Quantitative Evaluation of Adsorption and Desorption Behavior of Carbon Dioxide over Perovskite-Type Oxides

Tsutomu Sakai, Atsushi Murata, Jun-ichiro Hayashi,
Katsuki Kusakabe and Shigeharu Morooka

Department of Chemical Science and Technology, Kyushu University, Fukuoka 812-81, Japan

Scope

Separation of CO_2 from effluent gas is important for global environmental protection. Activated carbon and silica gel are good adsorbents of CO_2 but they loose their ability at high temperature. On the other hand, perovskite compounds posses CO_2 adsorptivity at elevated temperature and can be used as CO_2 adsorbent. In the present study, several perovskite compounds with high specific area were synthesized by different methods and their CO_2 adsorptivity was determined. Adsorption/desorption rate of CO_2 was also evaluated by a pulse response method and a temperature-programmed desorption technique.

Experimental

Perovskite compounds were synthesized by the following methods:
(1) Nitrates precipitation: Aqueous solutions of nitrates were mixed, and water was slowly evaporated by heating.
(2) Citrates precursor: Excess citric acid and ethylene glycol were added to an aqueous solution of nitrates. Water was evaporated in a rotary evaporator until a viscous liquid was obtained. The precursor was further dried in vacuum at 100°C.
(3) Cyanides precipitation: $La(NO_3)_3 \cdot 6H_2O$ and $K_3[Co(CN)_6]$ were dissolved in water and mixed to get a precipitate at 60°C.
(4) Diluted precipitation: An aqueous solution of nitrates was dropped slowly into a water-ethanol-ammonia solution. The gel was recovered by centrifugation.
(5) Alkoxides sol-gel: An iso-propanol solution of $Ba(iso\text{-}OC_3H_7)_2$ and $Ti(iso\text{-}OC_3H_7)_4$ was hydrolyzed at 80°C. The hydrated oxide was dried in vacuum.

The calcination temperature was varied in 400-700°C and was optimized to attain both high crystallinity and surface area of powders. Solids was characterized with XRD, EDX and BET. The morphology of particles was observed with SEM.

Total adsorption of CO_2 was determined with TG. The temperature was increased at a rate of 5 $K \cdot min^{-1}$ to 500°C. The total pressure was kept at 101 kPa. Dynamic CO_2 adsorption was evaluated for $LaAlO_3$ and $BaTiO_3$ by applying the impulse response method of gas chromatography. $LaAlO_3$ or $BaTiO_3$ powder was packed in a separation column through which argon flew as the carrier. Pulses of CO_2 and Ar mixture were injected every ten minutes into the column until a steady-state response curve was attained.

Dynamic CO_2 adsorption was also evaluated by applying the temperature programmed desorption. The carrier gas was helium containing 8 vol% of CO_2. After adsorption equilibrium was attained, the column was heated at a rate of 3-20 $K \cdot min^{-1}$ from 30°C to 550°C. The effluent gas was continuously introduced into a TCD-GC and the desorption rate was evaluated.

Results and Discussion

The X-ray diffraction patterns shown in **Fig. 1** reveal that the single phase $LaFeO_3$ crystal was obtained by the citrates precursor and diluted precipitation methods. Conditions of the other methods and crystallinity of products are summarized in **Table 1. Figures 2 (a) and (b)** respectively show the morphology of $LaFeO_3$ and $LaAlO_3$ particles prepared by the citrates precipitation method. **Figures 3 (a) and (b)** indicate their total CO_2 adsorption isotherms in a range of 25-500°C. The other perovskite compounds prepared show the similar tendency. CO_2 isotherms obeyed the Freundlich equation and the amount of adsorption was proportional to the $1/n$ power of CO_2 partial pressure. At a CO_2 partial pressure of 10 kPa, the amount of CO_2 adsorbed by $LaFeO_3$ was about 14 $\mu mol \cdot m^{-2}$ at 25°C and roughly whole surface was covered by a monolayer of CO_2 molecules. It decreased to about 7 $\mu mol \cdot m^{-2}$ at 500°C. Silica gel that adsorbed about 3.5 $\mu mol \cdot m^{-2}$ of CO_2 at 25°C exhibited no adsorptivity at 500°C.

Figure 4 illustrates typical impulse response curves obtained with the chromatographic column packed with $LaAlO_3$. The response curve was very broad at 100°C and peaks of N_2 and CO_2 were separated at 500°C. Thus a part of CO_2 molecules adsorbed at 500°C were mobile, but the mount of mobile CO_2 was not large. The mean residence time of CO_2 increased with increasing column temperature. This is quite different from the tendency with silica gel, whose adsorptivity decreased with increasing temperature.

Figure 5 shows TPD profiles of $LaCoO_3$, $LaFeO_3$ and $LaAlO_3$, suggesting widely distributed activation energies of adsorption. The maximum desorption rate was observed at 75-80°C for all samples tested. The total amount of CO_2 desorbed was determined by integrating the desorption rate between 30-550°C. The relationship among CO_2 coverage θ, desorption rate $(-\Delta\theta/\Delta t)/\theta$ and temperature T was obtained for different heating rates. Activation energy E and frequency factor k_0 were defined by $(-\Delta\theta/\Delta t)/\theta = k_0 \exp(-E/RT)$ and calculated from the Arrhenius plot of the desorption rate at a same CO_2 coverage.

As shown in **Fig. 6**, the activation energy for $LaFeO_3$ was 100-150 kJ/mol when the CO_2 coverage was smaller than 0.4 and decreased to 40-50 kJ/mol at larger CO_2 coverage in the lower temperature range. The frequency factor varied with the CO_2 coverage by five orders of

Table 1. Perovskite compounds prepared.

	Methods	Calcination temperature	Single phase	BET surface area $[m^2 \cdot g^{-1}]$
$LaCoO_3$	Nitrates precipitation	800°C,2h	X	-
	Citrates precursor	600°C,2h	O	9.8
	Diluted precipitation	650°C,4h	O	13.9
	Cyanides precipitation	650°C,4h	X	16.8
$LaFeO_3$	Nirtrates precipitation	600°C,2h	X	9.9
	Citrates precursor	600°C,1h	O	22.8
	Diluted precipitation	600°C,2h	O	7.2
$LaAlO_3$	Citrates precursor	800°C,1h	O	13.8
$LaNiO_3$	Nitrates precipitation	800°C,2h	X	-
	Citrates precipitation	800°C,2h	O	3.6
$LaCrO_3$	Nitrates precipitation	800°C,2h	O	2.8
$BaTiO_3$	Alkoxides sol-gel	600°C,2h	O	47
	Alkoxides sol-gel	800°C,2h	O	37

magnitude. The desorption rate $(-\Delta\theta/\Delta t)/\theta$ at 500°C was of the order of 10^{-2} s^{-1} at a CO_2 coverage of 0.5. This rate would be smaller than the permeation rate through a thin membrane for gas separation. Thus, $LaFeO_3$ that was prepared in this study may not be competent as a membrane-constructing material. However, its desorption rate is acceptable when it is used as a packed-bed adsorbent. The results for $LaAlO_3$ were fundamentally similar with those of $LaFeO_3$.

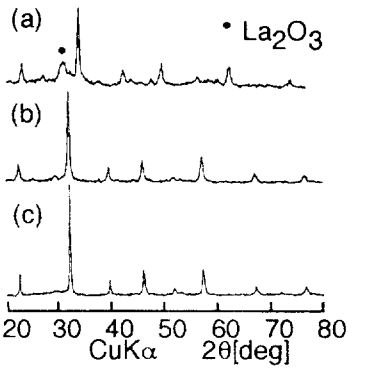

Figure 1. XRD patterns of $LaFeO_3$.
(a) Nitrates precipitation;
(b) citrates precusor; and
(c) diluted precipitation.

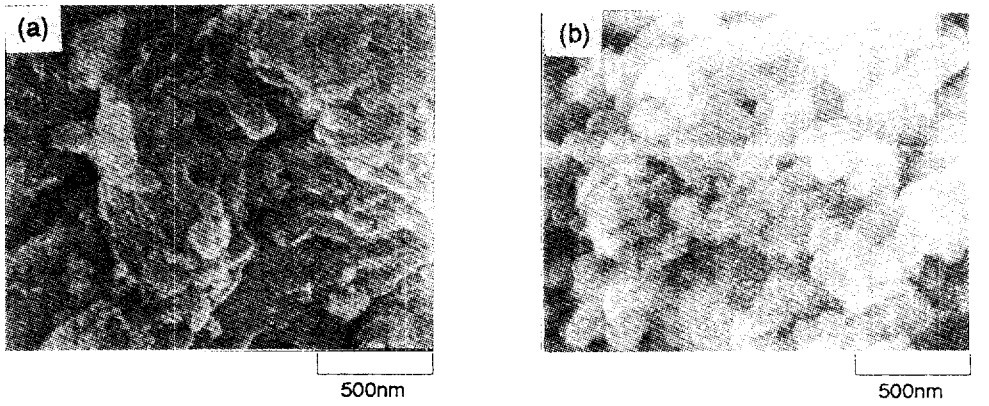

Figure 2. SEM images of perovskites; (a) $LaFeO_3$ and (b) $LaAlO_3$.

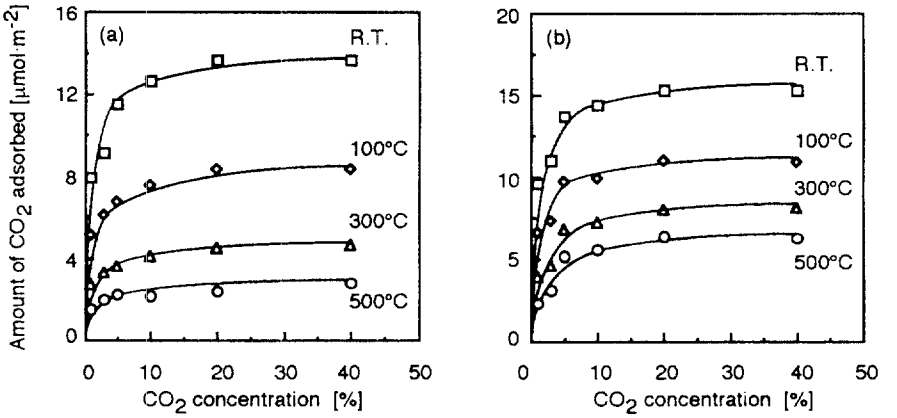

Figure 3. Adsorption isotherms of (a) $LaFeO_3$ and (b) $LaAlO_3$.

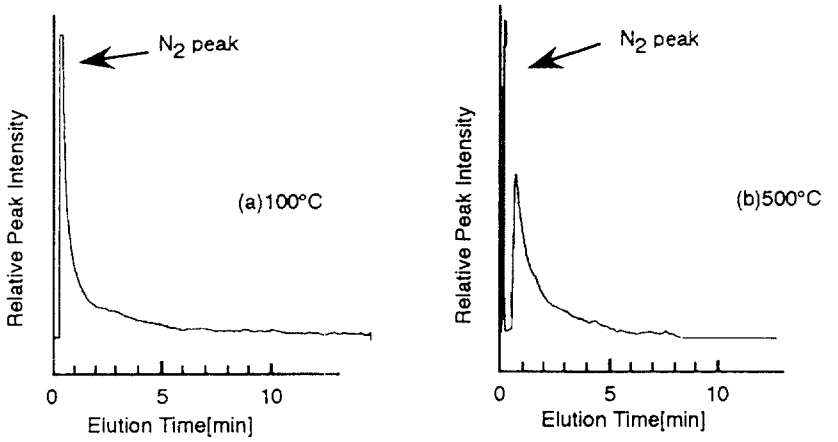

Figure 4. Impulse response curves of CO_2 through $LaAlO_3$ column

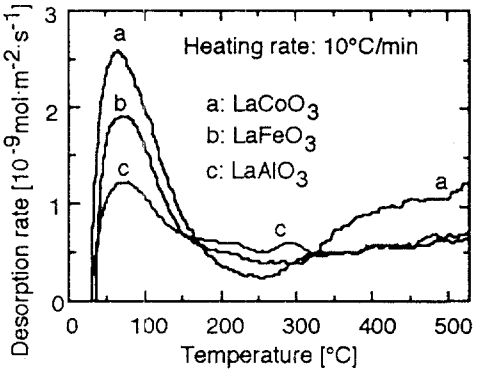

Figure 5. TPD profiles of $LaCoO_3$, $LaFeO_3$ and $LaAlO_3$

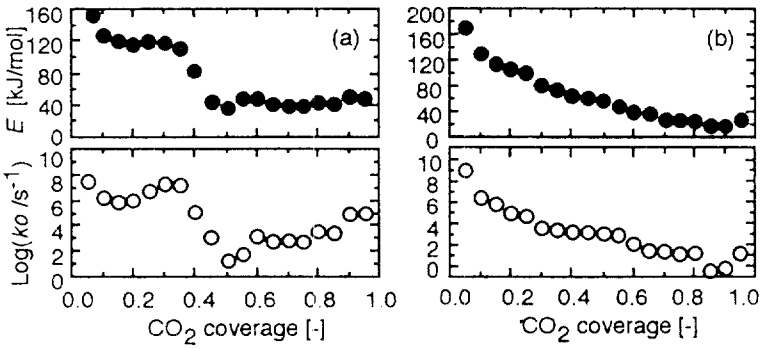

Figure 6. Effect of CO_2 coverage of E and k_0.
(a) $LaFeO_3$ and (b) $LaAlO_3$.