

THERMODYNAMICS AND KINETICS OF ADSORPTION OF ORGANOMETALLIC COMPOUNDS ON CARBON AEROGELS IN THE PRESENCE OF SUPERCRITICAL CARBON DIOXIDE

Y. Zhang and C. Erkey*
Department of Chemical Engineering
University of Connecticut
Storrs, CT 06269
e-mail: cerkey@engr.uconn.edu
fax: (860) 486 - 2959

In this study, both the thermodynamics and dynamics of adsorption $\text{Ru}(\text{cod})(\text{tmhd})_2$ from scCO_2 onto carbon aerogels with average pore sizes of 21 nm (CA-21) and 4 nm (CA-4) were investigated by the measurement of adsorption isotherms and concentration decay curves in batch mode. The adsorption isotherms were measured at 23 MPa and 343.5 K. A theoretical model was employed to describe the dynamics of adsorption of $\text{Ru}(\text{cod})(\text{tmhd})_2$ on CA-21 from scCO_2 . The model takes into account pore diffusion and assumes that there is local equilibrium in the pores.

INTRODUCTION

The thermodynamics and dynamics of adsorption of organometallic compounds from scCO_2 solutions onto porous substrates are important for development of large scale processes for preparation of supported nanoparticles.

RESULTS

The adsorption isotherms of $\text{Ru}(\text{cod})(\text{tmhd})_2$ on CA-21 and CA-4 from scCO_2 were measured at 343.2 K and 23 MPa. The isotherms are presented in Figure 1. The uptake of $\text{Ru}(\text{cod})(\text{tmhd})_2$ by CA-21 was always higher than that by CA-4 at the same fluid phase concentration. With the concentration of $\text{Ru}(\text{cod})(\text{tmhd})_2$ in scCO_2 increasing, the uptake of $\text{Ru}(\text{cod})(\text{tmhd})_2$ by both CA-21 and CA-4 increases. The concentration that can be reached in the fluid phase can be higher than 1.5 wt% in this condition. The two isotherms were fitted to Langmuir model, modified Langmuir model and Freundlich model.

Langmuir Model is one of the simplest and most useful model for description both physical and chemical adsorption. It can be represented by :

$$C_s = \frac{K_1 Q_0 C}{1 + K_1 C}$$

where C_s is the uptake by the adsorbent, K_1 is Langmuir adsorption constant, Q_0 is the adsorption capacity, and $K_1 Q_0$ is the relative affinity of the adsorbate toward the surface of the adsorbent and C is the solution concentration. It is often very useful to add simply a degree of freedom to the Langmuir equation through an additional linear term to describe the adsorption on carbon stationary phases since these adsorbents contain a lot of non-selective

sites (the linear term) and some competitive sites. The modified Langmuir isotherm is presented by:

$$C_s = \frac{K_1 Q_o C}{1 + K_1 C} + kC$$

where the kC term takes into account the heterogeneity of the sorbent surface. Freundlich Model is an empirical model that can be applied to nonideal adsorption on heterogeneous surfaces as well as multilayer adsorption. It is expressed by the following equation which relates the uptake, C_s to the concentration in solution, C by

$$C_s = K_f C^{1/n}$$

where K_f is the Freundlich adsorption constant and n is the Freundlich exponent. The fitted isotherms are shown in Figure 1 and the parameters calculated from the isotherms are listed in Table 1. The unit for the uptakes is g Ru(cod)(tmhd)₂/gCA-21 and for the solute concentration in solvent is mol Ru(cod)(tmhd)₂/mol solution.

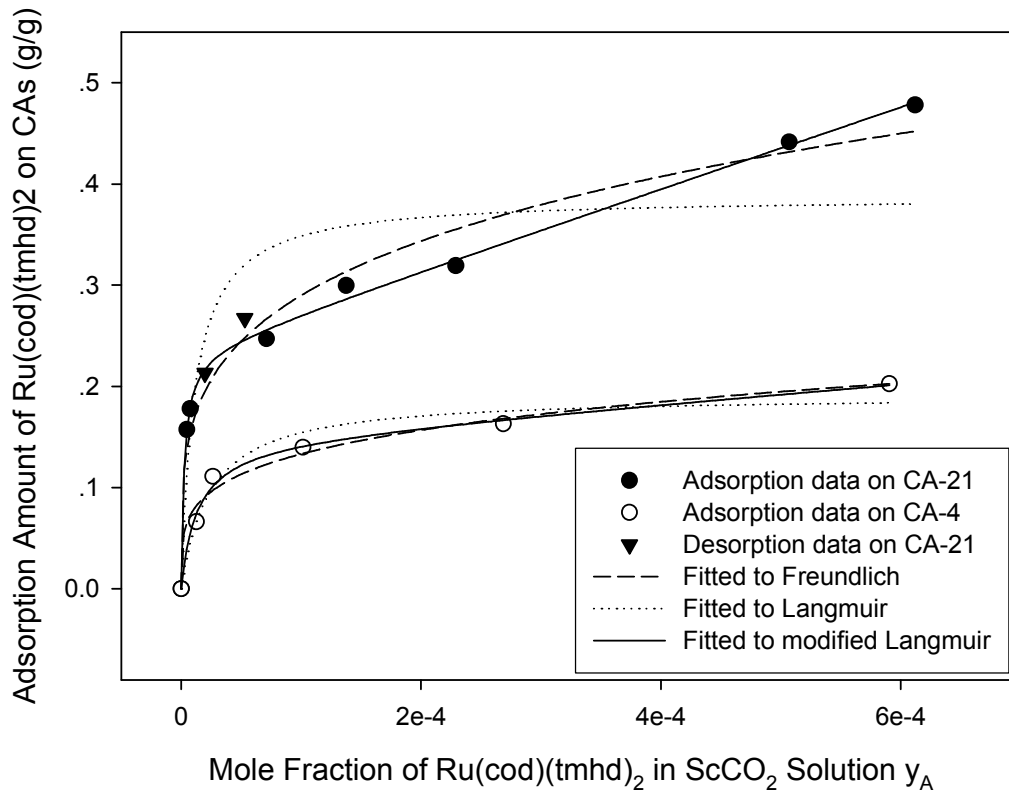


Figure 1 Adsorption isotherms of Ru(cod)(tmhd)₂ on CA-21 and CA-4 from scCO₂ at 343.2 K and 23 MPa.

Table 1. Parameters of Ru(cod)(tmhd)₂ adsorption isotherms on CA-4 and CA-21 from scCO₂ solution at 353.2 K and 27.6 MPa.

Adsorbent	Langmuir			Modified Langmuir				Freundlich		
	R ²	K _l	Q _o	R ²	K _l	Q _o	k	R ²	K _f	1/n
CA-4	0.968	4.19*10 ⁴	0.191	0.994	7.61*10 ⁴	0.148	99.5	0.982	1.174	0.236
CA-21	0.828	8.43*10 ⁴	0.387	0.998	3.97*10 ⁵	0.235	403.0	0.979	2.778	0.245

Dynamics of adsorption

Since the knowledge of both the adsorption capacity and the rate of adsorption is required in understanding and in designing large scale supercritical adsorption process, a model was developed to describe the dynamics of the batch adsorption process by identifying the individual steps in the process and incorporating them into the model. For SCFI, four steps were identified: 1) mass transfer from the bulk fluid to the adsorbent surface, 2) supercritical diffusion within the adsorbent, 3) adsorption onto the surface, and 4) surface diffusion within the adsorbent.

The first step is mass transfer from the bulk fluid to the exterior surface ($r = R$) of the adsorbent. This is best described by film diffusion where the flux is proportional to a mass transfer coefficient and the concentration difference between the bulk and surface.

$$N_A = k_m(C_{A,b} - C_{A,s})$$

For well-stirred solutions, the mass transfer resistance from the bulk fluid to the exterior surface can be neglected and the concentration at the exterior surface is equal to that measured in the bulk. In this work, the solutions were well stirred and this resistance is assumed negligible in the model.

The second step is diffusion of the solute in the fluid phase within the adsorbent in the radial direction. This is defined by Fick's first law, where $D_{e,p}$ is the effective pore volume diffusivity.

$$N_A = -D_{e,p} \frac{\partial C_A}{\partial r}$$

The effective diffusivity is the supercritical fluid phase molecular diffusivity, D_{AB} , adjusted for the porosity and tortuosity of the adsorbent.

$$D_{e,p} = \frac{\varepsilon_p D_{AB}}{\tau}$$

Since the porosity is less than one and the tortuosity is greater than one, the effective diffusivity is lower than the supercritical phase diffusivity.

For systems where the molecular size of the solute approaches the pore size, further reductions in the diffusivity are observed. This has been presented in several studies with the diffusivity reduced by a size restriction factor, $F(\lambda)$, where λ is the ratio of the critical solute diameter to the pore size.

$$D_{e,p} = F(\lambda) \frac{\varepsilon_p D_{AB}}{\tau}$$

The size restriction factor is calculated from the Chantong equation [1].

$$F(\lambda) = 1.03e^{-4.5\lambda}$$

The third step is adsorption onto the surface. In this work, local equilibrium was assumed within the adsorbent where the adsorbed phase concentration is related to the supercritical phase concentration through the isotherm.

$$q = f(C_A^*)$$

The fourth step is surface diffusion within the adsorbent. For this process, the solute is adsorbed onto the surface and then migrates along the surface under the concentration gradient in the adsorbed phase. The flux due to surface diffusion is defined as follows, where $D_{e,s}$ is the effective surface diffusivity coefficient.

$$N_A = -D_{e,s} \rho_p \frac{\partial q}{\partial r}$$

The surface diffusivity is a function of the physical properties of the adsorbent and the adsorption bond strength. Surface diffusion is most favorable in cases where the adsorbent has a high adsorption capacity and a weak adsorption bond. A more detailed discussion on surface diffusion can be found in the reference by Komiyama *et al.*². For this work, the effects of surface diffusion were neglected in the model.

Following identification of the individual steps in the adsorption process a shell balance on a spherical adsorbent particle was performed for the unsteady state adsorption process. The following equation was obtained, where $\partial C_A / \partial t$ represents the accumulation term, $\partial q / \partial t$ represents the adsorption term, and $\partial C_A / \partial r$ represents the flux term.

$$\varepsilon_p \frac{\partial C_A}{\partial t} + \rho_p \frac{\partial q}{\partial t} = D_{e,p} \left(\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right)$$

The first boundary condition for the above equation arises from symmetry around the center of the adsorbent and can be expressed as:

$$\frac{\partial C_A}{\partial r} = 0 \quad \text{at } r = 0$$

The second boundary condition is obtained from a macroscopic mass balance on the bulk liquid since the volume is finite and the concentration changes with time. The concentration

at the surface is equal to the concentration in the bulk due to the assumption of a well-stirred solution.

$$-V \frac{dC_A}{dt} = mSD_{e,p} \frac{\partial C_A}{\partial r} \quad \text{at } r = R$$

The initial conditions are given by the following equations. At time zero the adsorbent is solute free and the bulk fluid concentration is known.

$$C_A = 0 \quad \text{at } t = 0, 0 \leq r < R$$

$$C_A = C_{A,0} \quad \text{at } t = 0, r = R$$

Equations were converted to a set of ODEs by utilizing the Numerical Method of Lines (NMOL) and solved simultaneously in Polymath. The change in concentration with respect to radial position was represented using finite differences. For this work 20 increments in the radial direction were used, with $n = 1, 2, \dots, N$ representing the individual nodes. Test trials showed that 20 increments provided significant resolution to describe the adsorption dynamics.

The model was tested by the adsorption of $\text{Ru}(\text{cod})(\text{thmd})_2$ from scCO_2 over CA-21 performed in batch mode at 343.5 K and 23.0 MPa. For evaluation of the dq/dC_A term, the modified Langmuir model was used to represent the isotherm for adsorption. Freundlich model was not used because the derivative of the isotherm goes to infinity as the concentration approaches zero. The fit to the data are shown in Figure 2. The numerical solution provided a good fit in this case.

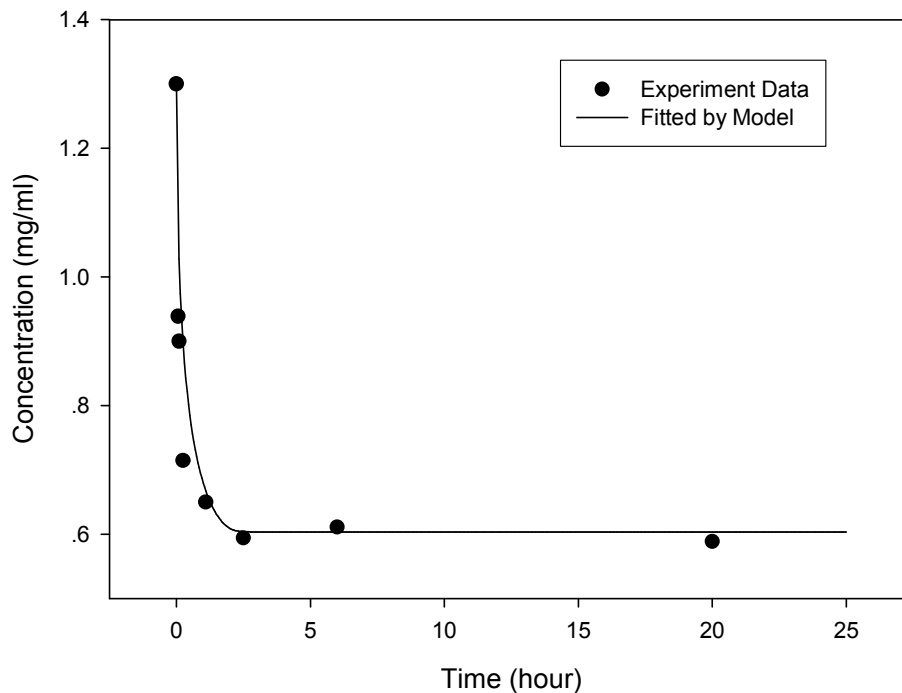


Figure 2. Experimental and predicted concentration decay.

In this study, the parameter effects on the model fit were also investigated. Figure 3 shows the effect of adsorbent particle size and fluid diffusivity on the adsorption dynamics. With increase of the particle size, and/or decrease of the diffusivity, the rate of approach to equilibrium slowed down. As expected, the equilibrium concentration is not changed since it is governed by the adsorption isotherm. With constant diffusivity, particle size affects the diffusion distance. Larger particle size will result in a longer diffusion time. Higher diffusivity results in shorter diffusion time.

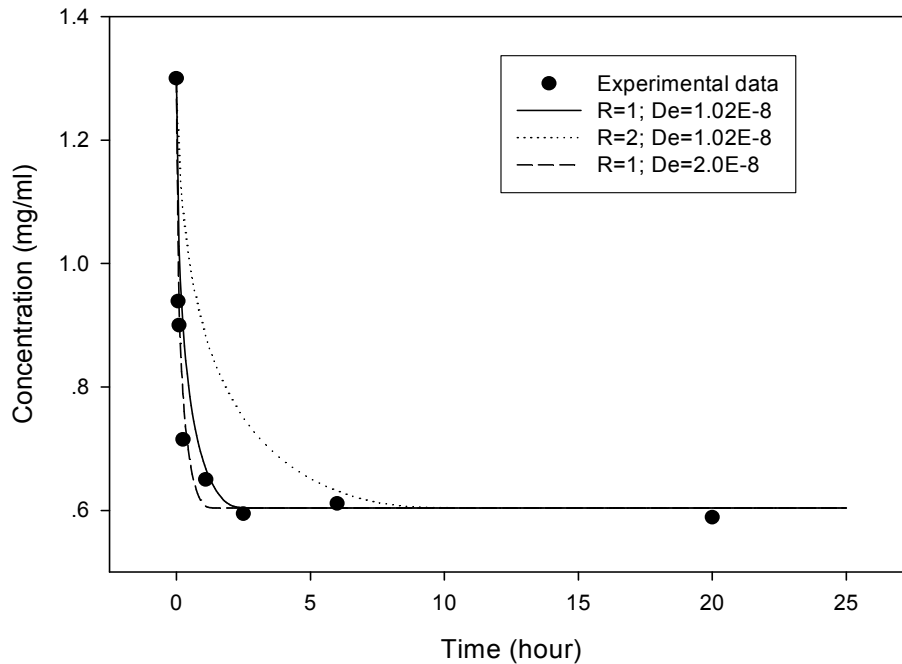


Figure 3. Effect of adsorbent particle size and fluid diffusivity on the adsorption dynamics

REFERENCES

-
- [1] CHANTONG, A., MASSOTH, F.E., AICHE J., Vol. 29, **1983**, p. 725.
 - [2] KOMIYAMA, H., SMITH, J.M., AICHE J., Vol. 20, **1974**, p. 1110.