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Desorption behavior of various volatile organic compounds from activated carbon in supercritical carbon dioxide: Measurement and kinetic modeling

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ABSTRACT

The desorption behavior of various volatile organic compounds (VOCs: toluene, acetone, n-hexane, n-octane, methanol, ethanol, 2-propanol, and propylene glycol monomethyl ether) from activated carbon was measured in supercritical carbon dioxide ($scCO_2$) using the fixed-bed method at 313–353 K and 10.0–15.0 MPa. The measured behavior strongly depended on the type of VOC, and the CO_2 density and volatility of the VOCs were the primary factors influencing this behavior. The desorption behavior was correlated with a kinetic model that assumed material balances in the bulk and pore phases with local adsorption equilibria in the adsorbed phase. The fitting parameters determined using these correlations were reasonably explained by the CO_2 density and properties of VOCs, and they provided quantitative information about the desorption phenomena in $scCO_2$.

1. Introduction

Activated carbon is one of the most effective adsorbents for removing hazardous substances such as volatile organic compounds (VOCs) [1,2]. Regeneration methods for activated carbon are required to reuse the adsorbent from environmental and economic viewpoints in industrial-scale adsorption processes [3]. Thermal treatments are widely used as conventional regeneration methods in many industries. However, they can cause carbonization and destroy the structure of activated carbon owing to the high operating temperatures over 1000 K in usual cases [4,5].

Supercritical carbon dioxide ($scCO_2$) is a promising solvent for regenerating activated carbon owing to its high diffusivity into the micropores of the adsorbent and the low damage caused to the structure of the adsorbent resulting from the extremely low surface tension and operation capability under relatively mild temperatures (critical temperature, T_c = 304.12 K [6]). Experimental data of the desorption behavior of organics from the adsorbent under $scCO_2$ is required for designing the regeneration process. Thus far, the desorption behavior of organics including VOCs from activated carbon in $scCO_2$ has been widely studied [7–20]. Many researchers have noted that the desorption behavior of VOCs strongly depends on the CO_2 density, which varies with temperature and pressure. However, most of them only studied one or two VOC species, and therefore, little information is available about the effects of the properties of VOCs on desorption phenomena from activated carbon in $scCO_2$.

For investigating the effects of the properties of VOCs on the desorption behavior, our previous work [21] demonstrated the desorption behavior of various types of VOCs (toluene, n-hexane, n-decane, methanol, and acetone) from activated carbon in $scCO_2$. It was found that the desorption behavior strongly depended on the physical and chemical properties of VOCs, especially the vapor pressure of the VOCs and affinity of the VOCs for the adsorbent. However, desorption data about other types of VOC species are urgently required to obtain a detailed understanding of the effects of the properties of VOCs on the desorption behavior.

Additionally, regeneration processes using $scCO_2$ can have many operating conditions with various types of VOCs that need to be removed from the adsorbent. Therefore, the desorption behavior

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Nomenclature

C_a	Concentration of VOCs in the adsorbed phase (mol/kg-adsorbent)
C_b	Concentration of VOCs in the bulk phase (mol/m^3)
C_p	Concentration of VOCs in the pore phase (mol/m^3)
DR	Desorption ratio of VOCs (%)
D_{az}	Axial dispersion coefficient (m^2/s)
D_e	Effective diffusion coefficient of VOCs in the pore phase (m^2/s)
D_m	Molecular diffusion coefficient of carbon dioxide (m^2/s)
d_p	Mean particle diameter of the activated carbon (m)
K	Adsorption equilibrium constant (m^3/mol)
k_f	Mass transfer coefficient (m/s)
L	Axial length of the column (m)
M	Molar mass of VOCs (g/mol)
m_{ac}	Mass of activated carbon loaded in the column (kg)
N	Number of data points (−)
Q	Mass flow rate of CO_2 in the column (kg-CO_2/s)
q_{ads}	Initial amount of adsorbed VOC (mol/kg-adsorbent)
q_{des}	Amount of desorbed VOC (mol/kg-adsorbent)
q_{sat}	Saturated amount of adsorbed VOC (mol/kg-adsorbent)
R_p	Mean particle radius of the activated carbon (m)
r	Radial coordinates of the particle (m)
t	Time (s)
u	Superficial velocity in the column (m/s)
V_p	Pore volume of the adsorbent (m^3/kg-adsorbent)
z	Axial coordinate of the column (m)

Greek letters

ε_p	Porosity of the activated carbon (−)
ε_b	Void fraction in the column (−)
μ	Viscosity of carbon dioxide in the column (Pa · s)
ρ	Density of carbon dioxide in the column (kg-CO_2/m^3)
ρ_s	Solid density of the activated carbon (kg-adsorbent/m^3)
σ_{vdW}	van der Waals diameter of VOCs (nm)

Subscripts

0	Initial value
exp	Experimental value
calc	Calculated value

must be theoretically analyzed using an appropriate model for the efficient design of the processes along with experimental data. One of the most popular models for correlating the desorption behavior was represented by partial differential equations of material balances in the bulk phase and effective diffusion in the pores of the adsorbent. It showed high applicability to the desorption behavior of organics from activated carbon in $scCO_2$ [8,9,11,16,19,20]. The application of such types of kinetic models to the desorption behavior of various VOCs can provide an important basis for designing regeneration processes using $scCO_2$ in consideration of the properties of VOCs.

In this study, eight types of VOCs with different chemical and physical properties (aromatics, paraffin, ketone, alcohol, and ether)—toluene, n-hexane, n-octane, acetone, methanol, ethanol, 2-propanol, and propylene glycol monomethyl ether (PGME)—were chosen as target adsorbates. Then, the desorption behavior of these VOCs from activated carbon was studied over a wide range of $scCO_2$ conditions (T = 313–353 K, P = 10.0–15.0 MPa) via measurements and kinetic modeling to investigate the effects of the VOC properties on the desorption phenomena. The first part of this paper discusses the experimental data of the desorption behavior of four VOCs (n-octane, ethanol, 2-propanol, and PGME) from activated carbon that were newly measured in this study. Then, the correlations of the measured data by a kinetic model and the determined fitting parameters are discussed with the desorption data of other VOCs (n-hexane, methanol, acetone, and toluene) that were reported previously [21].

Table 1
Properties of activated carbon.

Property	Value
Specific surface area (m^2/g)[a]	1300
Mean pore diameter (nm)[a]	0.69
Pore volume (cm^3/g)[a]	0.441
Mean particle diameter (μm)	100
Solid density (g/cm^3)[b]	2.21
Porosity[c]	0.494

[a] Determined by a nitrogen adsorption measurement with *t* method [22].
[b] Determined by the helium buoyancy with a magnetic suspension balance [23].
[c] Calculated from the solid density, pore volume and mass of the adsorbent.

Table 2
Characteristics of desorption column.

Property	Value
Inner diameter (mm)	4.35
Length (mm)	100
Volume (cm^3)	1.485
Mass of activated carbon (g)	0.705
Void fraction (−)[a]	0.576

[a] Determined with the column volume, solid density, pore volume and mass of the adsorbent.

2. Experimental

2.1. Materials

Carbon dioxide (purity: 99.99 vol%) was obtained from Showa Denko Gas Products Co., Ltd., Japan. n-octane (purity: 98.0 mass%), ethanol (purity: 99.5 mass%), and 2-propanol (purity: 99.7 mass%) were purchased from Wako Pure Chemical Industries, Japan. PGME (purity: 99.5 mass%) was obtained from Sigma-Aldrich Co. LLC., USA. These chemicals were used without further purification. Activated carbon was obtained from Cambridge Filter Japan, Ltd.; its properties are listed in Table 1. The specific surface area, mean pore diameter, and pore volume of activated carbon were determined by the *t* method [22]. The solid density of the adsorbent was determined by helium buoyancy with a magnetic suspension balance [23]. The adsorbent was loaded into an adsorption (and also desorption) column (1/4-inch SUS316 steel tube) and pretreated by heating in argon gas atmosphere at 573 K for 8 h to remove physisorbed water and possible impurities. The characteristics of the column are summarized in Table 2.

2.2. Method

The desorption behavior of VOCs from activated carbon in $scCO_2$ was measured by using the fixed-bed method at 313–353 K and 10.0–15.0 MPa. The details of the experimental apparatus and procedure are described in our previous paper [21].

The experimental desorption ratio of VOCs (DR_{exp}) is given as follows:

$$DR_{exp}[\%] = \frac{q_{des,exp}(t)}{q_{ads}} \times 100 \quad (1)$$