

# CO<sub>2</sub>-Pressure Swing Activation for Efficient Production of Highly Porous Carbons

*Shuwen Wang, Katsumi Kaneko\**

Center for Energy and Environmental Science, Shinshu University, Wakasato, Nagano, 380-8553, Japan.

\*To whom correspondence should be addressed. E-mail: kkaneko@shinshu-u.ac.jp

Tel: +81-(0)26-269-5743 Fax: +81-(0)26-269-5737

**Abstract:** In this work, we describe a new type of activation method of carbon materials using pressure-swing of CO<sub>2</sub>. The porosity development markedly depends on the pressure swinging frequency, and the porous carbon obtained from pressure-swing activation shows high porosity development without pitting corrosion on surface, being superior to that obtained from activation without pressure-swing. This phenomenon is ascribed to the enhancement of Knudsen diffusion and/or configurational diffusion which is caused by an exterior stimulus from the pressure swing.

---

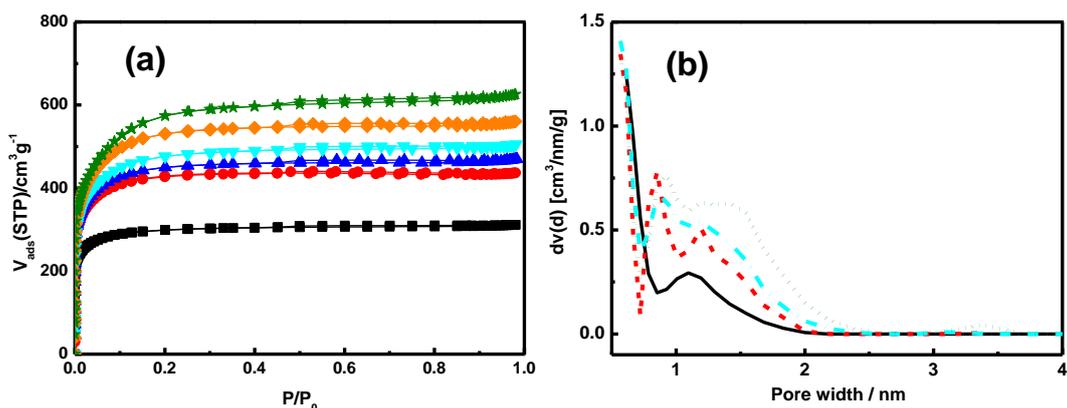
Enhancing the mass transfer of a reactant gas in the solid matrix as well as in pores is a key to accelerate the solid-gas phase reactions. The mass transfer processes in solid-gas phase reactions are classified into external mass transfer and internal mass transfer, being the transportation of a gas reactant from bulk phase to the external surface of the solid, and from the external surface of solid into the pores inside the solid, respectively. The necessity for improvement of the mass transfer has invented fluidized-bed reactors and moving-bed reactors in chemical engineering. However, the enhancement of the mass transfer inside the micropores is not easy. This is because the diffusion molecules are strongly interacted with the pore walls when the mean free path ( $\lambda$ ) of the reactant molecules is comparable to the pore size. Moreover, the interaction becomes too strong for the molecules to transport freely when the pore size is comparable to the reactant molecules. These two types of mass transfer belong to the internal mass transfer, being named as the Knudsen diffusion and configurational diffusion, respectively [1]. On the other hand, an intensive confinement effect of molecules in micropores accelerates the chemical reaction due to the in-pore high pressure effect

[2]. Consequently, if we can accelerate the diffusion of molecules in micropores and shift a pseudo-equilibration to the product side by an external stimulus, an enhancement even in intra-micropore reaction can be expected. The pressure swing technology, which has been applied to gas separation through repeating the adsorption and desorption process by fluctuating the pressure, can also be applied as a stimulus for intra-micropore diffusion. In this work, we describe a new type of pressure-swing method for activation of carbon materials.

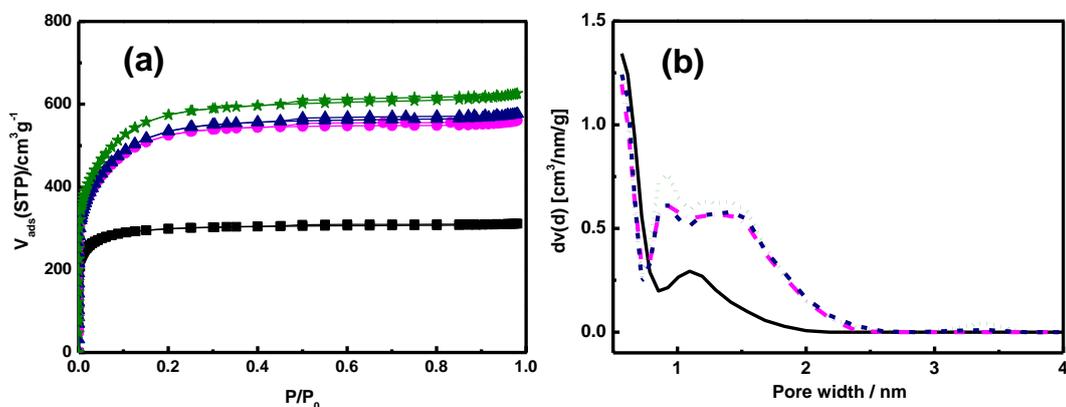
Two kinds of microporous carbon materials are used in this work for further activation. One is a coconut shell-based activated carbon (AC) and the other is a pitch-based activated carbon fiber (ACF). The new activation was conducted with a horizontal reaction tube which combines with the vacuum line having a pressure gauge and inlet CO<sub>2</sub>, as shown in Figure S1. A carbon sample was loaded in a ceramic boat and then heated from room temperature to a target temperature at a heating rate of 20 K min<sup>-1</sup> under a pure Ar flow (400 mL min<sup>-1</sup>). The tube was evacuated after the preheating and then CO<sub>2</sub> was injected into the tube up to 0.6 atm in a determined time. Subsequently the reaction tube was evacuated for 20 seconds and the pressure inside tube was below 20 Pa, then CO<sub>2</sub> was again injected in a similar way for a further CO<sub>2</sub> activation. Here such injection and evacuation cycles can be proceeded at different frequency from 1 to 20 times for 120 min, as shown in Figure S2. This activation method is named the CO<sub>2</sub>-pressure swing (CO<sub>2</sub>-PS) activation. Then sample was cooled down to room temperature under the Ar purging.

The porosity development was evaluated by N<sub>2</sub> adsorption isotherms at 77 K obtained by using a Micromeritics ASAP 2020 surface analyzer. Figure 1(a) shows the N<sub>2</sub> adsorption isotherms of pristine AC and the CO<sub>2</sub>-PS activated samples. The shapes of these isotherms are all of type I, indicating the predominate presence of micropore. The detailed porosity parameters are given in Figure 1(b), Table S1 and Figure S3. The surface area evaluated by  $\alpha_s$ -plots (SPE) method [3]

increases from 1720 to 2010  $\text{m}^2 \text{g}^{-1}$ , and the micropore volume evaluated by  $\alpha_s$ -plots method increases from 0.67 to 0.91  $\text{cm}^3 \text{g}^{-1}$  with increase of the  $\text{CO}_2$ -PS frequency from 1 to 20. The extent of activation is in good accordance with the pressure swing frequency. As discussed in supporting information, the  $\text{CO}_2$  supplied for each  $\text{CO}_2$ -PS cycle is sufficient for the gasification reaction, then the dependency of porosity development with the frequency of pressure swing should be attributed to the magnitude of diffusivity of reactant molecules; higher frequency of pressure swing gives a more efficient diffusion of  $\text{CO}_2$  in AC. The pore size distributions (PSD) determined by QSDFT method (using a slit pore model) shown in Figure 1(b) indicate the significant pore development in the pore width range of  $0.8 \text{ nm} < w < 2.3 \text{ nm}$ , being different from those activated by successive  $\text{O}_2$  adsorption /  $\text{CO}$  and  $\text{CO}_2$  desorption process [4], which gives the development of uniform pores.



**Fig. 1** – (a)  $\text{N}_2$  adsorption isotherms and (b) PSD of pristine AC and AC activated by  $\text{CO}_2$ -PS with different frequency of pressure swing at 1123 K for 2 h. AC:  $\blacksquare$  (—), 1 cycle:  $\bullet$  (---), 2 cycles:  $\blacktriangle$ , 5 cycles:  $\blacktriangledown$  (- · - ·), 10 cycles:  $\blacklozenge$ , 20 cycles:  $\blackstar$  (····). The symbols in ( ) are for PSD in Figure 1(b).



**Fig. 2** – (a)  $\text{N}_2$  adsorption isotherms and (b) PSD of pristine AC and AC activated by different frequency of pressure swing at 1123 K for 2 h.

methods for 2 h. AC: ■ (—), CO<sub>2</sub>-PS (20 cycles): ★ (⋯⋯), CO<sub>2</sub>-CF (1123 K): ● (— · —), CO<sub>2</sub>-CF (1143 K): ▲ (— —). The symbols in ( ) are for PSD in Figure 2(b).

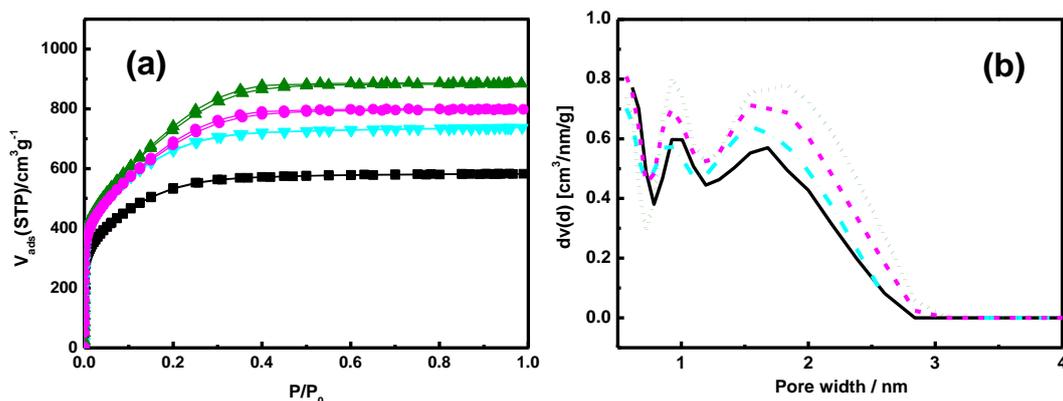
The porosity development by the CO<sub>2</sub>-PS activation is also compared with the activation with CO<sub>2</sub> flowing at a constant rate, which is named as CO<sub>2</sub>-constant flow (CO<sub>2</sub>-CF) activation in this work. The CO<sub>2</sub>-CF activation was conducted at 1123 K and 1143 K for 2 h with CO<sub>2</sub> flow rate of 48 ml min<sup>-1</sup>, which is equal to the CO<sub>2</sub> injection rate of CO<sub>2</sub>-PS activation at cycle number of 20. The corresponding N<sub>2</sub> adsorption isotherms are shown in Figure 2(a) and the porosity parameters are shown in Figure 2(b) and Table 1. AC obtained from CO<sub>2</sub>-PS activation shows similar burn-off but larger surface area and micropore volume than that from CO<sub>2</sub>-CF activation under comparable conditions, indicating CO<sub>2</sub>-PS method has a significant mass-transfer-accelerated effect comparing with CO<sub>2</sub>-CF method. Moreover, CO<sub>2</sub>-CF activation at a higher temperature of 1143 K gives a remarkable burn-off of 71%, while the surface area and micropore volume are still lower than that from CO<sub>2</sub>-PS activation, suggesting the diffusion limitation of the CO<sub>2</sub>-CF activation method.

**Table 1** – Porosity parameters of pristine AC and AC activated by different methods.

Sample	$S_{\text{us}} / \text{m}^2 \text{g}^{-1}$	$V_{\text{micro}} / \text{cm}^3 \text{g}^{-1}$	$w / \text{nm}$	burn off / wt%
Pristine AC	1290	0.47	0.73	--
AC (CO <sub>2</sub> -PS, 20 cycles, 1123K)	2010	0.91	0.91	46
AC (CO <sub>2</sub> -CF, 1123 K)	1930	0.84	0.87	47
AC (CO <sub>2</sub> -CF, 1143 K)	1960	0.86	0.88	71

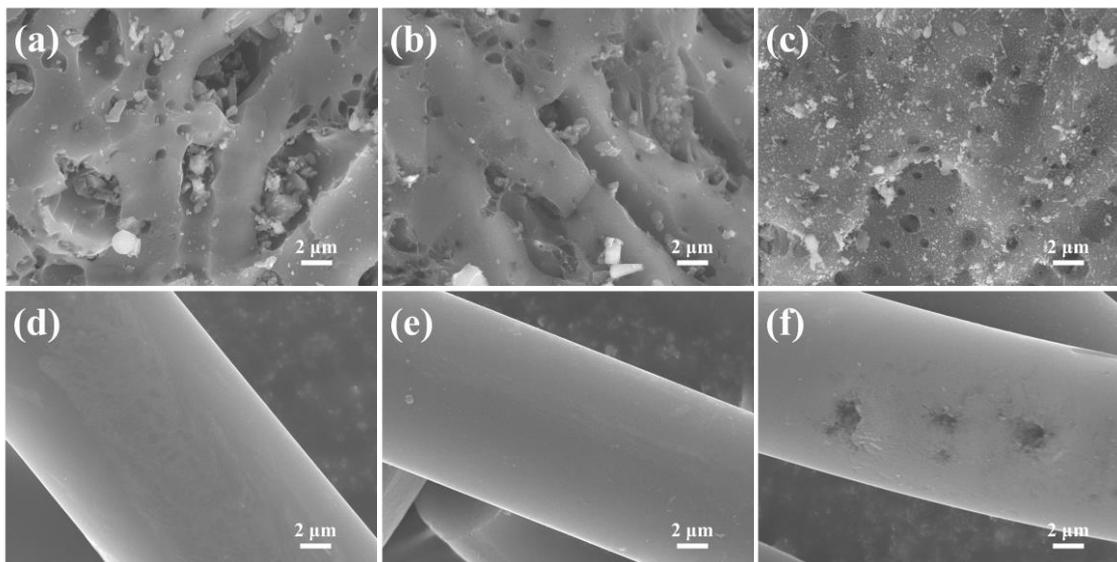
The roles of different types of mass-transfer in CO<sub>2</sub> activation are further discussed here. In this work the external mass transfer is not considered since it only affects the overall reaction rate at low temperature process [5]. The internal mass transfer includes bulk diffusion, Knudsen diffusion and configurational diffusion. The CO<sub>2</sub> activation with bulk diffusion limitation can lead to a radial anisotropy of porosity in the particle of the obtained sample [6]. In this work, the granular AC (150 μm ~ 250 μm) and that pulverized into smaller size (< 10 μm) are activated by CO<sub>2</sub>-CF method under the same condition at 1123 K with CO<sub>2</sub> flowing at 48 mL min<sup>-1</sup>, and their N<sub>2</sub> adsorption

isotherms are compared. The result shown in Figure S4 indicates that the N<sub>2</sub> adsorption isotherms of samples with larger size and smaller size are almost identical, suggesting the activation in the AC particle is almost homogenous and the bulk diffusion limitation should be negligible. Consequently, the diffusion limitation of CF-CO<sub>2</sub> activation in this work is ascribed to Knudsen diffusion and/or configurational diffusion, which can be reduced by using the pressure swing method.



**Fig. 3** – (a) N<sub>2</sub> adsorption isotherms and (b) PSD of pristine ACF and ACF activated by different methods at 1223 K for 2 h. ACF: ■ (—), CO<sub>2</sub>-PS (5 cycles): ▼ (— • —), CO<sub>2</sub>-PS (20 cycles): ▲ (••••), CO<sub>2</sub>-CF: ● (— —). The symbols in ( ) are for PSD in Figure 3(b).

The CO<sub>2</sub>-PS activation with the cycle numbers of 5 and 20 has also been compared with CO<sub>2</sub>-CF activation at 1223 K with CO<sub>2</sub> flow rate of 48 ml min<sup>-1</sup>. The N<sub>2</sub> adsorption isotherms of the resulting samples are shown in Figure 3(a) and the porosity parameters and burn-off are shown in Figure 3(b) and Table S2. The porosity increase remarkably with the cycle numbers of pressure swing during CO<sub>2</sub>-PS activation. Similar to that of AC, ACF obtained from CO<sub>2</sub>-PS method shows higher surface area and micropore volume than that from CO<sub>2</sub>-CF method under comparable conditions, suggesting CO<sub>2</sub>-PS method can be widely applicable for different porous carbons.



**Fig. 4** – SEM images of pristine AC (a) and ACF (d), those activated by CO<sub>2</sub>-PS method with 20 cycles of pressure swinging (b, e) and CO<sub>2</sub>-CF method under comparable conditions (c, f).

The morphology change of AC and ACF activated by different methods are examined by a field emission scanning electron microscope (FE-SEM: JEOL, JSM-6330F, Japan). Figure 4 (a) and (d) show the surface morphology of pristine AC and ACF, which don't change significantly after CO<sub>2</sub>-PS activation with 20 cycles of pressure swinging, as shown in Figure 4 (b) and (e). On the other hand, those obtained from CO<sub>2</sub>-CF activation show evident pitting corrosions, as shown in Figure 4 (c) and (f). This result indicates that the CO<sub>2</sub>-PS activation can induce a more uniform gasification in porous structure of carbon than CO<sub>2</sub>-CF activation. Similar results were shown in Figure S5 with wider scope of SEM image.

In conclusion, the CO<sub>2</sub>-PS activation, being a new technique for CO<sub>2</sub> activation on microporous carbon materials, can provide an enhancement on Knudsen diffusion and/or configurational diffusion comparing with the CO<sub>2</sub>-CF activation, resulting in the production of highly microporous carbon without pitting corrosion on the carbon surface. Therefore we can apply directly this method to carbon precursors to obtain highly microporous carbons in future.

**Acknowledgement:** S.W. is supported by Concert-Japan: Efficient Energy Storage and Distribution, JST. This work is partially supported by Grant-in-Aid for Scientific Research (A) (24241038).

## References:

- [1] Malone DM, Anderson JL. Hindered diffusion of particles through small pores. *Chem Eng Sci* 1978; 33(11): 1429–1440.
- [2] Fujimori T, Morelos-Gómez A, Zhu Z, Muramatsu H, Futamura R, Urita K, et al. Conducting linear chains of sulphur inside carbon nanotubes. *Nature Comm* 2013; 4: 2162–2169.
- [3] Kaneko K, Ishii C, Ruike M, Kuwabara H. Origin of superhigh surface area and microcrystalline graphitic structures of activated carbons. *Carbon* 1992; 30(7): 1075–1088.
- [4] Py X, Guillot A, Cagnon B. Activated carbon porosity tailoring by cyclic sorption/decomposition of molecular oxygen. *Carbon* 2003; 41(8): 1533–1543.
- [5] Thomas JM, Thomas WJ. Principles and practice of heterogeneous catalysis. Weinheim: VCH. 1997, 291.
- [6] Robau-Sánchez A, Aguilar-Elguézabal A, Torre-Sáenz L, Lardizábal-Gutiérrez D. Radial distribution of porosity in spherical activated carbon particles. *Carbon* 2003; 41 (4): 693–698.