

REACTIVE DECOMPOSITION OF METALS IN SUPERCRITICAL FLUIDS: INVESTIGATION OF THE SOLUBILITY AND DECOMPOSABILITY OF METAL ORGANIC SUBSTANCES

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In this work the reactive decomposition of metal organic substances in supercritical carbon dioxide (scCO₂) was demonstrated. For the choice of suitable precursor substances, precise knowledge of the solubility and decomposition in scCO₂ is required. In this work, the influence of the ligands and metal atoms of commercially available metal complexes on the solubility was investigated. Additionally, reaction conditions (temperature, pressure, and concentration of the metal complexes) were found, at which the total decomposition of the metal organic complexes through hydrogenation in scCO₂ is achievable. As an application of this process, the coating of a polymer membrane with a thin platinum layer for hydrogen fuel cell applications is demonstrated.

INTRODUCTION

The production of well-defined metal particles, coatings, and powders is of great interest for a variety of industrial applications such as catalysis. Synthesis in solutions is state of the art for the production of those, but these processes bring along a variety of problems such as a high amount of liquid waste. Supercritical Fluid Reactive Deposition (SFRD) of metals on supports offers an attractive alternative route [1-3]. In this process, an appropriate precursor is dissolved in the supercritical fluid and deposited as a pure metal on the support by reduction e.g. with hydrogen. Using CO₂ as a fluid offers a variety of advantages: moderate critical data (304 K, 7.4 MPa), low toxicity, and it is environmentally benign.

We applied this method to coat a Nafion[®] membrane with thin metal layers for fuel cell applications. In order to find appropriate precursor complexes for the coating of membranes, systematic studies of the solubility of the complex in scCO₂ and decomposition data are necessary. Several studies exist concerning the influence of ligands on solubility [4], [5], but almost no studies can be found about the influence of the metal on solubility of the complex. We systematically examined various β -diketonate, cyclopentadienyl and cyclooctadiene complexes with metals including platinum, palladium, rhodium, ruthenium, copper, nickel, iron, and cobalt. Guided by the solubility data, selected metal organic complexes were decomposed through hydrogenation in scCO₂ and adequate reaction conditions were determined.

MATERIALS AND METHODS

Materials

All complexes were obtained by a commercial supplier. We used complexes with the following ligands: 2,4-pentanedionate (acetylacetonate, *acac*); 2,2,6,6-tetramethyl-3,5-heptanedionate (*thd*); cyclopentadienyl (*cp*); methyl (*me*) and cyclooctadiene (*cod*). The following complexes were examined: Pd(*acac*)₂, Cu(*acac*)₂, Ni(*acac*)₂, Cu(*thd*)₂, Ni(*thd*)₂, Co(*thd*)₃, Ag(*thd*), Ru(*thd*)₃, Ru(*thd*)₂(*cod*), Ni(*cp*)₂, Ru(*cp*)₂, Fe(*cp*)₂, Os(*cp*)₂, Pt(*cod*)*me*₂, Rh(*acac*)(*cod*). All substances were used as received. Nafion[®] membrane was obtained from QuinTech, Germany.

Apparatus

The solubility experiments were performed in a modified extraction apparatus shown in Figure 1. The saturation cell (D), containing an excess amount of substance, is heated to the desired temperature. The cell is filled with CO₂ up to the desired pressure. A constant flow of CO₂ through the cell is maintained, the pressure being held constant. The flow rate must be low enough to ensure saturation, which has been shown in some earlier experiments with various flow rates. The saturated solution is decompressed to atmospheric pressure in the back pressure regulator. The dissolved solid precipitates and is sampled in a glass tube with a frit (G). The amount of precipitated substance is measured with a balance.

For the investigation of solubility of Pt(*cod*)*me*₂ at different temperatures, a different kind of apparatus was used (not shown). This apparatus consists of a circuit with a saturation cell where the substance is filled in, a high pressure spectroscopy view cell, a sample loop, and a gear pump. After pressurization with CO₂ and heating, the fluid in the apparatus is pumped through the saturation cell. The solution is pumped through the apparatus until saturation is reached. The saturation process can be observed with online UV/Vis spectroscopy. A sample is taken with a sample loop, decompressed and the solute is washed out with a known amount of hexane. The solution is analysed with UV/Vis spectroscopy.

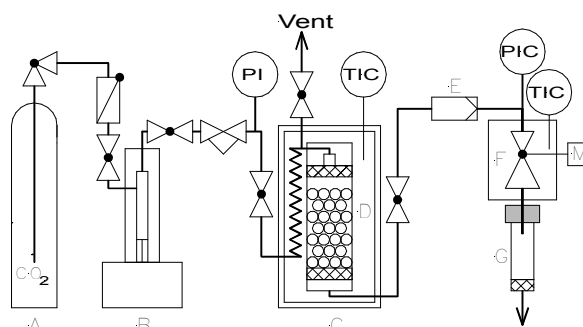


Figure 1: Apparatus for the investigation of solubility of organometallic complexes in scCO₂

The deposition experiments were conducted in a 100-mL high-pressure stainless steel reactor as shown in Figure 2. In a typical deposition experiment, a substrate (~1×1 cm section of a polished Si wafer or a 1×5 cm section of Nafion[®] 117 membrane) and a known quantity (10-50 mg) of the precursor were placed in the reactor. The vessel was purged with CO₂, heated to the reaction temperature and maintained under these conditions for a period of at least 10 minutes to ensure complete dissolution of the precursor. The reaction was started through injection of hydrogen gas (~10-fold molar excess) and carried out for 1 h. The decomposition

in the autoclave was directly monitored through the measurement of the absorbance (UV-Vis). The coated samples were examined with SEM using a Leo 1530 (Zeiss) microscope.

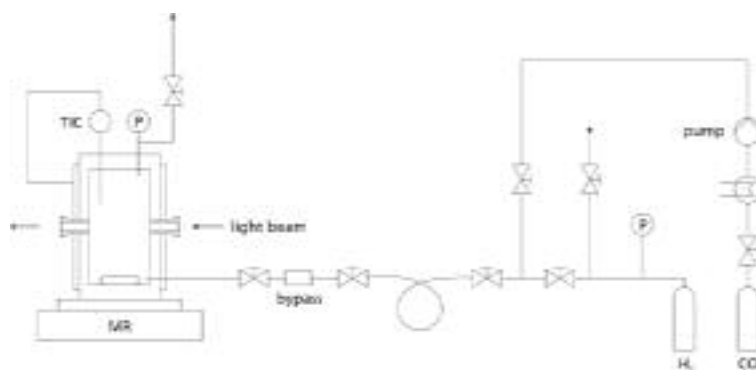


Figure 2: Scheme of the high-pressure reactor used for decomposition experiment.

RESULTS

In order to find suitable ligands, we examined the solubility of several types of complexes with different metal atoms. All investigated *acac* complexes showed only low solubility in *scCO*₂ in agreement with the results reported in literature [6]. In almost all cases the solubility of the corresponding *thd* complex was about 10 times higher. Most of the cyclopentadienyl and cyclooctadiene complexes exhibited high solubility in *scCO*₂. Figure 3 shows as an example the solubility of selected nickel and ruthenium complexes in *scCO*₂.

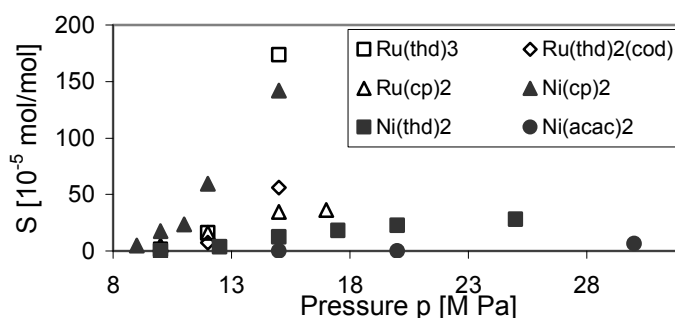


Figure 3: Solubility (S) of nickel and ruthenium complexes in carbon dioxide at 333 K

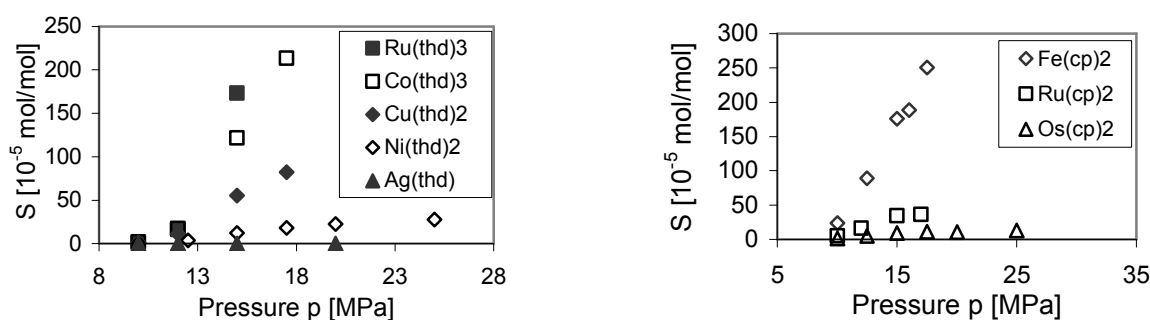


Figure 4: Solubility (S) of thd complexes in carbon dioxide at 333 K (left), Solubility (S) of ferrocene, ruthenocene and osmocene in carbon dioxide at 333 K (right)

Not only the ligand, but also the metal has great influence on the complex solubility. Figure 4 (left graph) shows the solubility of various *thd* complexes in *scCO*₂ at 333 K. It can be observed that, in general, the solubility increases with a higher number of ligands per molecule. This is due to a better shield of the positive charge of the metal by the ligands [7].

In order to investigate the influence of the metal on complex solubility in *scCO*₂, we used *cp* complexes which all have the same sandwich structure. Figure 4 (right graph) shows the solubility of the complexes of nickel, ruthenium, and osmium at 333 K. These metals belong to the same group of the periodic system and differ only in the atomic weight and size. It is obvious from Figure 4 (right graph) that the solubility is higher with lower mass and size of the metal atom.

We also investigated the parameters (temperature and precursor concentration) for the reactive decomposition of selected metal organic complexes (Table 1). Platinum, palladium and rhodium complexes decompose at lower temperatures (313 – 353 K) than copper and ruthenium complexes which decompose beyond the temperature of 453 K see table 1).

Table 1: Investigated metal organic complexes

precursor	T [K]	p [MPa]	c [mol/L]	S (60 °C, 15 MPa) [mol/mol]	decomposability
Pt(cod)me ₂	313 - 353	15,5	$0,4 - 1,8 \cdot 10^{-3}$	0,00063	yes
Cu(thd) ₂	453 - 493	21 - 30	$0,4 - 2,3 \cdot 10^{-3}$	0,00055	yes
Rh(acac)(cod)	323 -343	15,5	$1 - 2 \cdot 10^{-3}$	0,00018	yes
Ru(thd) ₃	473	17 - 19	$3,5 \cdot 10^{-5}$	0,0017	yes
Ru(cp) ₂	513	21,6	$5,2 \cdot 10^{-4}$	0,00034	yes
Ru (thd) ₂ (cod)	473	18,9	$8,9 \cdot 10^{-4}$	0,00056	yes
Pd(acac) ₂	333	15,5	$1,5 \cdot 10^{-4}$	0,00002	yes
Fe(cp) ₂	443 - 463	18	$1,3 \cdot 10^{-3}$	0,00176	no

From the complexes that decompose at moderate temperatures, Pt(cod)me₂ has the highest solubility in *scCO*₂. For this reason, this complex was chosen for more detailed investigations. We determined the solubility of Pt(cod)me₂ in *scCO*₂ in a wide pressure and temperature range to provide sufficient data for the decomposition process. The pressure was varied from 9 to 30 MPa at different temperatures (313 to 353 K). The results are shown in Figure 5.

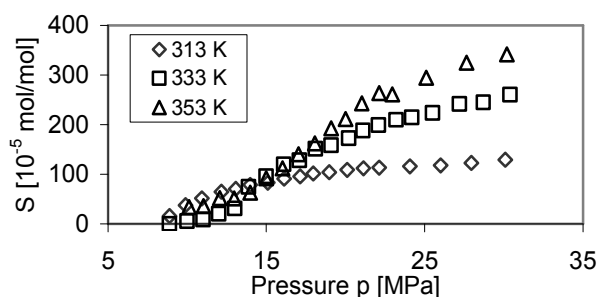
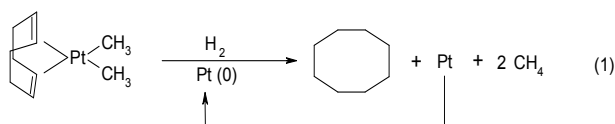


Figure 5: Solubility (S) of Pt(cod)me₂ in *scCO*₂ at different pressures and temperatures

The decomposition of Pt(cod)me₂ via hydrogenation to platinum (eq. 1) has been shown to be autocatalytic [8].



We determined the overall decomposition rate at adequate reaction conditions to ensure the total decomposition of the precursor in coating experiments. Figure 6 shows the monitoring of the precursor concentration over the course of the reaction time for a typical decomposition experiment. It was carried out in a homogenous phase. After a short induction period (Figure 6), the concentration declines linearly with the reaction time, typically for zero-order kinetics.

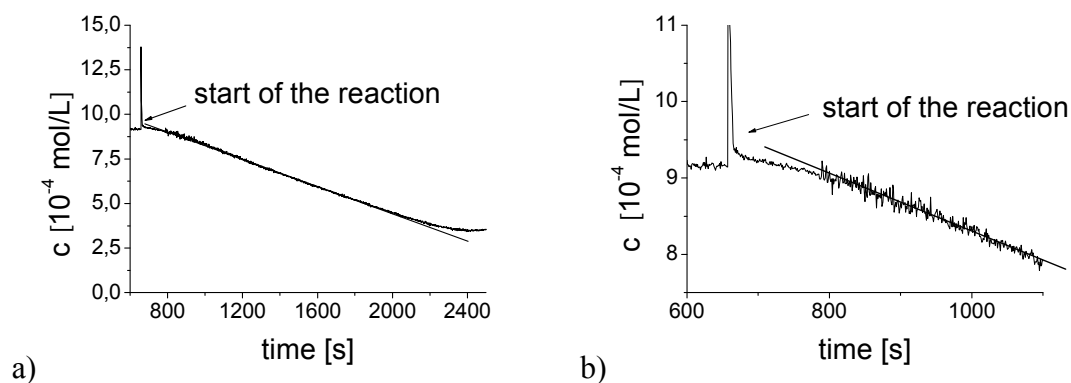


Figure 6: a) Decomposition rate of $\text{Pt}(\text{cod})\text{me}_2$ at 333 K and 15,5 MPa, $c(\text{Pt}(\text{cod})\text{me}_2) = 9,76 \cdot 10^{-4} \text{ mol/L}$, $k = 0,0038 \cdot 10^{-4} \text{ mol/(L}\cdot\text{s)}$ b) magnification of the induction period

We further deposited platinum onto Nafion[®] membranes resulting in the formation of continuous and reflective films. Figure 7 shows a typical SEM image of deposited Pt nanoparticles onto a Nafion[®] membrane. To avoid the formation of cracks in the continuous platinum film caused by swelling of the membrane with scCO_2 (Figure 7 b) we used water as a swelling agent prior to the deposition. The as-prepared deposited films were free of cracks (Figure 7 a). EDX analysis of the deposited film indicated that the film was free of contamination.

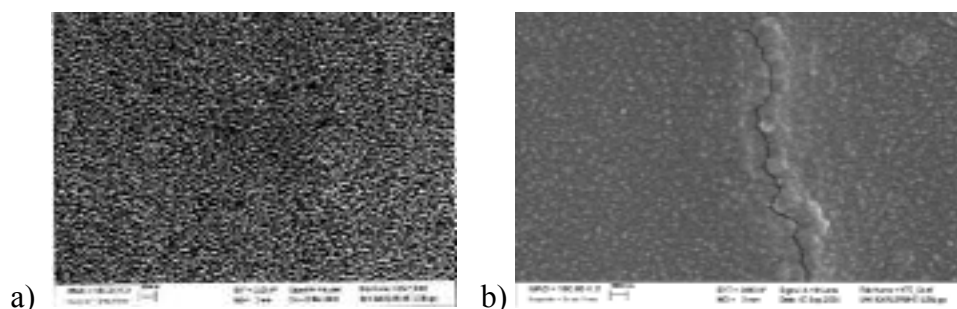


Figure 7: a) Crack free Pt film deposited onto Nafion[®] (333 K, 15 MPa, H_2O as swelling agent) b) Pt film with cracks deposited onto Nafion[®] (333 K, 15 MPa)

Figure 8 a) shows a cross-section of a coated Nafion[®] membrane. The platinum film was approximately 5 μm thick. It further shows that platinum is present not only at the surface of the membrane but also deeper inside as indicated by the brighter areas adjacent to the distinct platinum films. Figure 8 b) shows the platinum concentration as a function of the membrane thickness determined by EDX. In the coating experiment, the membrane was swollen by the scCO_2 and the therein dissolved complexes. Therefore, the complex was transported into the membrane. Upon hydrogenation, platinum is generated at the membrane surface as well as inside, in close proximity to the surface, resulting in good adhesion of the platinum film.

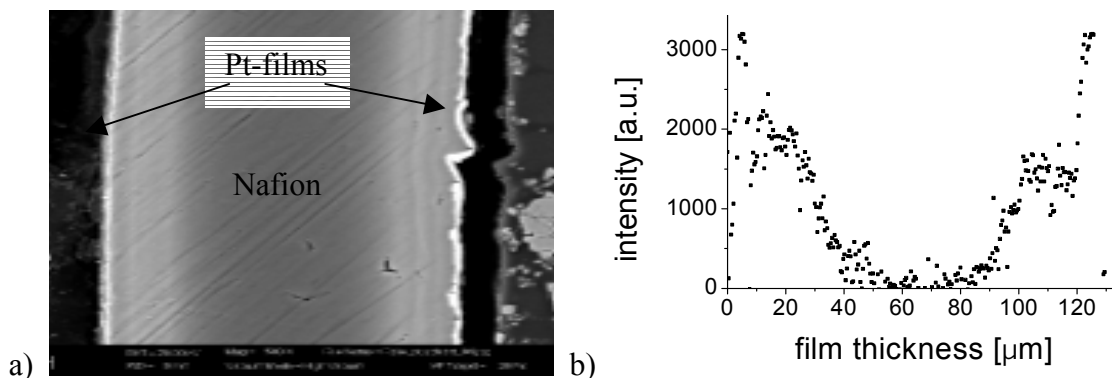


Figure 8: a) SEM micrograph of a cross section of a coated Nafion[®] membrane (film thickness 130 μm, reaction conditions: T = 333 K, p = 15 MPa, t = 1 h reduction time) b) Platinum concentration as a function of membrane thickness

CONCLUSION

In this work we demonstrate the coating of Nafion[®] membranes with a thin platinum film by SFRD. These coated membranes could serve as catalysts for hydrogen fuel cell application. For the choice of metal organic precursors, we investigated their solubility in scCO₂ and determined adequate deposition conditions. The ligands and the metal in the complex influence the solubility of the complex in scCO₂. Concerning the influence of the ligands on complex solubility, a general trend can be observed: *acac* complexes show in general a lower solubility in comparison to *thd*, *cp* and *cod* complexes. The oxidation state and the mass of the metal atom influence also the solubility of the complex in scCO₂. Complexes including Pt, Pd and Rh decompose at moderate temperatures (313 – 333 K), whereas Cu, Ru and Fe complexes decompose beyond 453 K. The deposition of a continuous and reflective platinum film on a Nafion[®] membrane was carried out successfully.

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