Adsorption Of Dimethyl(1,5-Cyclooctadiene)Platinum On Porous Supports In Supercritical Carbon Dioxide

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ABSTRACT

Adsorption experiments in supercritical carbon dioxide were carried out at 333 and 353 K at a constant pressure of 15 MPa with dimethyl(1,5-cyclooctadiene)platinum. Additionally, the solubility of the platinum compound at the experimental conditions was determined. The influence of concentration, temperature and two different types of support material (a monolithic cordierite with washcoat and silica gel tablets) on the adsorption was investigated. Therefore, a new experimental method was developed, allowing for monitoring the uptake of the organometallic compound by online-UV-spectroscopy. The monolithic support material shows a sharp increase in the uptake of the platinum compound already in the first few minutes. The rate of uptake can be increased by increasing the geometric surface of the support material for a better contact between the fluid and the solid support. Furthermore, the results obtained at different temperatures indicate that mass transport plays an important role in the process of adsorption from the supercritical solution. The higher equilibrium uptake observed for the silica gel tablets compared to the monolithic support material is probably due to the higher internal surface. This is important as it shows the ability of the dissolved compound to access the pores. Analyses of the loaded support material will have to be performed in order to confirm this conclusion.

INTRODUCTION

The deposition of dissolved compounds on solid support materials in supercritical fluids for surface functionalization is a complex process. An important part of this process is the diffusion and adsorption of the dissolved substance onto the solid surface. In order to understand, develop and to optimise such a supercritical fluid deposition process, knowledge of the influence of parameters such as pressure, temperature and precursor concentration on the adsorption is essential.

The only study on the adsorption of a metal precursor on a porous support in supercritical CO_2 so far has been carried out by Zhang [1] who also investigated the kinetics of the adsorption. The adsorption was very fast, and the equilibrium uptake increased with increasing precursor concentration. However, the process of adsorption in supercritical fluids is still largely unexplored [2]. There is particularly little information on the kinetics of the adsorption process. In this study, the adsorption of an organometallic platinum compound on porous support materials in supercritical carbon dioxide has been investigated as part of a joint research project aiming at the development of a catalytic converter e.g. for flue gas treatment. Special attention was given to the increase of the uptake with time.

Therefore a new experimental method had been developed. The influence of support material, compound concentration and temperature is reported.

EXPERIMENTAL

High purity grade 6.0 carbon dioxide (Messer Griesheim) was used in the experiments. Dimethyl(1,5-cyclooctadiene)platinum (Pt(cod)(me)$_2$; Strem) with a purity of 99% was used without further purification. Two different support materials were used: A monolithic cordierite with washcoat, as it is typically used for catalytic converters in cars, was kindly provided by the Institute for Chemical Process Engineering at the University of Stuttgart, Germany. The material was used in pieces of 20 mm length and 7 x 7 mm width, containing 25 parallel channels per piece. Silica gel tablets with a diameter of 11 mm were obtained from Fluka. The tablets were cut in half, and four such halves were used for each experiment. The materials were dried at 120-140 °C for several days prior to use.

A new experimental method was developed in order to measure adsorption kinetics in supercritical carbon dioxide. A scheme of the self-designed experimental setup is shown in Fig. 1. The device consists of a fluid circuit with a gear pump, a 3 ml equilibrium cell with 2 μm frits to hold the organometallic substance, a 3 ml adsorption cell containing the support material, and a high pressure UV spectroscopy cell attached to a calibrated UV/VIS spectrometer. The adsorption cell can be connected to or disconnected from the circuit via a two-way valve. Carbon dioxide is supplied to the circuit via a syringe pump. The whole apparatus is placed in a water bath for adjusting temperatures. The maximum temperature was 353 K (accuracy $\pm\,0.5$ K) and the maximum pressure 30 MPa (accuracy $\pm\,0.1$ MPa).
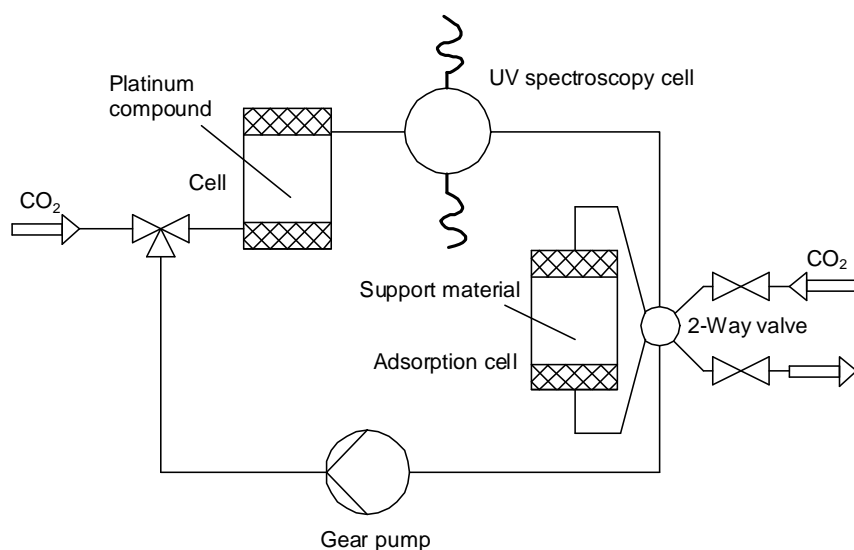

Fig. 1: Schematic of the experimental setup for studying adsorption kinetics in supercritical solution.

Prior to each experiment, the apparatus was heated to the experimental temperature and filled with pure carbon dioxide up to the experimental pressure. A UV spectrum (at 258 nm) was then taken and used as reference spectrum. The adsorption cell, disconnected from the circuit, was filled with a known amount of support material. The equilibrium cell remaining in the circuit was then filled with a known amount of Pt(cod)(me)$_2$, the concentration which in the supercritical fluid being calculated from the amount of substance, the amount of carbon dioxide at given temperature and pressure and the volume of the apparatus. To keep below the saturation concentration, the solubility of the platinum compound in carbon dioxide was measured in separate experiments at the relevant conditions [3].

The circuit as well as the adsorption cell were then flushed with gaseous carbon dioxide, sealed, heated to the experimental temperature and filled with carbon dioxide up to the experimental pressure. The gear pump was switched on to start circulation and mixing of the fluid in the circuit, by-passing the adsorption cell. The dissolution of the platinum compound in the supercritical fluid (1-2 hours) could be observed online by monitoring the increase in concentration recorded by the UV spectrometer. The two-way valve was then switched and the adsorption cell connected to the circuit. Spectra were recorded in intervals of 20 s to monitor the decrease in the concentration of the dissolved platinum compound (Fig. 2). Experiments were performed at a pressure of 15 MPa and temperatures of 333 and 353 K. The concentration of $Pt(cod)(me)_2$ was varied. Analogous experiments were carried out without support material to determine the decrease in Pt-compound concentration arising from the volume increase after connecting the adsorption cell to the circuit.

The resulting curves were approximated by a linear fit method as shown in Fig. 2. Fit parameters were the start time t_s and the end time t_e of the decrease in concentration. The start time represents the time between switching the two-way valve and the visible registration of the decrease in concentration. This delay is caused by the distance between the adsorption cell and the spectroscopic cell. To account for the decrease in concentration due to the adsorption cell volume, the starting concentrations c_0 were subtracted from the concentrations c_a obtained for the adsorption experiments. The resulting concentrations were multiplied by the volume of the circuit V_c (20.0 ml) to obtain the amount of adsorbed substance m_a and divided by the amount of support material, m_s. This gives the specific uptake in mg substance per g support material (eq 1).

$$m_a = \frac{(c_a - c_0)V_c}{m_s} \qquad \text{(eq 1)}$$

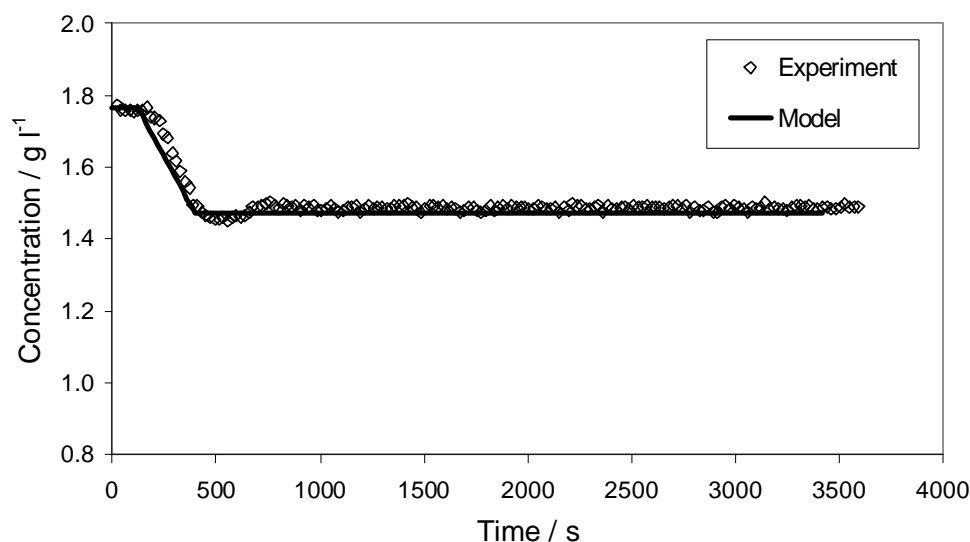The reproducibility of the uptake curves was about ± 3 mg g^{-1}.

Fig. 2: Decrease in concentration of $Pt(cod)(me)_2$ in carbon dioxide due to the increase in volume of the apparatus after connecting the adsorption cell to the circuit; experiment with 30 mg $Pt(cod)(me)_2$ at 333 K and 15 MPa, no support material.

RESULTS AND DISCUSSION

The uptake curves for two different support materials at a temperature of 333 K for a high and a low concentration of $Pt(cod)(me)_2$ are shown in Fig. 3. For the monolithic support, uptake increases sharply from the beginning at both concentrations. Equilibrium uptake is reached after about 1 hour. The silica gel tablets exhibit a much slower uptake of the platinum compound, and even after several hours equilibrium is not reached. The rate of the uptake is higher for the monolithic material, whereas the total equilibrium uptake and therefore the adsorption capacity are higher for the silica gel tablets. Due to the parallel channels in the monolithic material, the fluid solution can flow through the channels, whereas the fluid can only flow over the outer surface of the compact silica gel tablets. For the same reason, the geometric surface of the monolithic material is much higher than that of the silica gel tablets, leading to a higher contact area between solution and support. This is probably the reason for the higher uptake rate for the monolithic material compared to the silica gel tablets. The internal surface of the porous structure is about 3.5 times higher for the silica gel tablets than for the monolithic material. This may explain the higher adsorption capacity of the silica gel tablets compared to the monolithic material. It indicates that the platinum compound dissolved in the supercritical fluid actually penetrates into the pores of the support material.
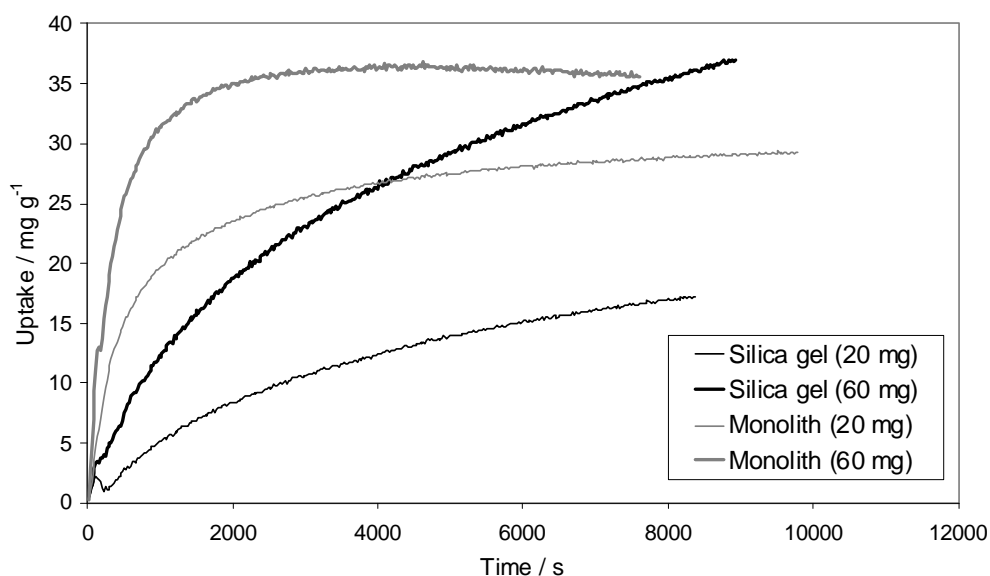

Fig. 4: Uptake of $Pt(cod)(me)_2$ versus time for monolithic support material and silica gel tablets at initial amounts of 20 and 60 mg of $Pt(cod)(me)_2$ in carbon dioxide at 333 K and 15 MPa.

The concentration dependence of the uptake of $Pt(cod)(me)_2$ versus time at 333 K is shown in Fig. 4 at the example for the silica gel tablets. Both support materials exhibit a similar influence of concentration on the uptake curves. Increasing concentration of the platinum compound in supercritical carbon dioxide increases both, the rate of uptake and the equilibrium uptake, which finally reaches a limit that cannot be exceeded with further increase of concentration. In case of the monolithic material, an increase in the amount of $Pt(cod)(me)_2$ from 40 to 60 mg does not result in higher uptake. The same is valid for the silica gel tablets at an increase from 50 to 60 mg $Pt(cod)(me)_2$. The limit values of the maximum adsorption capacity for the support materials at the given temperature was observed at 35 mg g^{-1} for the monolithic material and is estimated to be around 50 mg g^{-1} for the silica gel tablets, but which could not be reached in the experimental time interval.
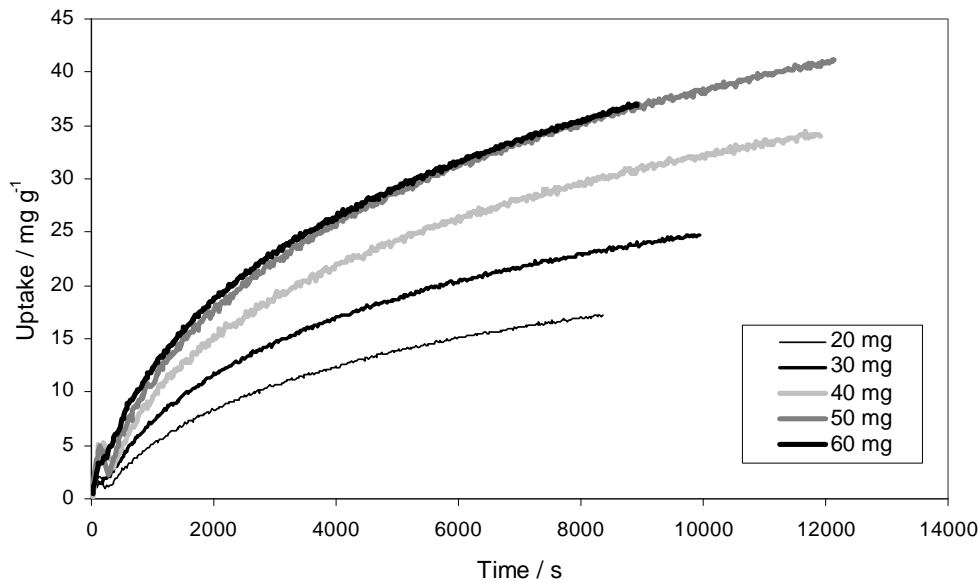
Fig. 4: Uptake of Pt(cod)(me)$_2$ versus time for silica gel tablets at various initial amounts of Pt(cod)(me)$_2$ in carbon dioxide at 333 K and 15 MPa.

Fig. 5 shows the influence of temperature on the uptake of Pt(cod)(me)$_2$ on the monolithic material. For the same initial weight of the platinum compound, the uptake increases with increasing temperature. However, the density of the supercritical fluid strongly depends on temperature. For pure carbon dioxide, the density is 427 kg m^{-3} at 353 K and 604 kg m^{-3} at 333 K [4]. This means the concentration of Pt(cod)(me)$_2$ per amount of carbon dioxide is about 40 % higher at 353 K. The respective concentration values are also given in Fig. 5.
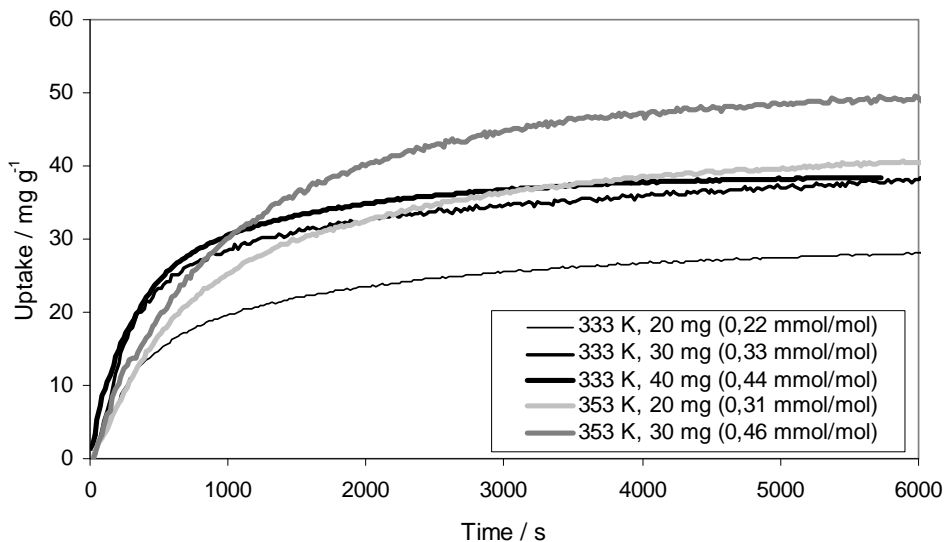

Fig. 5: Uptake of Pt(cod)(me)$_2$ in carbon dioxide versus time for the monolithic support material at 333 and 353 K and 15 MPa at different absolute amounts of Pt(cod)(me)$_2$.

Considering the carbon dioxide density difference, the experiments with 30 mg substance at 333 K and 20 mg substance at 353 K represent similar concentrations of about 0.3 mmol Pt(cod)(me)$_2$ per mol carbon dioxide. A comparison of the respective graphs shows that the equilibrium uptake is similar in

both cases. It can be concluded that the essential parameter for the adsorption is the relative amount of dissolved substance per amount of carbon dioxide rather than the absolute amount of substance in the fluid. However, the rate of uptake seems to be slightly lower at the higher temperature.

At 333 K the maximum adsorption capacity is nearly the same for the two concentrations given in Fig. 5: At 353 K, however, there is still a significant increase of the equilibrium uptake when the concentration of the platinum compound increases. This may be a hint, that the uptake is not dominated by adsorption equilibrium but by mass transport. Increasing temperature enhances mass transport due to higher diffusion coefficients and therefore may result in an increase in uptake.

CONCLUSIONS

A new experimental method to study the influence of concentration, temperature and support material on the adsorption of organometallic substances (here $Pt(cod)(me)_2$) in supercritical carbon dioxide was developed where the substance is allowed to dissolve in the supercritical fluid before getting into contact with the solid support. By switching a two-way-valve, a homogeneous supercritical solution with defined concentration of the organometallic compound enters the adsorption cell. Thus, the start of the uptake can be clearly defined. For further details, see [3] and [5].

The monolithic support material shows a sharp increase in the uptake of the platinum compound already in the first few minutes. This is an advantage for processes comprising a reaction of the platinum compound on the surface of the support material. The rate of uptake can be increased by increasing the geometric surface of the support material for a better contact between the fluid and the solid support. Furthermore, the results obtained at different temperatures indicate that mass transport plays an important role in the process of adsorption from the supercritical solution.

The higher equilibrium uptake for the silica gel tablets compared to the monolithic support material is probably due to the higher internal surface. This is important as it shows the ability of the dissolved compound to access the pores. Analyses of the loaded support material will have to be performed in order to confirm this conclusion.

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REFERENCES

GLAESER 2003: Gläser R., Weitkamp J., Ind. Eng. Chem. Res. 42, **2003**, p. 6294

[1] Zhang Y., Kang D., Aindow M., Erkey C., J. Phys. Chem. B 109, **2005**, 2617

[2] Zhang Y., Erkey C., J. Supercrit. Fluids 38, **2006**, p. 252

[3] Aschenbrenner, O., Dahmen, N., Schaber, K., Dinjus, E.,
submitted to Ind. Eng. Chem. Res in 2007

[4] Span R., Wagner W., J. Phys. Chem. Ref. Data 25, **1996**, p. 1509

[5] Aschenbrenner, O., Dissertation, University of Karlsruhe 2007
http://www.uvka.de/univerlag/volltexte/2008/290/pdf/Aschenbrenner_Ortrud.pdf