

SUPERCRITICAL FLUID REACTIVE DEPOSITION FOR THE PREPARATION OF METAL CATALYSTS ON POROUS MODEL SUPPORTS

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Platinum catalysts supported on micro-, meso-, and macroporous silica (silicalite-1, MCM-41, silica gel) were prepared via supercritical fluid reactive deposition (SFRD). The porous model supports were first impregnated with the complex 1,5-(cyclooctadiene)dimethylplatinum(II) dissolved in supercritical carbon dioxide (scCO₂) at 80 °C and 15.5 MPa for 2 h. For SFRD, the complex was reduced to platinum metal in scCO₂ by addition of hydrogen. In order to identify appropriate conditions for SFRD, the three-phase S–L–G coexistence curve was measured in the pressure range of 0.1 to 25.0 MPa for the mixtures investigated. The supported Pt(COD)Me₂ complex and the platinum composites were characterized by elemental analysis (ICP-AES), TGA, DSC, XRD, and N₂ adsorption. DSC and XRD support a homogenous distribution of the complex over the MCM-41 support. High platinum dispersions were obtained by SFRD on the macro- and mesoporous supports, but not on the microporous silicalite-1. The Pt/MCM-41 catalysts are active for the combustion of toluene in air as a test reaction for the oxidative destruction of volatile organic compounds (VOCs).

INTRODUCTION

Supercritical fluids are attracting increasing attention as processing solvents in materials chemistry due to their unique and tunable properties such as high diffusivity, low viscosity, and high solvent strength [1,2]. For instance, supercritical carbon dioxide (scCO₂) was used in the preparation of metal or metal oxides nanoparticles on porous substrates [3,4]. An interesting approach for catalyst preparation is the deposition of metal precursors on supports from supercritical solutions. Saquing et al. [5] reported the decomposition of a platinum complex deposited on activated carbon from scCO₂. Further, Dhepe et al. [6] demonstrated the preparation of bimetallic catalysts on FSM-16 using scCO₂ and tested these catalysts in the hydrogenolysis of butane. Metal particles can also directly be deposited on solid supports by reduction of metal complexes with hydrogen in scCO₂ (supercritical fluid reactive deposition, SFRD) [7-9]. However, the influence of the pore size of the supports on the preparation of supported platinum nanoparticles in scCO₂ by SFRD was not yet investigated systematically.

In this study, we present first results in exploring the opportunities of using scCO₂ for the preparation of platinum on various siliceous porous supports with different pore sizes. The crystalline microporous silicalite-1 ($A_{\text{BET}} = 373 \text{ m}^2 \text{ g}^{-1}$, $d_p = 0.5 \text{ nm}$), ordered mesoporous MCM-41 ($A_{\text{BET}} = 1200 \text{ m}^2 \text{ g}^{-1}$, $d_p = 2.4 \text{ nm}$) and disordered macroporous silica gel ($A_{\text{BET}} = 288.2 \text{ m}^2 \text{ g}^{-1}$, $d_p = 12.8 \text{ nm}$) were chosen as model supports. The platinum complex 1,5-(cyclooctadiene)dimethylplatinum(II) (Pt(COD)Me₂) served as a precursor to metallic platinum. Appropriate conditions for SFRD were derived from studies on the high-pressure phase behavior and the solubility of Pt(COD)Me₂ in scCO₂. Finally, the supported Pt-catalysts were tested as catalysts in the total oxidation of toluene with air.

EXPERIMENTAL SECTION

The porous silica supports silicalite-1 and all-silica MCM-41 were prepared according to procedures adopted from the literature [10,11]. Silica gel 62 was obtained from Sigma Aldrich and 1,5-(cyclooctadiene)dimethylplatinum(II) (Pt(COD)Me₂) from ABCR (99 %).

The three-phase S–L–G coexistence curve (SLG-line) of Pt(COD)Me₂ under CO₂ pressure was measured according to the first melting point method [12]. For deposition of the complex, physical mixtures of Pt(COD)Me₂ and the support were placed in a tubular reactor and treated in scCO₂ at 80 °C and 15.5 MPa for 2 h before releasing the pressure to ambient. The resulting samples are designated as CO₂-treated. For SFRD, H₂ was added to the Pt(COD)Me₂/support-mixture in scCO₂ at constant temperature and pressure, and the mixture was kept for 2 h. The samples were characterized by powder X-ray diffraction (XRD, Siemens D5000), differential scanning calorimetry (DSC, DSC 204 Phoenix, Netzsch), thermogravimetric analysis (TGA, setsys TG-16, Setaram) and N₂ adsorption (Micromeritics ASAP 2010). The platinum content of the samples was determined by atomic emission spectrometry (ICP-AES, Perkin Elmer, Plasma 400) and from the weight loss upon oxidative decomposition of the complex observed by TGA in air. Samples are labeled according to the content of the supported component, e.g., 9.0Pt/silicalite-1 for a silicalite-1 containing 9.0 wt.-% Pt. The Pt particle size was calculated from the Scherrer-Equation using the full-width-at-half-height of a Gaussian function fitted to the Pt(111)-reflection ($2\theta = 38^\circ - 42^\circ$, step size = 0.01° , step time = 20 s).

Toluene oxidation by air was carried out in a flow-type apparatus with a fixed-bed reactor holding pelletized samples of the SFRD products ($WHSV = 300 \text{ h}^{-1}$, $m_{\text{Pt}} = 0.65 \text{ mg}$, $p_{\text{Tol}} = 2.9 \text{ kPa}$). The reaction temperature was continuously increased from 150 to 350 °C with a heating rate of $0.07 \text{ }^\circ\text{C min}^{-1}$. Samples were periodically taken from the gaseous reaction mixture and analyzed by capillary GC.

RESULTS AND DISCUSSION

High-pressure phase behavior and complex solubility

The experimental SLG-data for CO₂/Pt(COD)Me₂ and for He/Pt(COD)Me₂ are shown in Figure 1. In case of the first mixture, the melting point decreases with increasing pressure from 105 °C at 0.1 MPa to 87 °C at 25.6 MPa. For the second mixture, the melting point increases with increasing pressure from 105 °C at 0.1 MPa to 111 °C at 25.6 MPa. For both

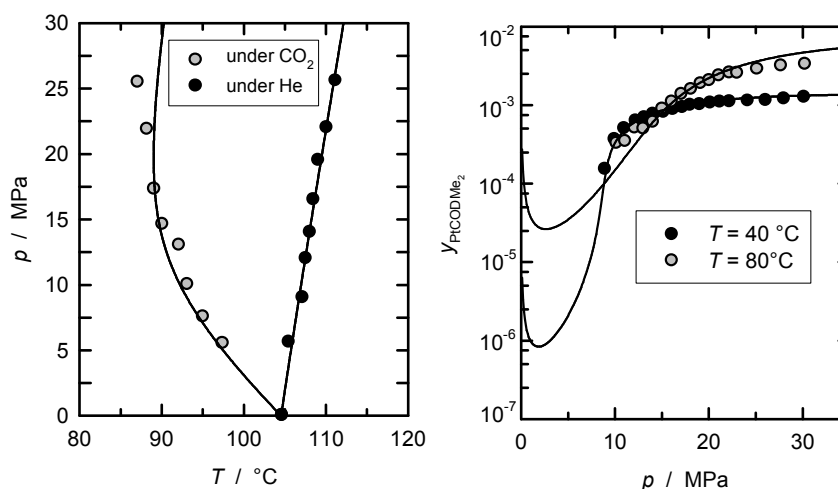


Figure 1: SLG-line of Pt(COD)Me₂ under CO₂ or Helium pressure (left part) and solubility of Pt(COD)Me₂ in CO₂ (right part, experimental data from [13]).

mixtures, the binary interaction parameter in the attraction term of the PR-EoS was fitted to the experimental data of the SLG-line. As shown in Figure 1, this approach enables a good correlation of the SLG-line and of the solubility of Pt(COD)Me₂ in CO₂ [13] in the range of interest for the SFRD process (5 MPa ≤ p ≤ 25 MPa, 37 °C ≤ T ≤ 87 °C).

Deposition of Pt(COD)Me₂ from scCO₂ on silicalite-1, MCM-41 and silica gel

In a first set of experiments, the supports were loaded with the complex Pt(COD)Me₂ by treating a physical complex/support-mixture with scCO₂. In Table 1, the fractions of the complex in the starting mixture $X_{\text{Pt(COD)Me}_2}$ are compared to the complex loadings X_{calc} calculated assuming that all complex dissolved in scCO₂ is lost after the deposition experiments. Expectedly, X_{calc} is lower than $X_{\text{Pt(COD)Me}_2}$. For complex loadings above 0.100 g g⁻¹, the values calculated by the PR-EoS agree reasonably well with those determined experimentally by TGA. This also holds, if helium was added to the scCO₂-phase as a non-reactive replacement for hydrogen. For lower initial complex fractions below the solubility limit, more complex is found on the support than expected from the calculation. This may be explained by adsorption of the complex on the support. Thus, a minimum fraction of 5.1 wt.-% complex is adsorbed on MCM-41. In order to evaluate the efficiency of the complex deposition, the experimentally found loading was divided by the calculated one. The resulting efficiency E is close to one in all cases, except for initial complex fractions below the solubility limit. Thus, the complex deposition from scCO₂ represents a highly economic process with a low loss of noble metal, especially, if the complex-containing CO₂-phase can be recycled.

Table 1: Calculated and experimentally determined complex loading after deposition of Pt(COD)Me₂ on MCM-41, silicalite-1, and silica gel (deposition conditions: 15.5 MPa, 80 °C, 2 h).

model support	y_{He} / %	$X_{\text{Pt(COD)Me}_2}$ / g g ⁻¹	X_{calc} / g g ⁻¹	X_{TGA} / g g ⁻¹	E / g g ⁻¹
MCM-41	-	0.01	-	0.028	∞
MCM-41	1.17	0.01	-	0.026	∞
MCM-41	1.17	0.03	-	0.034	∞
MCM-41	-	0.03	-	0.037	∞
MCM-41	-	0.05	-	0.051	∞
MCM-41	-	0.10	0.029	0.095	3.28
MCM-41	-	0.21	0.132	0.146	1.11
MCM-41 ^{a)}	-	0.22	0.143	0.179	1.25
MCM-41	1.17	0.21	0.146	0.152	1.04
MCM-41	2.34	0.20	0.152	0.179	1.18
MCM-41	4.68	0.20	0.167	0.190	1.14
MCM-41	10.00	0.20	0.177	0.186	1.05
MCM-41	-	0.41	0.333	0.340	1.02
MCM-41	1.17	0.41	0.346	0.321	0.93
MCM-41	-	0.81	0.735	0.656	0.89
MCM-41	1.17	0.81	0.748	0.750	1.00
silicalite-1	-	0.21	0.131	0.172	1.31
silicalite-1	-	0.21	0.137	0.241	1.76
silica gel	-	0.20	0.181	0.156	0.87

^{a)}duration of deposition: 24 h

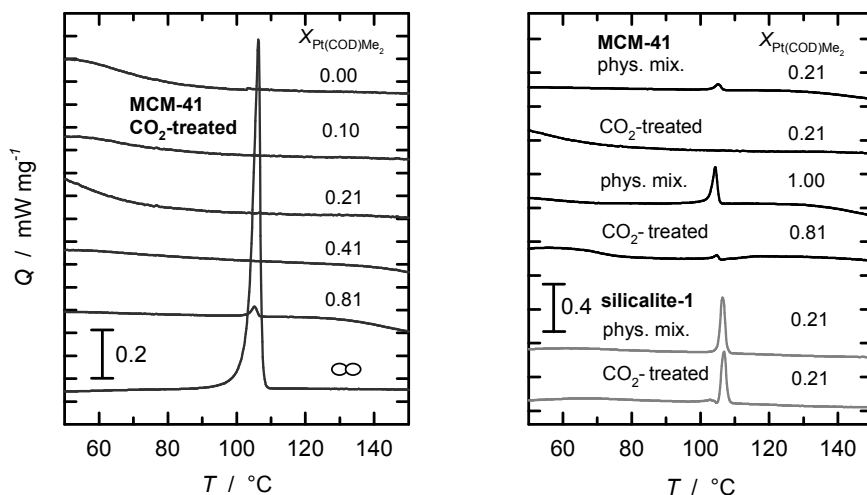


Figure 2: DSC curves for CO₂-treated Pt(COD)Me₂/MCM-41-mixtures (left part) and for physical mixtures of Pt(COD)Me₂ with MCM-41 or silicalite-1 before and after treatment in scCO₂ (right part) with different complex loadings $X_{\text{Pt(COD)Me}_2}$.

Figure 2, left part, shows the DSC curves for scCO₂-treated Pt(COD)Me₂/MCM-41-mixtures with different complex contents $X_{\text{Pt(COD)Me}_2}$ before the treatment. For comparison, a curve for the pure complex is shown, too. The pure complex Pt(COD)Me₂ melts at 105 °C. The absence of a defined melting peak up to complex loadings of 0.41 indicates that the complex was homogeneously distributed over the surface of the MCM-41 support by deposition from scCO₂. A small melting peak was noticed for a high complex loading of 0.81 only. However, a melting peak is clearly visible in the DSC curve of an untreated, physical mixture with $X_{\text{Pt(COD)Me}_2} = 0.21$ (Figure 2, right part). The difference between the physical mixture before and after treatment with scCO₂ is more pronounced at an even higher initial complex loading of 0.81. However, the physical mixture and the scCO₂-treated sample based on silicalite-1 exhibit essentially the same DSC curve with a larger melting peak. This clearly shows that the complex is unevenly distributed and still possesses bulk melting behavior. Evidently, the complex can not enter the pores of the microporous silicalite-1.

The XRD patterns for the parent MCM-41 and a Pt(COD)Me₂/MCM-41-mixture before (17.9 wt.-% complex) and after treatment with scCO₂ (14.6 wt.-% complex) are displayed in Figure 3. In all samples, the typical reflections for ordered mesoporous MCM-41-type materials are obtained [11]. Therefore, a structural damage of the mesoporous host can be excluded. However, the intensity of the reflections is lower for the physical mixture and the CO₂-treated sample with respect to the complex-free, parent MCM-41. This may be attributed to a stronger scattering of the sample in the presence of the solid complex. The particularly low intensity for the CO₂-treated sample may be taken as evidence for a homogeneous distribution of the complex, also within the pores of MCM-41.

Supercritical fluid reactive deposition of platinum on silicalite-1, MCM-41 and silica gel

As shown by the XRD pattern in Figure 3, the structural integrity of the ordered mesoporous MCM-41-material is also maintained when the platinum complex is reduced by hydrogen

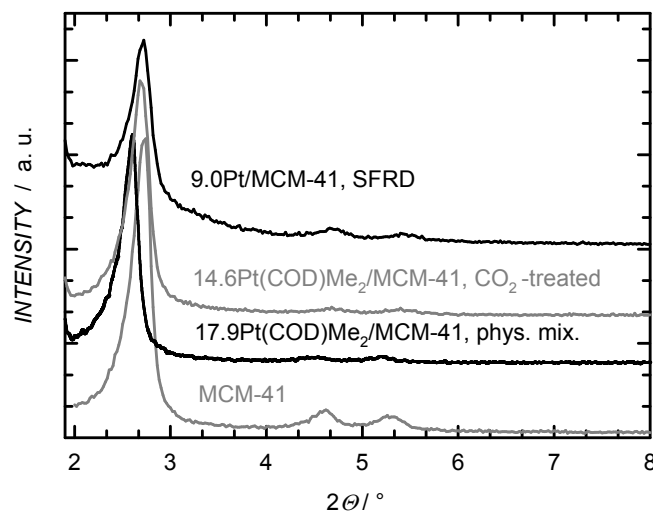


Figure 3: XRD patterns of the parent MCM-41, a Pt(COD)Me₂/MCM-41 physical mixture, a CO₂-treated Pt(COD)Me₂/MCM-41-mixture and of Pt/MCM-41 obtained by SFRD.

added to the scCO₂-phase (supercritical fluid deposition (SFRD) of platinum). The intensity (peak area) of the major reflection around $2\theta = 2.7^\circ$ is significantly lower with respect to that of the reflections at higher 2θ -values (4.6 and 5.3°) than for the parent MCM-41. This lower relative intensity is a clear indication for the presence of scattering material inside the pores of the ordered mesoporous support. It can, therefore, be concluded that platinum has been deposited, at least to a major extent, within the mesopores of MCM-41. This is corroborated by a reduction of the specific surface area A_{BET} for 9.0Pt/MCM-41 prepared by SFRD compared to the parent MCM-41-type material by approx. 30 % as determined by N₂ adsorption. Nevertheless, the pore size distribution remains effectively unchanged after SFRD. This points at a blockage of the MCM-41 pores or, in other words, at the presence of platinum particles with sizes in the range of the pore diameter of the MCM-41 ($d_p = 2.4$ nm).

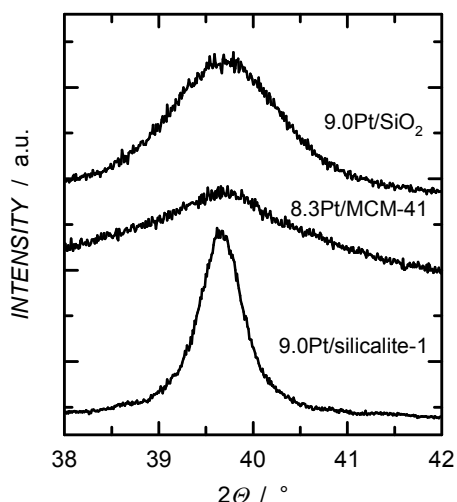


Figure 4: Pt(111) reflection for Pt on silica gel, MCM-41, and silicalite-1 prepared by SFRD.

Figure 4 shows the Pt(111) reflection for samples obtained from SFRD of similar amounts of platinum on silicalite-1, MCM-41 and silica gel. Evidently, the platinum particles on these supports have different average sizes. 9.0Pt/silicalite-1 shows a narrow peak, which reflects rather large platinum particles with a diameter of approx. 28.4 nm. While on silica gel the platinum particle size was 11.4 nm, the smallest particles with an average size of 5.8 nm were obtained with MCM-41 as the support. This indicates that a high specific surface area is advantageous for the formation of smaller platinum particles by SFRD. In the case of silicalite-1, the complex was not able to enter the micropores (*vide supra*). Therefore, only the outer surface of the crystals was accessible for the distribution and reduction of the complex. On MCM-41, the complex and the platinum particles can obviously be deposited from scCO₂ into the mesopores.

The fact that the average particle size is larger than the mesopore diameter of 2.4 nm points at the presence of larger particles on the outer surface and/or to a non-spherical particle shape of the Pt inside the MCM-41 channels.

The supported platinum materials obtained from SFRD were active catalyst for the total oxidation of toluene in air. An additional reductive treatment of the catalyst was not necessary. For instance, the light-off temperature of a 5.6 Pt/MCM-41 was 150 °C, whereas it was at least 20 °C higher on a 1.0 Pt/SiO₂ catalyst prepared via conventional impregnation of silica gel with a platinum salt and subsequent reduction in hydrogen.

CONCLUSIONS

Supercritical fluid reactive deposition (SFRD) is a promising way to prepare noble metal nanoparticles on porous siliceous supports for use as catalysts. As shown here for the platinum complex Pt(COD)Me₂, organometallic precursors can be homogeneously distributed over solid supports with sufficiently large pore diameters. They should be at least higher than those of typical microporous solids such as silicalite-1 ($d_p = 0.5$ nm). A high dispersion of platinum, i.e., the formation of small platinum particles, by SFRD is also favored by a high specific surface area of the support like that of the mesoporous MCM-41-type materials. The extension of SFRD to other porous catalyst supports and other metals as well as metal mixtures for controlled catalyst preparation is currently investigated in our laboratories.

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