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Supercritical deposition of Pt on SnO_2-coated Al_2O_3 foams: Phase behaviour and catalytic performance

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Abstract

Deposition and reduction of an organometallic platinum complex from a supercritical Pt(COD)Me_2/CO_2 solution was carried out to produce Pt/SnO_2 catalysts supported on Al_2O_3 foams for CO oxidation at moderate temperatures. The phase behaviour of the complex in supercritical carbon dioxide was investigated to find the optimum pressure and temperature conditions for the deposition. For the Pt(COD)Me_2/CO_2 mixture, the melting point decreased with increasing pressure from 378 K at 0.1 MPa to 360 K at 25.6 MPa. Additional investigations showed that the solubility of Pt(COD)Me_2 in CO_2 increases from 5.9×10^{-4} mol/mol at 11.2 MPa and 313 K to 3.4×10^{-3} mol/mol at 29.6 MPa and 353 K. The supercritical deposition yielded catalysts with highly dispersed platinum nanoparticles of approx. 3 nm having a narrow size distribution and thus, a superior activity towards oxidation of carbon monoxide in comparison to a catalyst prepared by the conventional aqueous impregnation of Pt.

Keywords: Supercritical fluid; Platinum; Nanoparticle; CO oxidation; Ceramic foam

1. Introduction

The catalytic oxidation of carbon monoxide is an important purification step downstream to, e.g. reforming and combustion processes. In the context of fuel cell technology, in particular, CO removal gained increasing importance since the catalysts of the low-temperature fuel cells are extremely sensitive to poisoning by CO. Here, the CO concentration needs to be reduced from about 1% to below 10 ppm in the presence of excess hydrogen. The preferential oxidation (PROX) of CO, i.e. the selective oxidation of CO to CO_2 with minimum H_2 consumption, could be an option to reach this goal. However, PROX has to be carried out at low temperatures in order to avoid the occurrence of the reverse water gas shift-reaction which produces CO [1] and, therefore, requires highly active catalysts.

The system Pt/SnO_2 has been studied for many years because it has shown to catalyze the CO oxidation at moderate temperatures, where neither platinum nor tin dioxide alone are catalytically active. The high activity is ascribed to a synergistic bifunctional mechanism in which Pt provides the adsorption sites for CO, while oxygen adsorbs dissociatively on SnO_2 [2,3]. The reaction between the adsorbed species occurs at the Pt/SnO_2 boundary. If this synergistic mechanism holds, it should be of extreme importance for a high catalytic activity to realize a large boundary surface area, i.e. to achieve a high dispersion of the platinum particles on the tin dioxide phase.

The preparation of fine dispersed platinum particles of 1–2 nm size on γ-alumina supports is a well-studied process. The precursor here is chloroplatinic acid and the fine dispersion of platinum is achieved by an intercourse of ion exchange and chloride interaction with the amphoteric carrier. In the case of SnO_2, platinum is usually deposited by means of wet impregnation of the SnO_2 washcoat with aqueous solutions of platinum tetramine nitrate [4]. Owing to the relatively low surface area of SnO_2 and the capillarity effects during drying, the achievement of high Pt dispersions is difficult. Here, we report on the deposition and reduction of an organometallic

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Table 1
Thermo-physical properties of gases, supercritical fluids, and liquids [6]

	Gas 0.1 MPa, 285–300 K	Supercritical fluid	Liquid 285–300 K
ρ (kg/m^3)	60–200	200–500	600–1600
D_{ij} (cm^2/s)	0.1–0.4	0.7×10^{-3}	$(0.2–2) \times 10^{-5}$
η (Pa s)	$(1–3) \times 10^{-5}$	$(1–3) \times 10^{-5}$	$(0.2–3) \times 10^{-3}$

platinum complex from supercritical solution. This process is known as supercritical fluid reactive deposition (SFRD) [5].

Thermophysical properties of supercritical fluids are between those of gases and liquids: they offer low viscosity (η), high diffusion rate (D_{ij}) and the absence of surface tension (Table 1).

One of the most promising supercritical fluids for many engineering purposes is carbon dioxide. It exhibits low critical pressure and temperature values ($T_c = 304.13$ K; $P_c = 7.38$ MPa), low toxicity and is chemically inert. These properties have led to the use of scCO$_2$ in various extractive processes such as the decaffeination of coffee, and to the development of novel methods like SFRD for the preparation of nanostructured materials [7–9]. SFRD not only enables the deposition of Pt nanoparticles in narrow size distributions, it also allows for a homogeneous distribution of the metal on carriers with complex geometric structures or tortuous pore networks where impregnation with liquids tends to yield maldistributions under the effects of gravity, surface tension and capillary forces. In this work, supercritical deposition was applied to produce Pt/SnO$_2$ catalysts supported on Al$_2$O$_3$ foams. In the first section, the thermodynamic behaviour of supercritical Pt-solutions is described. In the second part, we compare Pt/SnO$_2$/Al$_2$O$_3$-foam catalysts produced by means of wet-chemical and by supercritical Pt deposition with respect to their physico-chemical properties and to their catalytic activity in the CO oxidation.

2. Experimental

The platinum complex selected for SFRD was dimethyl-(1,5-cyclooctadien)-platinum (Pt(COD)Me$_2$), purchased from Strem Chemicals.

2.1. Phase behaviour of Pt(COD)Me$_2$/CO$_2$ mixtures

The knowledge of solid–liquid–gas (S–L–G) and solid–fluid (S–F) phase behaviour is important to the understanding and design of processes with supercritical fluids. In the case of the SFRD process, an insufficient solubility of the organometallic precursor limits the practical applicability. In addition, the properties of the produced particles such as particle size, size distribution, and morphology are often strongly influenced by the melting behaviour of the mixtures involved.

2.1.1. Melting point depression

For the determination of the pressure–temperature (p–T) projection of the S–L–G curve, the widely used method has been the first melting point method. This measurement technique was applied because of its simplicity and quickness of operation. Usually, the melting point of Pt(COD) under CO$_2$ pressure was determined by finding the melting temperature at a constant system pressure. The static equilibrium cell with an inner volume of 3.3 cm^3 is designed for pressures up to 100 MPa and temperatures up to 473 K and is equipped with three sapphire windows (8 mm in diameter), which allow the observation of the solute and the fluid at high pressure. In a typical experiment, the temperature was increased slowly until the onset of melting was observed. Thereby a heating rate of either 0.05 K/min or 0.1 K/min was used and the constant system pressure is adjusted with the manual piston pump.

2.1.2. Solubility

The solubility of Pt(COD)Me$_2$ in CO$_2$ was determined with a high-pressure variable volume cell. The heatable cell has an internal variable volume that allows changes in cell volume ($V = 3.3$–7.3 cm^3) and pressure via a movable piston. Two sapphire windows (8 mm in diameter) enable a visual observation of the phase behaviour. Phase separation was defined as the point when precipitation of the solid was observed. Cloud points were determined visually by noting the pressure where the organometallic precipitated out of the solution. Repeated measurements were performed to minimize the influence of kinetic effects on the onset of precipitation. Therefore, the system pressure was slowly reduced in the range from 0.6 MPa/min to 1.2 MPa/min. Each cloud point determination was conducted three times giving reproducibility within ±0.2 MPa.

A more detailed description of both apparatus and the experimental procedure is given in literature [10,11].

2.2. Catalyst preparation

45 PPI α-Al$_2$O$_3$ foams (Vesuvius Inc.) were used as supports for the Pt/SnO$_2$ catalysts. The blank foams were coated with tin dioxide by dipping in a 250 g/L SnO$_2$ sol. The sol was prepared by dissolving metallic tin in nitric acid, washing repeatedly the resulted precipitate with aqueous ammonia solution and subsequently with distilled water. The precipitate was then dispersed with cyclohexylamine to form a sol. A detailed description can be found elsewhere [12]. The carrier pieces were coated two times in order to ensure full coverage of the surface. Each impregnation was followed by drying at 353 K and calcining at 623 K.

2.2.1. Supercritical fluid reactive deposition of platinum

The setup used for supercritical deposition comprised a deposition vessel connected by pipes and needle valves on both sides to two screw presses for controlled filling of carbon dioxide and hydrogen under pressure. The stainless steel deposition vessel (49 cm^3) was equipped with carbon/PTFE O-rings, thermocouple, pressure transducer, rupture disk, and a ventilation line with filters to prevent loss of solid organic metal complex. Prior to each experiment, Pt(COD)Me$_2$ and 3–5 SnO$_2$-coated foam pieces were placed into the vessel in two