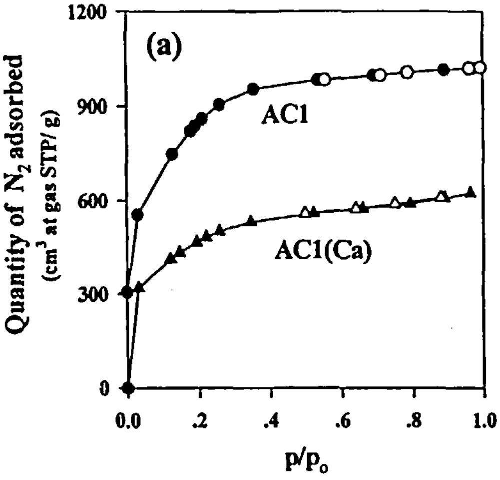


FIG. 6 Adsorption of nitrogen on the carbon adsorbents at 77 K: (a) AC1 and AC1(Ca), (b) AC2 and AC2(Ca), (c) CB and CB(Ca). The filled symbols and the open symbols were obtained from the adsorption and the desorption experiments, respectively.

(*continued*)

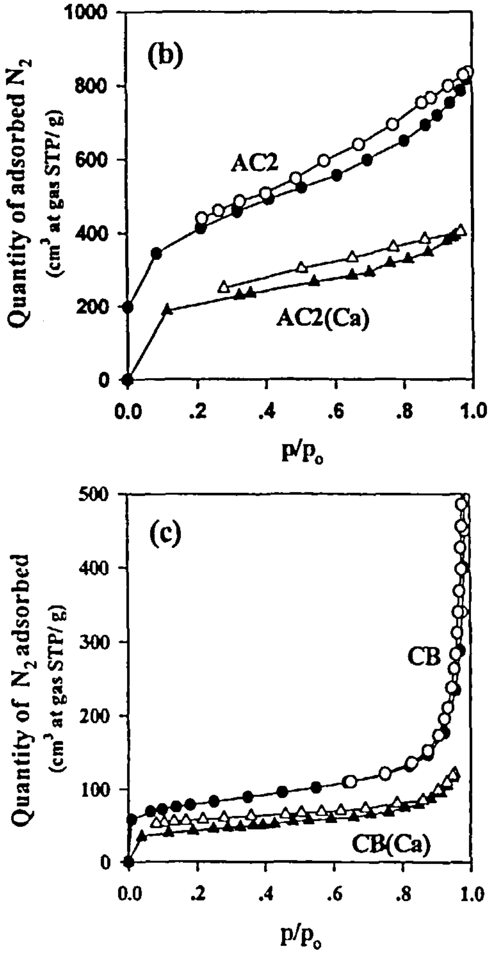


FIG. 6 Continued.

bents before and after chemical modification. Chemical modification led to decreases in pore volume and surface area for all adsorbents. However, the average pore radius of activated carbons increased a little after the modification while that was not the case with carbon black. Here, the average radius was calculated with the assumptions of the cylindrical pore model. Therefore, the value is twice the hydraulic radius, the ratio of pore volume to surface area, used in the MP method.

The increase in the average pore radius is due to the removal of pores smaller than the average pore radius in carbon adsorbents due to the

TABLE 1
Microstructures of the Carbon Adsorbents

	Surface area, S_{BET} (m^2/g)	Total volume, V_{tot} (cm^3/g)	Average radius, r_{avg} (Å)	CaO load (%)
AC1	3,000	1.6	11	—
AC1(Ca)	1,500	0.97	13	27.65
AC2	1,371	1.26	18.4	—
AC2(Ca)	630	0.62	19.7	27.35
CB	225	0.31	28	—
CB(Ca)	141	0.19	27	26.72

impregnation of salts. Activated carbon adsorbents are included in this case since they are microporous. On the other hand, the average pore radius of carbon black decreased after the impregnation of salts since their pores are too large to be removed. Such an argument can be supported by the pore size distribution of the adsorbents shown in Figs. 7, 8 and 9.

Surface morphologies of the chemically modified adsorbents were shown in the SEM photographs of Figs. 10, 11, and 12. Also included in these figures are x-ray maps of calcium atoms distributed on the surfaces. A uniform distribution of calcium, and thus of calcium oxide, is obvious in these figures.

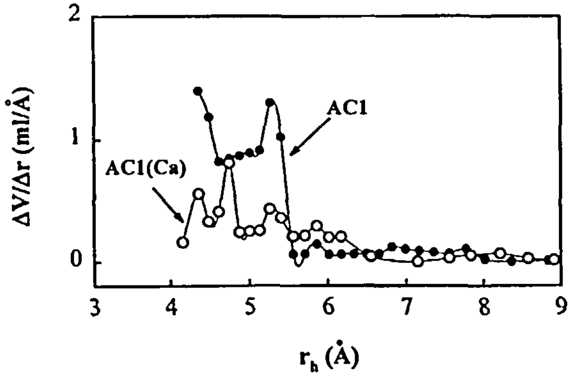


FIG. 7 Pore size distribution of AC1 and AC1(Ca).

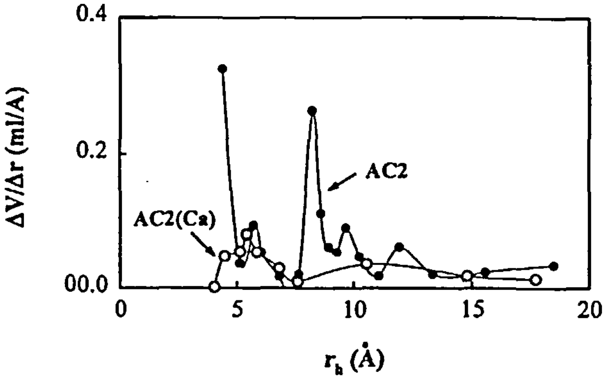


FIG. 8 Pore size distribution of AC2 and AC2(Ca).

Adsorption of Carbon Dioxide

Separation of gases based on adsorption requires reversibility in adsorption and desorption. The chemically modified carbon adsorbents prepared in this work possess highly irreversible surfaces due to strong chemisorption. This irreversibility, however, can be circumvented by pretreating the adsorbents with carbon dioxide. Reversible adsorption–desorption was observed after one dose of carbon dioxide adsorption for all experiments.

Adsorption experiments of carbon dioxide were carried out at 25, 100, and 250°C with the chemically modified carbon adsorbents. Similar experiments

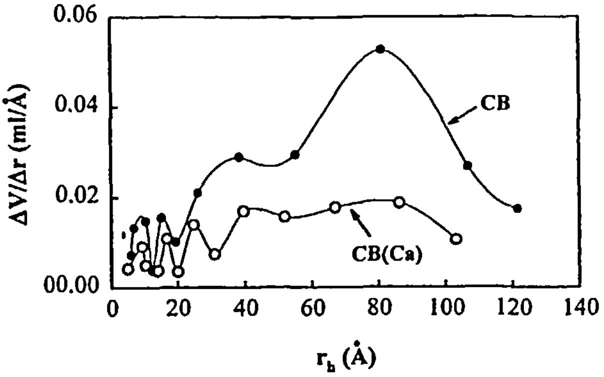


FIG. 9 Pore size distribution of CB and CB(Ca).

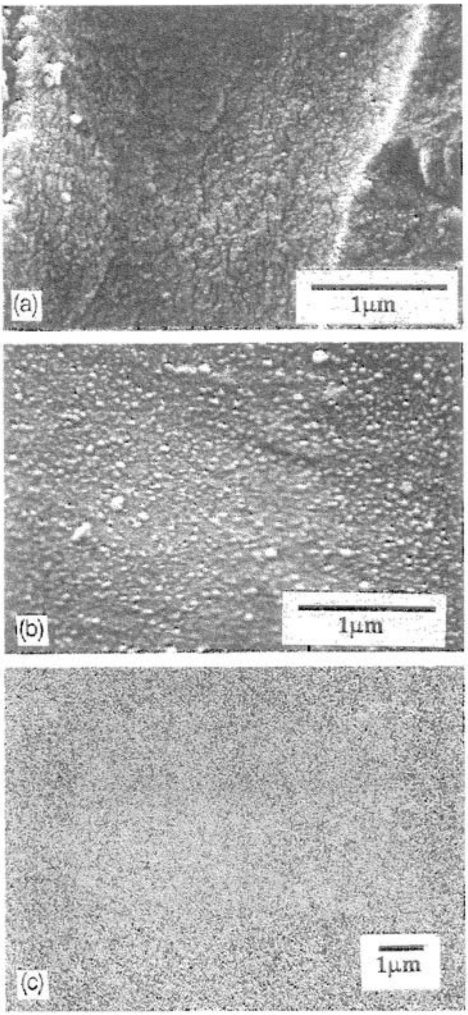


FIG. 10 Surface morphologies of the carbon adsorbents AC1 and AC1(Ca): (a) SEM photograph of AC1 (×30,000), (b) SEM photograph of AC1(Ca) (×30,000), (c) x-ray map of Ca (×10,000).

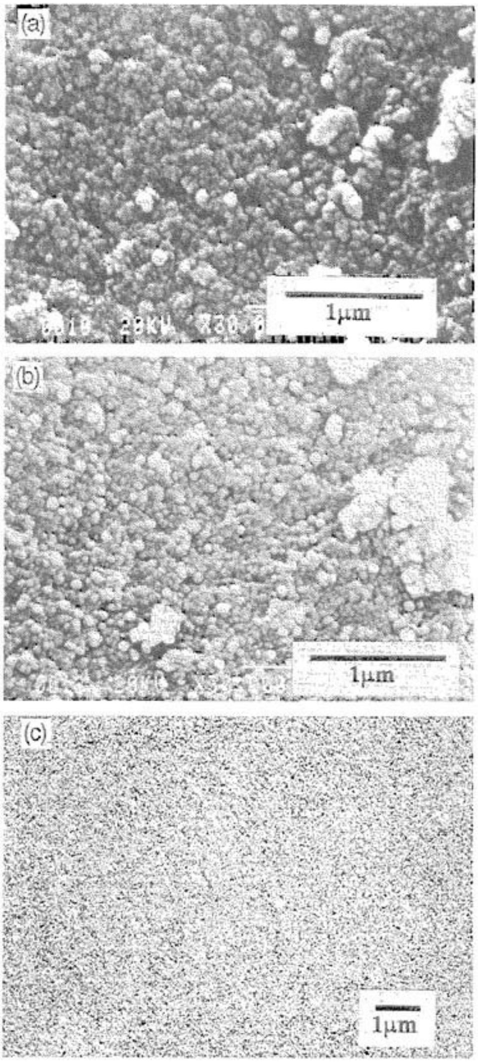


FIG. 11 Surface of the carbon adsorbents AC2 and AC2(Ca): (a) SEM photograph of AC2 (×30,000), (b) SEM photograph of AC2(Ca) (×30,000), (c) x-ray map of Ca (×10,000).

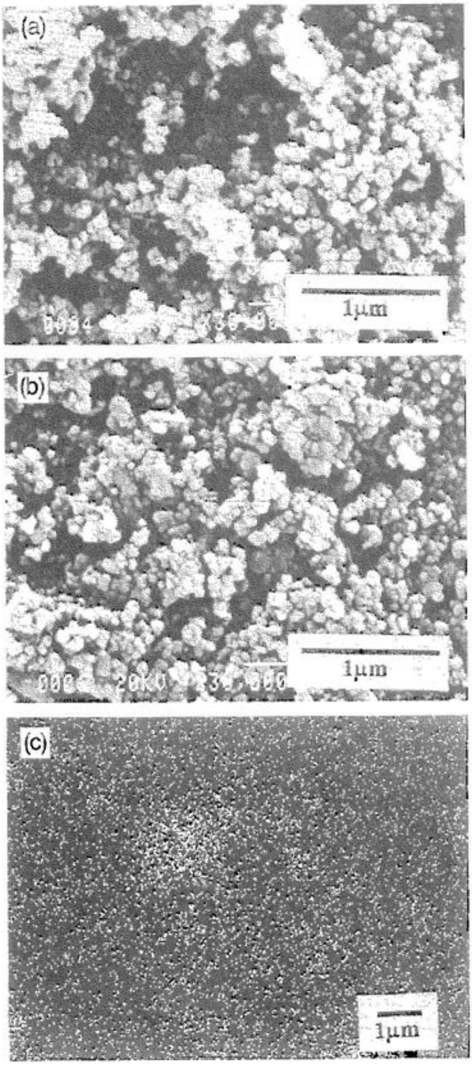


FIG. 12 Surface of the carbon adsorbents CB and CB(Ca): (a) SEM photograph of CB (×30,000), (b) SEM photograph of CB(Ca) (×30,000), (c) x-ray map of Ca (×10,000).

were also done with unmodified carbon adsorbents to investigate the effect of chemical modification on the adsorption of carbon dioxide.

Figure 13 shows the results of adsorption experiments. The amounts of adsorbed carbon dioxide on the carbon adsorbents decrease with increasing temperature, and the same is true for the chemically modified carbon adsorbents. However, since the interaction between base site and carbon dioxide is stronger than that between carbon and carbon dioxide, a considerable amount of carbon dioxide can be adsorbed on the chemically modified carbon adsorbent at temperatures as high as 250°C. The infrared spectra confirm that chemisorbed carbon dioxide on calcium oxide is the unidentate species (7). The unidentate species is considered to induce a stronger affinity for carbon dioxide than for carbon surface. Adsorption of carbon dioxide on the carbon adsorbents are more difficult at this temperature without chemical modification.

The amount of physically adsorbed gas becomes proportional to the partial pressure at low relative pressures. The adsorption isotherms follow Henry's law in this case, and the adsorptivity of a given adsorbent can

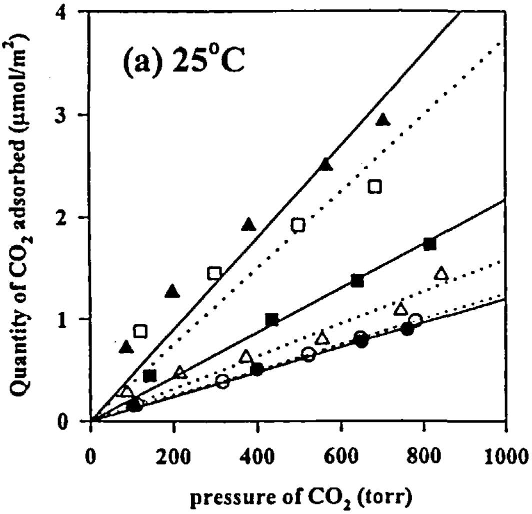
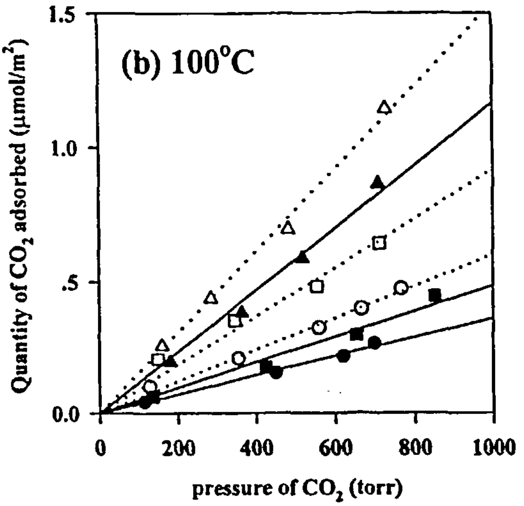


FIG. 13 Adsorption of carbon dioxide on the carbon adsorbents: (a) 25°C, (b) 100°C, (c) 250°C. The following symbols are used in the figure: (●) AC1, (○) AC1(Ca), (■) AC2, (□) AC2(Ca), (▲) CB, (△) CB(Ca).



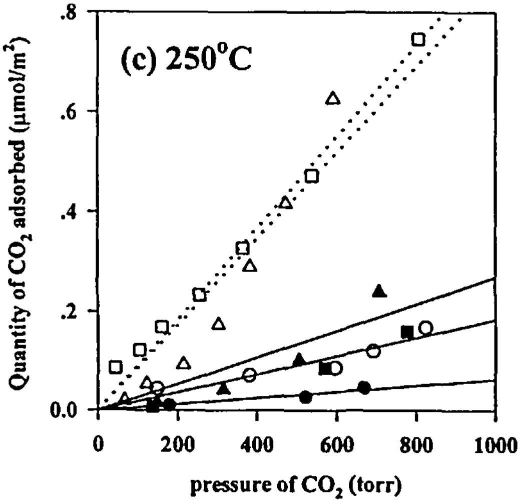


FIG. 13 Continued.

TABLE 2
Henry's Constants for the Reversible Adsorption of Carbon Dioxide

	Henry's constant (μmol/m²/atm)		
	25°C	100°C	250°C
AC1	0.92	0.27	0.05
AC1(Ca)	0.95	0.46	0.14
AC2	1.65	0.37	0.14
AC2(Ca)	2.84	0.70	0.70
CB	3.41	0.88	0.20
CB(Ca)	1.21	1.16	0.66

be represented by Henry's constant. Table 2 shows Henry's constants of carbon adsorbents before and after chemical modification. It is obvious that the values of Henry's constants for reversible adsorption became much larger with chemical modification except for CB at 25°C.

CONCLUSION

The surface properties of carbon adsorbents can be modified by simple chemical treatments. The base sites thus generated have a strong affinity for carbon dioxide. Since the chemically modified carbon adsorbents adsorb considerable amounts of carbon dioxide at high temperatures, they can be used for the separation of carbon dioxide directly from the effluent gas. The same principle can be widely applied for the separation of other gases using adsorbents.

ACKNOWLEDGMENTS

This work was partially supported by the School of Environmental Engineering and by the Automation Research Center, both at POSTECH, Korea.

REFERENCES

1. R. A. Kerr, *Science*, *270*, 1565 (1995).
2. I. M. Smith, *Proceedings of the International Energy Agency Carbon Dioxide Disposal Symposium*, Oxford, UK, 1993, p. 729.

3. S. H. Cho, J.-N. Kim, K. T. Joo, and K. S. Park, *Chem. Ind. Technol.*, *13*, 8 (1995).
4. S. Sircar, T. C. Golden, and M. B. Rao, *Carbon*, *34*, 1 (1996).
5. R. M. Barrer, *J. Colloid Interface Sci.*, *21*, 415 (1965).
6. R. C. Weast, *CRC Handbook of Chemistry and Physics*, 66th ed., CRC Press, Boca Raton, FL, 1985–1986, p. E-68.
7. A. Auroux and A. Gervasini, *J. Phys. Chem.*, *94*, 6371 (1990).
8. R. J. R. Uhlhorn, K. Keizer, and A. J. Burggraaf, *J. Membr. Sci.*, *46*, 225 (1989).
9. Y.-K. Cho, K. Han, and K.-H. Lee, *Ibid.*, *104*, 219 (1995).
10. *Ceramics*, *8*, 145 (1994).
11. H. Kusakawa, T. Kato, T. Kuwabara, W. Ueda, Y. Morikawa, Y. Moro-oka, and T. Ikawa, *J. Catal.*, *126*, 208 (1990).
12. B. C. Lippens, B. G. Linsen, and J. H. de Boer, *Ibid.*, *3*, 32 (1964).
13. D. Beruto, M. G. Kim, and A. W. Searcy, *High Temp. High Pressures*, *20*, 25 (1988).
14. S. Budavari, *The Merck Index*, 11th ed., Merck & Co., Rahway NJ.
15. D. Cazorla-Amoros, A. Linares-Solano, J. P. Joly, and C. Salinas Martinez de Lecea, *Catal. Today*, *9*, 219 (1991).

Received by editor September 29, 1997
Revision received January 1998