

Development of Functional Micro Porous Materials

Hiroyuki Muramatsu, Jun-ichi Kadokawa, Masa Karasu and Hideyuki Tagaya

Department of Materials Science & Engineering, Faculty of Engineering, Yamagata University,
Yonezawa, Yamagata 992-8510, Japan

FAX:81-238-26-3413, E-mail: tc021@dipfr.dip.yz.yamagata-u.ac.jp

It is well known that nano porous compounds such as active carbon and layered compounds with a large surface area have a large ability to adsorb gas molecules. In this study, a mixture of nitrogen and carbon dioxide gases was adsorbed on the active carbon whose surface was modified with organic materials. It was confirmed that the active carbon which was modified with polyethylene glycol adsorbed carbon dioxide as much as the active carbon without modification, and adsorbed carbon dioxide selectively than nitrogen. This result suggests that carbon dioxide was adsorbed selectively on the functional groups of active carbon having high polarity. Oxygen was separated from the mixture of oxygen and nitrogen gases by using modified active carbon and organic-inorganic layered compound. The surface modified active carbon has low separation ability. When organic-inorganic layered compound having polar molecules was used, however, oxygen was adsorbed more than nitrogen.

Key words:adsorption, active carbon, layered inorganic compound

1. INTRODUCTION

Nano porous materials are expected as separation materials. Active carbon is one of such nano scale porous compound and known as gas adsorbate. The active carbon can be modified by introducing functional groups such as OH and COOH. In this study, mixture of nitrogen and carbon dioxide gases was adsorbed on the active carbon whose surface was modified with organic materials.

NO_x is known as a cause of acid rain. If separation of oxygen from mixture of oxygen and nitrogen gases is possible, only oxygen can be provided to engine resulting the reduction of the production of NO_x. Therefore, in this study separation of oxygen from mixture of oxygen and nitrogen gases was carried out. Active carbon was used for the separation of nitrogen and oxygen gases. We have already reported the adsorption properties of Zn-Al layered double hydroxides (LDHs) in which mixture of nitrogen and carbon dioxide gases was adsorbed⁽¹⁾. The Zn-Al LDH(CO₃²⁻) adsorbed carbon dioxide selectively. And the amount of carbon dioxide adsorbed into the Zn-Al LDH (CO₃²⁻) increased with an increase in the Al content. Also, Zn-Al LDH(OH) adsorbed carbon dioxide effectively. Therefore organic-inorganic layered compounds such as layered

double hydroxides (LDHs) and Zn(OH)₂ were used as adsorbates.

2. EXPERIMENTAL

2.1 Preparation of surface modified active carbon

(i) Preparation of oxidized active carbon by carboxyl groups

Surface of active carbon was oxidized by treating in the nitric acid (3.6 M) at 363 K for 1 h. The active carbon was then washed in water by irradiating ultra sonic wave, filtered and dried at 333 K for 48 h. After drying, products were characterized by IR and TG/DTA.

(ii) Preparation of modified active carbon by organic compounds

The obtained oxidized sample was refluxed in acetonitrile or water with organic compounds such as alkyl alcohol, carboxylic acid and amine at 333 K for 8 h. Then the products were washed, filtered and dried at 333 K for 48 h. After drying, the products were characterized by IR and TG/DTA to confirm the presence of carboxyl groups and ester groups.

2.2 Preparation of organic-inorganic layered compounds

(i) Preparation of Zn-Al LDH(CO₃²⁻)

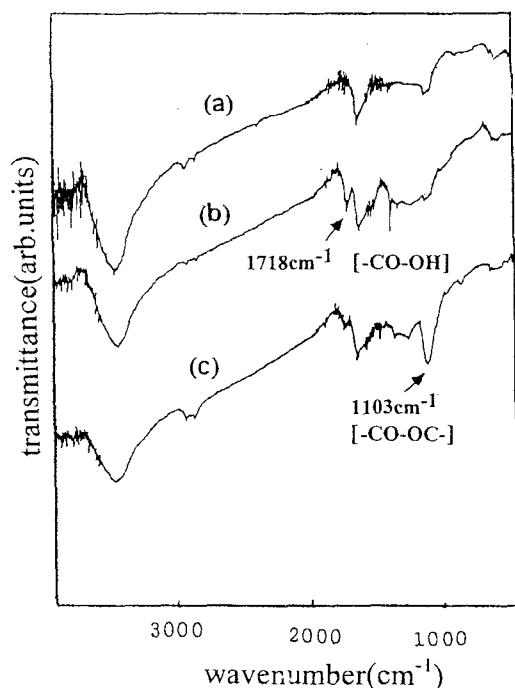


Figure 1. IR spectra of (a) active carbon and the reaction products of active carbon with (b) nitric acid and (c) polyethylene glycol

Zn-Al LDH(CO_3^{2-}), $[\text{Zn}_{0.7}\text{Al}_{0.3}(\text{OH})_2]^{0.3}[(\text{CO}_3)_{0.15}]^{0.3-}$ was prepared by adding the mixture of $\text{Zn}(\text{NO}_3)_2$ (0.03 mol) and $\text{Al}(\text{NO}_3)_3$ (0.013 mol) to a Na_2CO_3 (0.0058 mol) solution, and the pH-value of the solution was kept to 10 with a NaOH solution at 333 K for 2 h. The products were then washed, filtered and dried at 333 K for 48 h. After drying, the products were characterized by XRD to confirm the constitution of layered structures.

(ii) Preparation of Zn-Al LDH oxides

Zn-Al LDH oxide, $[\text{Zn}_{0.3}\text{Al}_{0.7}\text{O}_{1.15}]$, was prepared by calcination of the Zn-Al LDH(CO_3^{2-}) at 773 K for 3 h.

(iii) Preparation of Zn-Al LDHs which intercalated carboxylate anion⁽²⁾

Organic carboxylate anions were intercalated into Zn-Al LDHs in which Zn-Al LDH oxide was added to a solution including carboxylate anion and was stirred at 333 K for 8 h. The products were dried and characterized by XRD to confirm the intercalation reaction.

(iv) Preparation of layered compounds by the

reaction of $\text{Zn}(\text{OH})_2$ with organic carboxylic acid

$\text{Zn}(\text{OH})_2$ was prepared from $\text{Zn}(\text{NO}_3)_2$ (0.12 mol) solution (300 ml) which were added to NaOH (0.078 mol) solution (300 ml) and stirred at 277 K for 0.5 h. The products were dried and obtained $\text{Zn}(\text{OH})_2$ was reacted with organic carboxylic acid at 333 K for 8 h. XRD patterns of these organic-inorganic layered compounds were shown in Figure 2.

2.3 Procedure for gas adsorption

Sample was treated in an evacuated vessel for 30 min at room temperature or 423 K before gas adsorption. The mixture gases of nitrogen and carbon dioxide or nitrogen and oxygen (mol ratio=1:1) was injected into the vessel. After 30 min, the gas in the vessel was analyzed by gas chromatography. The typical gas adsorption properties of the organic-inorganic materials were obtained after 30 or 60 min.

2.4 Characterization of prepared organic-inorganic layered compounds and gas analysis

Powder XRD patterns were analyzed on a Rigaku powder diffractometer unit, using $\text{CuK } \alpha$ radiation ($\lambda = 0.154 \text{ nm}$) at 40 kV and 20 mA between 1.8 and 50°. FT-IR spectra (KBr disk method) were recorded on a Horiba FT-200.

TG/DTA analysis of samples were performed with a Seiko SSC 5000 thermal analysis system (heating rate : 10 K/min, in flowing N_2). Gas analysis was performed with Shimadzu gas chromatography GC-8A.

3. RESULTS AND DISCUSSION

3.1 Gas adsorption properties of surface modified active carbon

Figure 1 shows IR spectra of active carbon without treatment (AC) and with treatment by nitric acid (N-AC) or by polyethylene glycol (PEG-AC). The other modified active carbons which was treated by alginic acid (A-AC) were analyzed in the same way. In IR spectrum of the N-AC, the new peak at 1718 cm^{-1} appeared. It corresponded to stretching vibration of carboxyl groups. And in the IR spectrum of the PEG-AC, the peak at around 1718 cm^{-1} disappeared and the peak at around 1103 cm^{-1} appeared. The new peak corresponded to stretching vibration of the ester bond.

Figure 3 shows the amount of adsorbed carbon dioxide and nitrogen gases on modified active

Table I. XRD dates of organic-inorganic compounds

No.	Host	Guest	H:G	<i>d</i> -value(nm)			
1	Zn(OH) ₂	sebacic acid	2:1	1.90	1.25	0.93	0.62
2	Zn(OH) ₂	sebacic acid	1:1	1.25	0.63	0.40	
3	Zn(OH) ₂	heptanoic acid	1:1	1.85	0.92	0.62	
4	LDH	indigocarmine	1:1	1.86	0.92	0.62	
5	AC	PEG	1:1	—			

※AC; active carbon PEG; poly ethyleneglycol

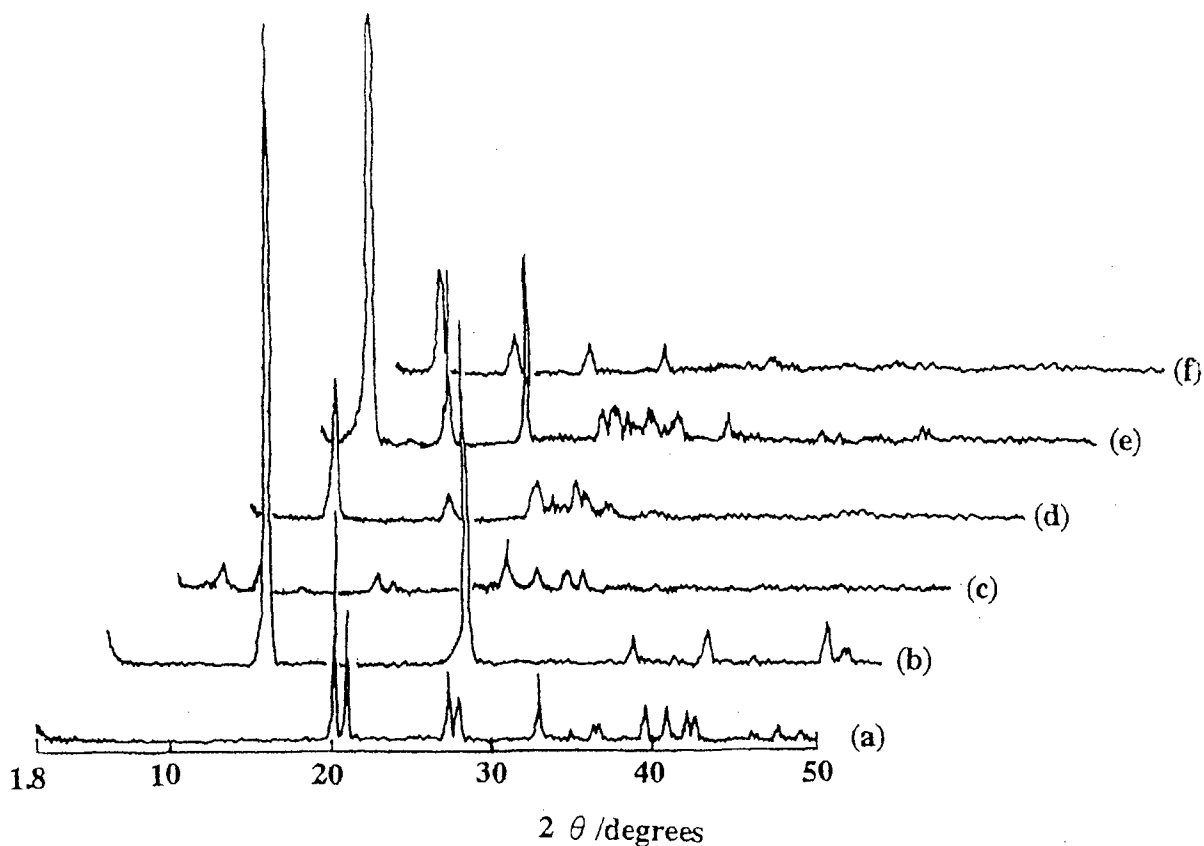


Figure 2. XRD patterns of organic-inorganic layered compounds. (a) Zn(OH)₂
(b) Zn-Al LDH (c)-(f) the sample of (1)-(4) listed in Table I, respectively.

carbon. The amount of the adsorbed gases increased in the following order:

active carbon >N-AC>PEG-AC.

The separation factor increased in the following order:

PEG-AC>N-AC>active carbon.

The carboxyl groups are polar more than alkyl groups and PEG is polar more than the carboxyl groups. Since carbon dioxide is polar more than

nitrogen, the present results indicate that the separation factor correlated well with polarity of modified active carbon.

3.2 Gas adsorption properties of layered organic-inorganic compounds

Table I shows the XRD data on the interlayer spacing of the Zn-Al LDH intercalation compounds and the reaction products of Zn(OH)₂ with organic carboxylic acids. Figure 2. shows XRD patterns of

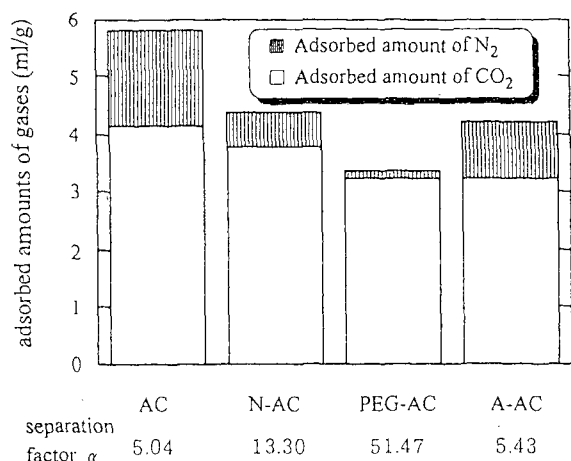


Figure 3. Adsorbed amounts of carbon dioxide and nitrogen gases on modified active carbon.

the organic-inorganic compounds. XRD patterns show (a) Zn(OH)₂, (b) Zn-Al LDH(CO₃²⁻) having a d-value of 0.76 nm, (c) reaction product of sebacic acid with Zn(OH)₂ having d-values of 1.90 and 1.25 nm, (d), (e) reaction products of sebacic acid and heptanoic acid with Zn(OH)₂ having d-values of 1.25 and 1.85 nm, respectively and (f) intercalation compound of indigocarmine into the Zn-Al LDH having a d-value of 1.86 nm. Figure 4 shows the adsorbed amounts of O₂ and N₂ gases into the layered organic-inorganic compounds. No.1 and No.2 were intercalation compounds of sebacic acid. However, No.2 has one peak at 1.25 nm and No.1 has two peaks at 1.25 nm and 1.90 nm in XRD patterns. The product has two peaks indicating that Zn(OH)₂ is assembled to two structure depending on host/guest ratio in the reactants. Therefore, it was considered that No.1 has larger adsorption site than No.2. Indeed the amounts of adsorbed gases on No.1 was larger than that on No.2. No.3 and No.1 have the same interlayer spacing at about 1.9 nm. However, No.3 was intercalation compound of monocarboxylic acid and No.1 was intercalation compound of dicarboxylic acid indicating that No.3 has bilayer structure and No.1 has monolayer structure. It was expected that No.1 has adsorption site more than

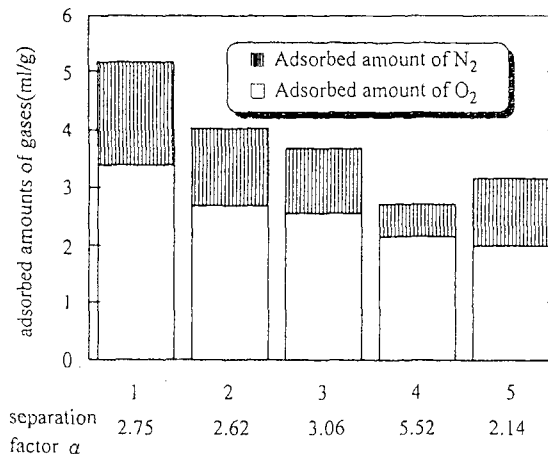


Figure 4. Adsorbed amounts of oxygen and nitrogen gases into the organic-inorganic compounds.

No.3. Indeed gas adsorption of No.1 was more than No.3. Moreover, though No.1, No.3 and No.4 have the same interlayer spacing at about 1.9 nm, No.4 has the highest separation factor although No.4 was the smallest amount of gas adsorption.

4. CONCLUSIONS

In this study, we have clarified the adsorption properties of active carbon and organic-inorganic layered compounds. Mixture of carbon dioxide and nitrogen was adsorbed on the active carbon. Because carbon dioxide has high polarity compared to nitrogen, carbon dioxide was adsorbed selectively by active carbon having high polarity. Mixture of oxygen and nitrogen was adsorbed on the organic-inorganic layered compounds. Because oxygen has a large polarity compared to nitrogen, oxygen was adsorbed selectively on active carbon with high polarity and interlayer of organic-inorganic layered compounds.

REFERENCES

- (1) Y. Tanno, H. Tagaya, M. Karasu, J. Kadokawa and K. Chiba, *Trans MRS. J.*, **1999**, *24*, 647
- (2) S. Miyata, *Clays Clay miner.*, **1986**, *28*, 50

(Received December 16, 1999; Accepted May 27, 2000)