One-Step Flame-Synthesis of Carbon-Embedded and -Supported Platinum Clusters

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ABSTRACT

Carbon-embedded or -supported Pt-clusters were made by a scalable, single-step flame spray pyrolysis (FSP) process. Pt-containing precursors was dissolved in xylene and sprayed and combusted in a controlled oxidation atmosphere resulting in nanostructured, carbon-embedded Pt-clusters. Combustion of xylene alone and subsequent addition of Pt-precursor downstream of the flame (onto the freshly-made carbon particles) led to carbon-supported Pt-clusters.

The majority of the Pt clusters are in the range of 2 – 5 nm. The presence of Pt decreased the carbon yield by catalytic burn-off. Changing the Pt loading, however, had only little effect. The presence of Pt on the surface was measured by CO-chemisorption. For carbon embedded Pt particles no CO was adsorbed and therefore also no catalytic activity for hydrogenation of cyclohexene was observed.

Carbon-supported Pt-clusters on the other hand were made by adding Pt downstream when carbon formation was finished. These carbon-supported Pt-clusters exhibited catalytic activity

Both carbon-embedded and -supported Pt-clusters possessed the self-preserving size distribution of aerosols grown by coagulation in the free-molecular regime. This indicates that homogeneous gas-phase formation rather than a heterogeneous pathway is present.

Keywords: Carbon black,, Flame spray synthesis, co-sythesis, catalytic soot combustion

1 INTRODUCTION

Most platinum-based catalysts consist of nanometer-sized metal particles embedded in or dispersed on high-surface-area supports [1].

Carbon embedded Pt nanoparticles find application in sensing applications such as for hydrogen peroxide or biomolecules such as glucose or choline [2]. They are produced by thermolysis incorporating them in glassy carbon [3] or by co-sputtering [4].

Carbon supported Pt nanoparticles are used in many catalytic processes, such as hydrogenation, oxidation, and reforming, but also in electrodes for fuel cells [5,6]. These particles are mainly produced in wet-phase processes [7].

Recently it has been shown that FSP is a suitable process for one-step flame-synthesis of carbon-embedded and -supported platinum clusters [8]
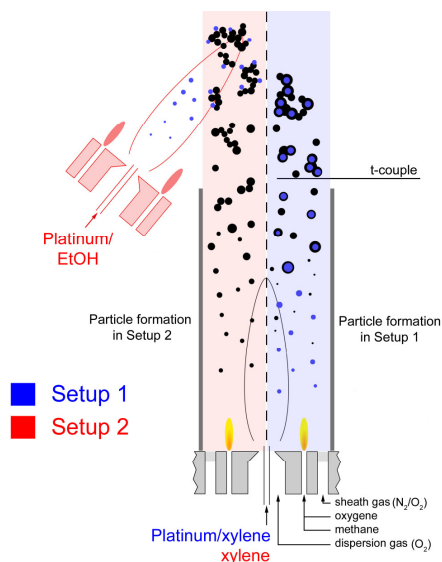

Figure 1: The Experimental setup consists of a flame spray pyrolysis (FSP) enclosed by a quartz glass tube, FSP1. C-embedded Pt clusters were made by dissolving Pt-precursor in xylene and co-oxidizing them. An additional FSP unit (FSP2) was used for synthesis of C-supported Pt clusters. The Pt precursor was dissolved in ethanol/water solution, sprayed, and combusted through the FSP2 unit at the top of the FSP1 chimney into the carbon-loaded effluents of FSP1.

2 EXPERIMENTAL

Figure 1 shows the experimental setup for synthesis of carbon-embedded and -supported Pt clusters by FSP. Xylene (Riedel-de Haën, >96%) was fed into the nozzle (of FSP1) by a syringe pump (Inotech R232) at 5 mL/min and dispersed by 5 L/min nitrogen (Pan Gas, >99.95%) into fine droplets. The spray was ignited and maintained by a premixed flame ring surrounding the spray capillary. This premixed methane/oxygen supporting flame ring was fed by 1.63 L/min CH_4 and 3.88 L/min O_2 throughout all experiments. The reactor is surrounded by a 50 mm outer diameter and 400 mm long quartz glass tube (wall thickness 2 mm). Oxygen and nitrogen were fed as sheath gas with a constant total flow of 7 L/min through a sinter metal ring. The stoichiometry during combustion was controlled by varying the sheath nitrogen to oxygen ratio. With aid of a vacuum pump the product particles were collected on a

glass fiber filter (GF/D Whatman, 257 mm in diameter). For synthesis of carbon-embedded Pt clusters, platinum acetyl-acetonate (Strem Chemicals, 98%) was dissolved in xylene and simultaneously fed into the flame, referred to as setup A in Figure 1 (only FSP1 operated). The Pt-precursor concentrations were chosen as to result in 1 to 5 wt % Pt loading of the final product, whereas the total precursor flow rate was in the range from 2.2 to 5 mL/min. For synthesis of carbon-supported Pt clusters, FSP1 (Figure 1) was used as carbon source while a second FSP unit (FSP2) delivering the Pt precursor was at the top end of the quartz glass tube at an angle of 45° (setup B). In FSP2, oxygen was used as dispersion gas at 3 L/min while the liquid precursor consisted of a mixture of ethanol (Fluka), water (deionized), and platinum acetyl-acetonate. The ethanol (EtOH) fraction in the EtOH/H_2O solvent was varied from 0.5 to 1.0 and platinum acetyl-acetonate concentrations were adjusted to obtain 2.7 to 12 wt % Pt in the product powder.

3   RESULTS AND DISCUSSION

3.1   Pt Clusters Embedded in Carbon.

Two conditions for carbon black synthesis were chosen to analyze formation of carbon-embedded Pt-clusters using only FSP1 (Figure 1). At a Equivalence ratio $\phi =1.31$ and 1.10 high yields of 2 - 5% of the total C in the precursor and the SSAs of 25 and 105 m^2/g, respectivel. Different Pt-contents in the final product (1 to 5 wt-%) were achieved by controlling the Pt concentration in xylene. The Pt clusters seem well dispersed; however, a few single Pt clusters in the size range of tens of nanometers can be observed in STEM pictures. This is attributed to incomplete Pt precursor droplet evaporation at short residence time at high temperatures. Increasing the Pt content also increased Pt cluster size as expected by coagulation and condensation. .
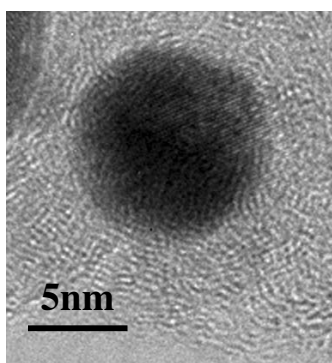
Setup [a]	Pt content [b] / wt%	Surface area / m^2g^{-1}	Pt disp.[c] / %
1	2.6	110	0
2	10	247	5.3
2	12	223	14.0

Table 1: Characteristics of selected Pt/C materials prepared by one-step flame synthesis. The absence of platinum on the surface results in a Pt dispersion of 0%.
[a]See Fig. 1 [b]Thermograviometrically determined [c]Derived from CO chemisorption measurements.

The Pt loading of the product depends not only on the Pt content in the precursor but also on the carbon yield. If the latter is reduced, the product Pt-loading increases without changing the Pt concentration in the precursor. Obviously some Pt clusters serve as nucleation sites for the carbon to grow layer-wise on their surfaces (surface growth) as seen in figure 2. No chemisorption of CO on Pt could be observed for all samples synthesized using only FSP1. Together with the inactivity of these samples for catalytic hydrogenation of cyclohexene, this indicates complete or hermetic coating of all Pt clusters with carbon.

3.2   Carbon-Supported Pt Clusters.

Using the FSP1 combined with the FSP2 carbon-supported Pt clusters were FSP2 provides the Pt while FSP1 served as a carbon black source. Lowering the temperature of the FSP2 unit (by using lower ethanol/water fractions) may have led to incomplete combustion and dissociation of the Pt precursor. This is supported by the lack of CO-adsorption (Table 1) and catalytic activity for this powder (as discussed further down). Only little, if any, Pt surface seemed to be available.
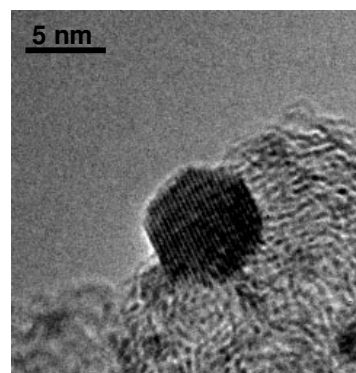

Figure 2: HR-TEM image of carbon embedded Pt nanoparticles. Crystalline Pt particles are surrounded by amorphous, layerwise built carbon.

Figure 3:HRTEM image of carbon supported Pt nanoparticles with Pt particles sitting on the carbon surface.

Figure 3 shows a typical HR-TEM image of these Pt/C particles made with pure ethanol as solvent for the Pt-precursor in FSP2. In contrast to carbon embedded Pt clusters (Figure 2), well-developed Pt clusters are located on the carbon surface being well-attached with a good fraction of Pt surface exposed for reaction.

4   CONCLUSIONS

The production of carbon black with FSP was investigated where the maximum carbon yield was observed at the minimum of the process temperature and the highest SSA was observed close to stoichiometric combustion accompanied with a small yield.

0.2-5.0 wt-% Pt nanoparticles embedded in carbon black were synthesized by introducing the respective amounts of Pt precursor to the xylene fuel (Fig. 1 setup 1). Co-formation of Pt nanoparticles and carbon results in carbon condensation on the freshly formed Pt particles. Pt particles were completely enclosed by carbon as shown by CO chemisorption. Few large Pt particles were detected by XRD and STEM, the majority though was in the range of 2 – 5 nm.

5-12 wt-% carbon black supported Pt nanoparticles were produced by using the above mentioned flame spray combusted xylene as the carbon source and introducing the Pt by aid of an additional gas assist nozzle. These particles were catalytically active for the hydrogenation of cyclohexene showing the accessibility of the Pt surface.

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