

Supporting Information for

Thermodynamic Control of Metal Loading and Composition of
Carbon Aerogel Supported Pt-Cu Alloy Nanoparticles by Supercritical
Deposition

by

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Synthesis of carbon aerogels (CAs)

CAs were synthesized by the pyrolysis of resorcinol-formaldehyde aerogels (RFAs) produced via the sol-gel route described by Pekala ¹ which involves the polymerization of resorcinol (R) and formaldehyde (F) with an alkali catalyst (C) in water (W) followed by gelation and cross-linking. Typically, mixtures of R, F and C in W were kept at ambient temperature for 1 day during which time substitution and condensation polymerization occurred. This was followed by a curing sequence that comprised one day at 50°C and then three days at 90 °C. The initial molar ratios of R/F, R/C and R/W were 0.5, 200 and 0.02, respectively. After curing, the resulting hydrogel was placed in an acetone bath to replace the water in the pores with acetone. Finally, acetone was extracted from the gels using scCO₂ at 13.8 MPa and 50 °C in an Applied Separations Spe-ed SFE extraction unit. Fresh CO₂ was fed to the system continuously with a flow rate of 0.35 l/h for 8 h. Then, the system was maintained at 13.8 MPa and 50 °C overnight without CO₂ flow. Finally, the system was depressurized slowly and RFAs were obtained. CAs were prepared via the pyrolysis of the RFAs at 1000°C in flowing N₂ (100 cm³/min).

Adsorption Measurement Method

Adsorption equilibrium measurements were carried out in the experimental setup presented in Figure 1. A custom-made stainless steel vessel with a volume of 57 mL was used. The vessel was equipped with two sapphire windows (2.5 cm in diameter (Sapphire Engineering, Inc., Pocasset; MA), a T-type thermocouple assembly (Omega Engineering), a pressure transducer (Omega Engineering), a vent line, and a rupture disk assembly (Autoclave Engineers) and was sealed with poly(ether ether ketone) O-rings. For each experiment, a certain amount of each of the metal precursors was placed in the vessel along with a stirring bar, and a certain amount of crushed carbon aerogel (CA) substrate (~2 mm in diameter). A stainless steel screen was placed in the middle of the vessel in order to separate the substrate

and the stirring bar. The system was sealed and heated to the desired temperature by a circulating heater/cooler (Cole Parmer, Model 12108-15). The system was pressurized with CO₂ using a syringe pump (ISCO, 260D) up to the desired pressure and kept at these conditions for the desired exposure time. During this process, Pt(cod)me₂ and CuDI6 dissolved in the scCO₂ and adsorbed onto the substrate from the fluid phase. Solubility of CuDI6 is higher than all of the initial concentrations used in this study since all of the CuDI6 dissolved instantaneously as it contacted with scCO₂ in all of the experiments.

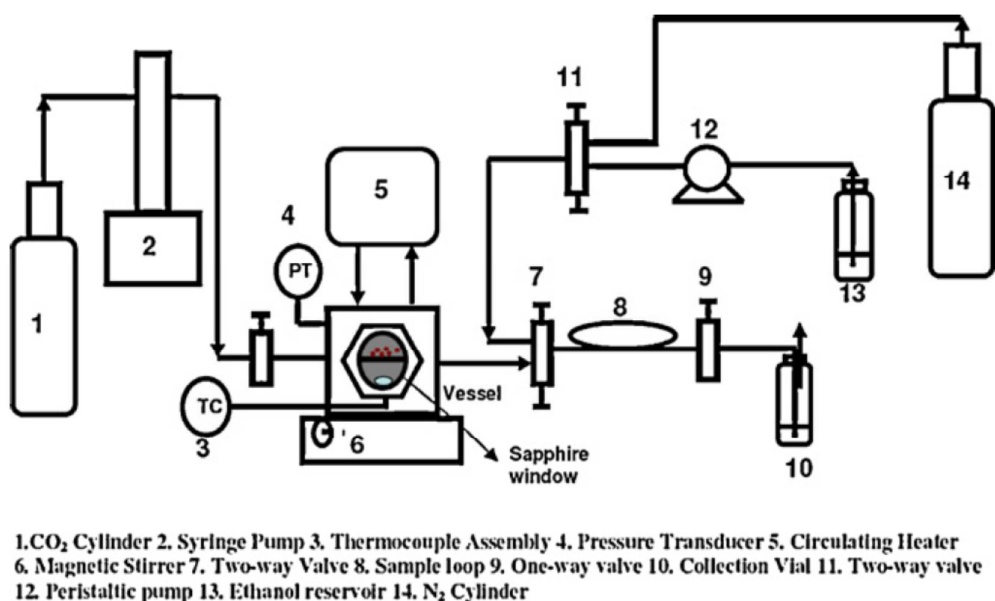


Figure 1. Diagram of the experimental setup

The adsorbed amounts of Pt(cod)me₂ and CuDI6 were determined by measuring the concentrations of Pt(cod)me₂ and CuDI6 in the fluid phase. The details of the procedure were given elsewhere.² Briefly, at a particular time, a small volume of the solution in the vessel was transferred and trapped in a sample loop with a volume of 0.20 mL. Subsequently, the sample loop was depressurized slowly. The CO₂ from the loop was bubbled through an ethanol solution to trap any Pt(cod)me₂ or CuDI6 that may be in the gas stream. Then, the sample loop was flushed with ethanol using a peristaltic pump (Gilson, Model Minipuls 3) to collect any Pt(cod)me₂ or CuDI6 that precipitated during depressurization. About 15mL of

ethanol was sufficient to dissolve all of the $\text{Pt}(\text{cod})\text{me}_2$ and CuDI6 since neither $\text{Pt}(\text{cod})\text{me}_2$ nor CuDI6 could be detected in additional washes. The solutions were collected in vials and analyzed by HPLC (Agilent Technologies, 1200 Series) with a Zorbax Eclipse XDB-C18 column with dimensions of 4.6 mm x150 mm. The column contains particles with a size of 5 μm . These analyses were performed using 100 % ethanol with a flow rate of 1 mL/min as the mobile phase and with the wavelength of the UV detector lamp set to 270 nm. This wavelength was selected based on the UV spectrum of a solution of $\text{Pt}(\text{cod})\text{me}_2$ – CuDI6 mixture in ethanol with a mass fraction of 100 ppm $\text{Pt}(\text{cod})\text{me}_2$ and CuDI6 . A series of binary metal precursor-ethanol solutions with mass fractions ranging from 0 to 200 ppm were used for the calibration. Calibration curves were prepared and updated before every measurement sequence. The HPLC analyses were repeated twice and the mean of the two results was used. To determine the adsorption isotherms, it is necessary to ensure that the system has reached equilibrium. Therefore, three or more samples were taken at different times. When the last two fluid phase concentrations were equal, the sampling was stopped. In order to minimize the errors associated with replacing the removed sample volume with pure CO_2 , the total volume of the samples removed from the vessel did not exceed 2 ml which is about 3 % of the total volume of the vessel. A series of experiments was conducted to test the accuracy of the sampling technique described previously. Experiments were carried out by dissolving a known amount of $\text{Pt}(\text{cod})\text{me}_2$ and CuDI6 in scCO_2 in the vessel without any aerogel present. Samples from the fluid phase were taken and the concentration in each sample was determined by HPLC. Fig. 2 is a plot of the measured concentration against the concentration calculated from the amount of $\text{Pt}(\text{cod})\text{me}_2$ and CuDI6 placed in the vessel. There is good agreement between the measured and calculated values showing that the sampling technique is quite accurate.

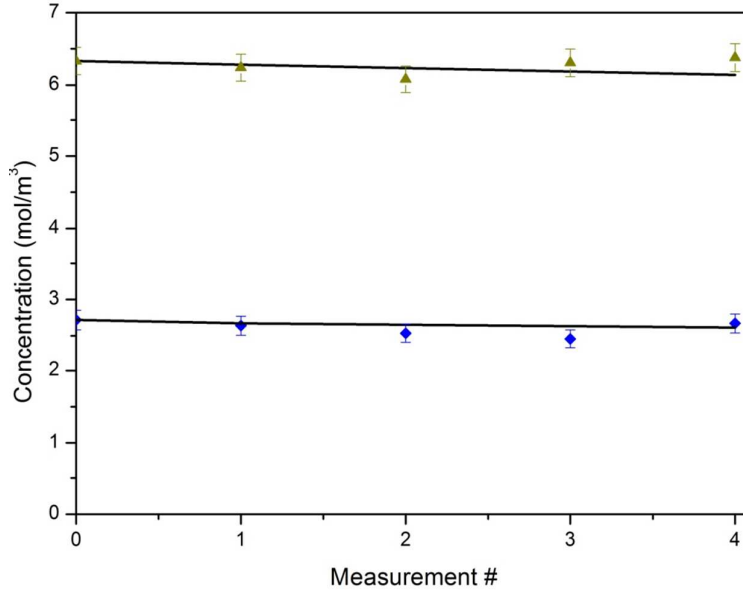


Figure 2. Calculated and measured concentrations of Pt(cod)me₂ and CuDI6 in scCO₂.

△: Pt(cod)me₂; ◇: CuDI6. The lines are the corresponding calculated metal complex concentrations.

Adsorption Models

The Langmuir equation takes the form:

$$q = \frac{K_1 Q_0 C}{1 + K_1 C} \quad (1)$$

where q (mol/kg) is the uptake amount of the adsorbate on the adsorbent, K_1 (m³ scCO₂/mol CuDI6) is the adsorption equilibrium constant, Q_0 is the uptake capacity (mole precursor/ kg adsorbent), C is the precursor concentration in scCO₂ (mol/ m³ scCO₂), and the $K_1 Q_0$ value is the relative affinity of the precursor towards the surface of adsorbent.

The Sips model is an empirical adsorption equation that is widely used for the interpretation of adsorption data and is also very important for the diagnosis of surface heterogeneity:

$$q = \frac{Q_s (\alpha C)^{1/n}}{1 + (\alpha C)^{1/n}} \quad (2)$$

where Q_s can be associated with the total number of binding sites, α , is the median association constant and $1/n$, is the heterogeneity factor. Values for $1/n$ close to zero indicate heterogeneous adsorbents, while values closer to 1.0 indicate a material with relatively homogenous binding sites. In this case, the Sips model reduces to the Langmuir equation.

Binary adsorption isotherms were modeled using an extended-Langmuir equation and IAST. The Langmuir model can be extended to describe the adsorption of metal precursors from a multicomponent solution. In this case, the extended Langmuir adsorption model can be expressed as:

$$q_i = \frac{K_{1,i} Q_{0,i} C_i}{1 + \sum_{j=1}^N K_{1,j} C_j} \quad (4)$$

The IAST adsorption model, which was proposed by Radke and Prausnitz ³, is usually employed for the prediction of adsorption in multi-component systems, using the respective single-solute isotherm parameters alone. ⁴⁻⁹ The model assumes that the solution is ideal which means that no interaction between adsorbent and adsorbate is considered. In IAST, the following equations are used to predict multicomponent behavior:

$$q_t = \sum_{i=1}^N q_i \quad (5)$$

$$z_i = \frac{q_i}{q_t} \quad (6)$$

$$q_i^0 = f(C_i^0) \quad (7)$$

$$\frac{1}{q_t} = \sum_{i=1}^N \frac{z_i}{q_i^0} \quad (8)$$

$$C_i = z_i C_i^0 \quad (9)$$

$$\pi_i^* = \int_0^{C_i^0} \frac{q_i^0}{C_i^0} dC_i^0 \quad (10)$$

$$\pi_1^* = \pi_2^* = \dots = \pi_N^* \quad (\text{at equilibrium})$$

where: C_i^0 is the hypothetical single-solute solution concentration in equilibrium with q_i^0 , z_i is the mole fraction of the solute in the adsorbed phase, and π_i^* is the modified spreading pressure. This modified spreading pressure is equal to $\pi_i A/RT$, where A is the area of the sites available for adsorption, R is the gas constant and T is the temperature. In IAST, one needs to utilize one of the previously mentioned single isotherm models to end up with binary isotherms. Experimentally obtained adsorption equilibrium data was simulated using IAST, i.e. the non-linear Equations 5-10 were solved in Mathcad using a Levensberg-Marquardt routine and the unknown parameters (π_i , C_i^0 , q_i^0 , z_i) were obtained.

Table 1. Values of the SSE function for the experimental data and the predictions of metal complex uptake on carbon aerogel

Model	Pt(cod)me ₂	CuDI6
Extended Langmuir	0.510	0.063
IAST-Langmuir	0.112	0.061
IAST-Sips	0.091	0.170

References

1. Pekala, R. W. Organic aerogels from polycondensation of resorcinol with formaldehyde. Journal of Materials Science. 1989, 24 3221-3227.

2. Bozbag, S. E.; Yasar, N. S.; Zhang, L. C.; Aindow, M.; Erkey, C. Adsorption of Pt(cod)me₂ onto organic aerogels from supercritical solutions for the synthesis of supported platinum nanoparticles. *The Journal of Supercritical Fluids* 2011, 56, 105–113.
3. Radke, C. J.; Prausnitz, J. M. Thermodynamics of multi-solute adsorption for dilute liquid solutions. *AIChE J.* 1972, 18 761-768.
4. Brunner, G.; Johannsen, M. New aspects on adsorption from supercritical fluid phases. *The Journal of Supercritical Fluids* 2006, 38 (2), 181-200.
5. Porter, J. F.; McKay, G.; Choy, K. H. The prediction of sorption from a binary mixture of acidic dyes using single- and mixed-isotherm variants of the ideal adsorbed solute theory. *Chemical Engineering Science* 1999, 54 5863-5885.
6. Lübbert, M.; Brunner, G.; Johannsen, M. Adsorption equilibria of α - and γ -tocopherol from supercritical mixtures of carbon dioxide and 2-propanol onto silica by means of perturbation chromatography. *J. of Supercritical Fluids* 2007, 42 180–188.
7. Bolten, D.; Johannsen, M. Influence of 2-Propanol on Adsorption Equilibria of α - and γ -Tocopherol from Supercritical Carbon Dioxide on Silica Gel. *J. Chem. Eng. Data* 2006, 51, 2132-2137.
8. Liu, B.; Yang, Q.; Xue, C.; Zhong, C.; Chen, B.; Smit, B. Enhanced adsorption selectivity of hydrogen/methane mixtures in metal-organic frameworks with interpenetration: A molecular simulation study. *Journal of Physical Chemistry C* 2008, 112 (26), 9854-9860.
9. Liu, J. C.; Keskin, S.; Sholl, D. S.; Johnson, J. K. Molecular Simulations and Theoretical Predictions for Adsorption and Diffusion of CH₄/H₂ and CO₂/CH₄ Mixtures in ZIFs. *Journal of Physical Chemistry C* 2011, 115 (25), 12560-12566.