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Adsorption kinetics of rhodium (III) acetylacetonate onto mesoporous silica adsorbents in the presence of supercritical carbon dioxide

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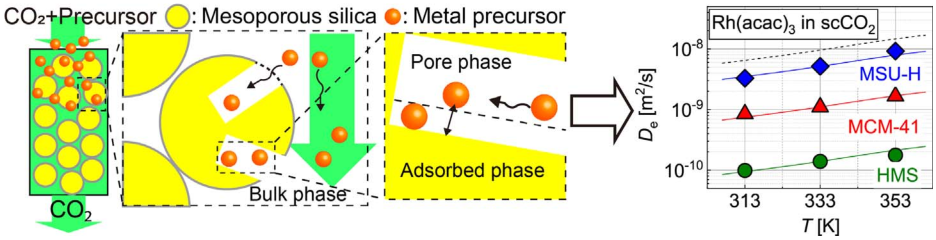
GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption kinetics of rhodium (III) acetylacetonate ($Rh(acac)_3$) onto three types of mesoporous silica adsorbents, MCM-41, HMS, and MSU-H, in the presence of supercritical carbon dioxide ($scCO_2$) at temperatures from 313 to 353 K and at a pressure of 15.0 MPa were studied using fixed-bed adsorption measurements. The breakthrough curves obtained with the measurements were correlated by a mathematical kinetic model using only one fitting parameter, the effective diffusion coefficient of $Rh(acac)_3$ in pores (D_e). The determined D_e values depended strongly on the temperature and the types of mesoporous silica used, which could be described using a generalized model that includes the parameters in consideration of the pore structure of the adsorbents (porosity and tortuosity) and the diffusion coefficient of $Rh(acac)_3$ in the bulk $scCO_2$ phase.

1. Introduction

Mesoporous silica has attracted much interest as a catalytic support because of its uniform pore size distribution, high specific surface area, and capability to adsorb metal particles into its structure [1]. Methods for impregnation of metal particles using supercritical carbon dioxide ($scCO_2$) can achieve dissolution of metal precursors and transportation of them into pores of the support owing to the high diffusivity of $scCO_2$ and the extremely low interfacial tension compared to conventional liquid solvents [2–6]. In addition, $scCO_2$ has useful advantages for industrial applications, such as not requiring a drying process, non-reactivity, non-toxicity, and non-flammability. Therefore, some studies have been conducted on the impregnation of metal particles into various mesoporous materials with $scCO_2$ [1–4,6–10]. We have recently reported the impregnation of rhodium [11] and cobalt [12,13] metal nanoparticles into mesoporous silica materials and demonstrated their high catalytic activity for hydrogenation of cinnamaldehyde [11] and Fischer-Tropsch synthesis [12] in comparison to conventional methods using liquid solvents.

The $scCO_2$ impregnation process mainly consists of three steps

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Nomenclature

a_i	Coefficient in Eq. (17)
C	Concentration of $Rh(acac)_3$ in $scCO_2$ at the column outlet (mol/m^3)
C_a	Concentration of $Rh(acac)_3$ in the adsorbed phase (mol/kg-adsorbent)
C_b	Concentration of $Rh(acac)_3$ in the $scCO_2$ bulk phase (mol/m^3)
C_p	Concentration of $Rh(acac)_3$ in the pore phase (mol/m^3)
D_{az}	Axial dispersion coefficient (m^2/s)
D_b	Molecular diffusion coefficient of $Rh(acac)_3$ in the $scCO_2$ bulk phase (m^2/s)
D_e	Effective diffusion coefficient of $Rh(acac)_3$ in the pore phase (m^2/s)
D_m	Molecular diffusion coefficient of carbon dioxide (m^2/s)
d_p	Mean particle diameter of mesoporous silica particles (m)
K	Adsorption equilibrium constant of the langmuir equation (m^3/mol)
k	Tortuosity factor of mesoporous silica adsorbents
k_f	Mass transfer coefficient (m/s)
L	Axial length in the adsorption column (m)
M	Molar mass (g/mol)
N	Number of data points (−)
q_{sat}	Saturated adsorption amount of $Rh(acac)_3$ in $scCO_2$ (mol/kg-adsorbent)
R_p	Mean particle radius of mesoporous silica particles (m)
r	Radial coordinates of mesoporous silica particle (m)
t	Time (s)
u	Superficial velocity in the adsorption column (m/s)
v	Molar volume of CO_2 (m^3/mol)
v_0	Hard-sphere closed-packed volume of CO_2 (m^3/mol)
z	Axial coordinate in the adsorption column (m)

Greek letters

ε_p	Porosity of the mesoporous silica adsorbents (−)
ε_b	Void fraction in the adsorption column (−)
μ	Viscosity of carbon dioxide (Pa s)
ρ	Density of carbon dioxide (kg/m^3)
ρ_p	Particle density of mesoporous silica adsorbent (g-adsorbent/cm^3)
σ	Hard-sphere diameter of molecules (nm)
σ_{vdW}	Van der waals diameter of molecules (nm)

Subscripts

Prec	Metal precursor
0	Initial value

[5,14]: (i) dissolution of the metal precursor in the $scCO_2$, (ii) adsorption of the metal precursor onto the support, and (iii) reduction of the precursor to its metallic or metal oxide forms. Therefore, design of the impregnation process requires quantitative understanding of each step. Regarding the dissolution step of the metal precursor in $scCO_2$, a relatively large amount of solubility data for metal precursors is available over a wide range of $scCO_2$ conditions [15–22]. In addition, effects of conditions on the precursor calcination and reduction steps have been investigated in detail [11,23,24].

For step (ii), equilibrium data for the adsorption of metal precursors on mesoporous silica adsorbents is indispensable for the design process. The adsorption equilibria of metal precursors onto SBA-15 and MCM-48 mesoporous silica adsorbents using the $scCO_2$ batch method have previously been reported [25–27]. Other studies on the adsorption equilibria of metal precursors onto several types of aerogel adsorbents have also been reported [28–33]. In our previous study [34], a dynamic method was developed using fixed-bed adsorption and in-situ measurement of fluid concentration. The measured concentrations were used to assess the rate of adsorption and the approach to adsorption equilibrium by monitoring the breakthrough curve of a metal precursor with a UV–vis detector. Using this method, the adsorption equilibria of rhodium (III) acetylacetonate ($Rh(acac)_3$) on mesoporous silica adsorbents were measured, and the effects of the adsorbents properties on the adsorption equilibria were revealed [34].

In order to design the adsorption processes in step (ii), a kinetic study of the adsorption behavior of metal precursors is also essential to estimate the impregnation time required by the $scCO_2$ methods. Zhang et al. [30] investigated the adsorption kinetics of $Ru(cod)(tmhd)_2$ (bis(2,2,6,6-tetramethyl-3,5-heptanedionato)(1,5-cyclooctadiene)ruthenium) onto carbon aerogel particles in $scCO_2$ in batch systems and simulated the effect of pore size on the adsorption kinetics. Bozbag and co-workers [32] also reported the adsorption kinetics of $Pt(cod)Me_2$ (dimethyl(1,5-cyclooctadiene)platinum) onto organic aerogels in $scCO_2$ using a batch method and found good agreement with simulated results using a mass transfer model with experimental data. However, these kinds of kinetic studies on the adsorption of metal precursors onto mesoporous materials are insufficient for the design of the $scCO_2$ impregnation process probably because of the experimental limitations for measuring adsorption kinetics using conventional batch methods. On the other hand, our proposed method of using dynamic fixed-bed measurements [34] can be applied to obtain detailed information on the adsorption kinetics of metal precursors in $scCO_2$ by in-situ analysis of breakthrough curves.

In the present work, the adsorption kinetics of $Rh(acac)_3$, a precursor of rhodium frequently used in hydrogenation reactions of organic compounds [11,35], onto three types of mesoporous silica materials (MCM-41, HMS, and MSU-H) in $scCO_2$ were measured with the fixed-bed method at temperatures from 313 to 353 K and at a pressure of 15.0 MPa. Then, correlations of the measured breakthrough curves with a kinetic model were performed, and the effective diffusion coefficient of the metal precursor inside pores (D_e) was determined. Finally, values of D_e determined with the correlations were discussed using a generalized model of D_e that considers the pore structure of the adsorbents and the diffusion coefficient of $Rh(acac)_3$ in the bulk $scCO_2$ phase.

2. Experimental

2.1. Materials

Mesoporous silica materials (MCM-41, HMS, and MSU-H) and $Rh(acac)_3$ (purity 97 mass%) were purchased from Sigma-Aldrich Co. LLC., U. S. A. The properties of the mesoporous silica adsorbents are summarized in Table 1.

Carbon dioxide (purity 99.99 vol.%) and methanol (purity 99.7 mass%) were supplied from Showa Denko Gas Products Co., Ltd., Japan and Wako Pure Chemical Industries, Japan, respectively. These chemicals were used without further purification. The pore volume, mean pore diameter, and specific surface area of the mesoporous silica materials were determined with the BJH [36] and BET [37] methods using an apparatus for nitrogen adsorption measurements (Belsorp mini, MicrotracBEL Corp., Japan). The adsorbent was loaded into an adsorption column (1/4-inch SUS316 steel tube), and the inner diameter, length, and volume of the column were 3.05 mm, 3.5 cm, and 0.256 cm^3, respectively. The pretreatment of the column was performed by heating at 623 K for 8 h in argon gas atmosphere to remove possible