ADSORPTION PROPERTIES AND PORE STRUCTURES OF ALLOYED CARBON AEROGELS

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Introduction

Carbon aerogels (CAs) have gathered much attention from industrial and fundamental aspects. The previous studies on CAs have focused on the porosity control by changing conditions of RF polycondensation [1, 2], activation [3], and heat treatment. If we can control the pore wall chemistry of CAs, the science and technological potentials should extend.

The interest in Ce as the catalyst for NO conversion stems from the high oxygen storage capacity and unique behavior of storage and release of oxygen [4]. In addition, the study about redox property of CeO_2 based materials is reported that their reducibility is greatly enhanced by coexistence of ZrO_2.

Therefore, we tried to prepare CAs alloyed with Ce and Zr in order to donate a new surface function [5]. We report the interesting adsorption properties of Ce, Zr-doped CAs, and their unique porosities

Experimental

The preparation method by sol-gel polycondensation is similar to the one reported [1]. An aqueous solution of resorcinol (R) and formaldehyde (F) is fixed at R/F mole ratio 1:2. $Ce(NO_3)_3$ and $ZrO(NO_3)_2$ are added to the solution (Ce/Zr mole ratio was approximately 1:1) at pH = 3 and 7. The initial pH was adjusted with NaOH for the sample prepared at pH=7. The solution was cured one day at room temperature, one day at 333 K and two days at 353 K. (The gelation depends on the initial pH of the solution. Typically, gelation occur in several hours for solution with low initial pH and it starts on the next day for the solution with pH=7.) The gel was washed with acetone until water is completely removed, then dried using supercritical CO_2 and carbonized at 1323 K for 3 h under N_2 flow. In this time, the Ce, Zr-doped CAs are obtained at pH7 and pH3 (a-CZ-CA-l and n-CZ-CA), and different concentration of the aqueous solution (a-CZ-CA-l and a-CZ-CA-h). In addition, the Ce or Zr doped CAs are also prepared (C-CA and Z-CA)

The pore structures of the prepared carbon aerogels were determined by N_2 adsorption at 77 K using α_S-analysis with subtracting pore effect method [6], listed in Table 1.

Results and Discussion

The transmission electron microscopy (TEM) images for the Ce, Zr-doped CAs are shown in Figure 1. The preparation at pH=7 provides the uniform mesoporous frame structure, composed of loosely bound particles about 20nm, same as non-doped CAs. The nanosized particles of dopant metals are distributed homogeneously throughout the sample, and they don't aggregate up to 1323 K. On the other hand, preparation at pH=3 gives a macroporous agglomerated form of spherical particles of 2-5 μm. Under acid condition, rapid gelation completes before colloidal sol particles make cross-link of frame works in ordinary CAs. If mesoporosity and/or microporosity are present, they should be formed inside of micrometer-sized particle, or should be the structural defects. The dopant metals are also distributed homogeneously.

Adsorption isotherms of nitrogen at 77 K on the Ce, Zr-doped CAs derived from different acidity of solution are shown in Figure 2a. For n-CZ-CA at pH 7, the adsorption isotherm is of type IV, with type H3 hysteresis, similar to non-doped CAs. This isotherm has a steep uptake at low pressure, meaning the presence of microporosity. In contrast, a-CZ-CA-l at pH 3 shows type I isotherm, indicating microporosity. Also type I isotherms are observed for the doped CAs prepared at low pH.

Comparison of the dopant concentration is shown in Figure 2b. Neither the shape nor the amount of adsorption is strongly affected by the dopant concentration, but the microporosity is slightly developed with increase in dopant. Especially, doping of Zr (Z-CA) is effective for development of microporosity, as much as CZ-CAs (Table 1). In contrast, doping of Ce results in poorly developed microporosity (C-CA).

Not only the initial pH of the solution but also the amount of dopant metal, Ce and Zr affects the sol-gel chemistry, and then the morphology and porosity of CAs can be controlled.

References

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Table 1. Porosity parameters for Ce, Zr-doped carbon aerogels

Sample	a_{total} / $m^2 \cdot g^{-1}$	V_{micro} / $ml \cdot g^{-1}$	V_{micro} / $m^2 \cdot g^{-1}$	a_{ext} / $m^2 \cdot g^{-1}$	$w_{ave.}^{\dagger}$ / nm
n-CZ-CA	800	0.17	520	280*	0.65
a-CZ-CA-l	500	0.17	489	11	0.70
a-CZ-CA-h	595	0.20	587	8	0.68
Z-CA	596	0.20	582	14	0.69
C-CA	87	0.03	76	11	0.91

*) Including the contribution of mesoporosity

†) Average pore width by Wicke's method: $w = 2\ V_{micro} / V_{micro}$

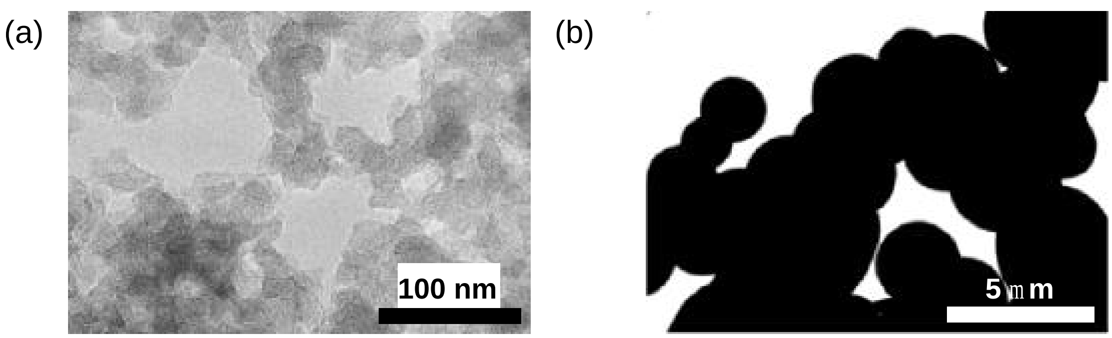

Figure 1. TEM images of Ce,Zr-doped carbon aerogel synthesized at (a) pH 7 and (b) pH 3.

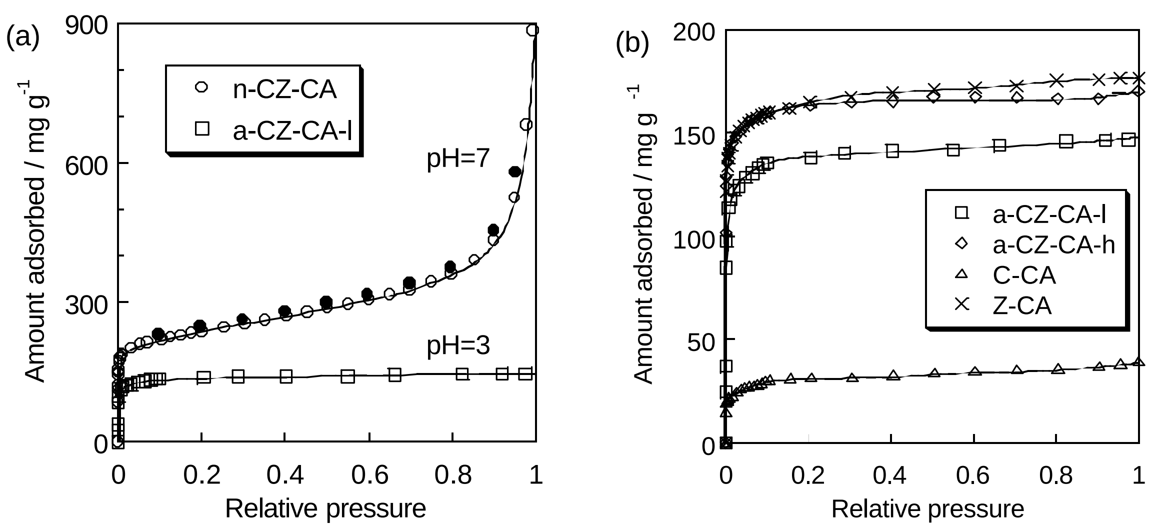

Figure 2. Adsorption isotherms of nitrogen at 77 K. (a) effect of acidity of solution and (b) comparison of dopant concentration in solution.