



# Efficient aerosol assisted delivery of low-volatility precursor for CVD applications

Laila Pasin<sup>a,\*</sup>, Jörg Meyer<sup>a</sup>, Elisabeth Eiche<sup>b</sup>, Frederik Weis<sup>c</sup>, Gerhard Kasper<sup>a</sup>

<sup>a</sup> Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology (KIT), Strasse am Forum 8, 76131 Karlsruhe, Germany

<sup>b</sup> Institute of Applied Geosciences, Karlsruhe Institute of Technology (KIT), Adenauer-ring 20b, 76131 Karlsruhe, Germany

<sup>c</sup> Palas GmbH, Greschbachstraße 3B, 76229 Karlsruhe, Germany



## ARTICLE INFO

### Keywords:

Aerosols  
Chemical vapor deposition  
Fluidized bed  
Noble metals  
Catalysts

## ABSTRACT

An improved lab-scale process for coating of carrier particles by aerosol assisted chemical vapor deposition (CVD) is described and characterized to produce a highly dispersed, supported noble-metal catalysts. The process is based on a fluidized bed (FB) operated at atmospheric pressure and focusses on an efficient and lossless delivery of precursor vapor, including vapors of low-volatility precursors, to the bed. Precursor is aerosolized (at ambient temperature) applying a suitable solution and then delivered into the FB from above via a double-walled heated tube in which the aerosol is sublimated, the vapor is adsorbed on the carrier particles and then decomposed.

Degree of sublimation, delivery rates and usage efficiencies were investigated applying a tandem-DMA set-up with two precursor substances, namely Pd(TMHD)<sub>2</sub> and MeCpPtMe<sub>3</sub> dissolved in butanone. At 150 °C and a residence time of about 2.5 s, precursor aerosol particles up to about 700 nm were found to sublime to  $\geq 99\%$ . The degree of sublimation could have been increased further by extending the residence time in the sublimation zone. For higher volatility precursors, vaporization/sublimation can be assumed to be complete.

Based on a mass balance of precursor amounts generated, delivered to the bed, and noble metal amounts recovered on the bed material it was found that the method of precursor delivery to the FB from above in combination with aerosol assisted precursor sublimation permits a quasi-lossless method of supplying and using precursor for coating.

The produced catalysts showed superior noble metal dispersion when compared with a commercial sample of same mass loading. The distribution of noble metal nanoparticles (in the range 1–2.2 nm) on an Al<sub>2</sub>O<sub>3</sub> support was found to be very uniform.

## 1. Introduction

The functionality of heterogeneous catalysts depends strongly on their dispersion, i.e. the particle size and specific surface area of the active phase. In order to achieve a stable dispersion on the nanoscale, the active phase, in our application noble metals, is usually deposited onto much larger oxide support particles. There are several commonly used methods to synthesize such supported noble metal catalysts, including crystallization, flame spray pyrolysis, wet impregnation, co-precipitation or sol-gel routes, and chemical vapor deposition (CVD). CVD is a direct deposition process from the vapor to a solid phase, known to offer excellent control over the entire synthesis route, and thus over the physical structure of the catalyst. Other advantages include the achievability of very high

\* Corresponding author.

E-mail address: [laila.pasin@kit.edu](mailto:laila.pasin@kit.edu) (L. Pasin).

<https://doi.org/10.1016/j.jaerosci.2018.09.003>

Received 9 June 2018; Received in revised form 9 September 2018; Accepted 14 September 2018

Available online 14 September 2018

0021-8502/ © 2018 Elsevier Ltd. All rights reserved.

noble metal dispersions and the absence of solvents in direct contact with the product.

Two principal routes of CVD process design have been investigated in recent years: There is an “aerosol route”, where the support particles are first synthesized and dispersed in a gas stream at ambient pressure and then mixed with precursor vapor in a flow reactor, in which the decomposition reaction is initiated. Typically, vapor adsorption and decomposition occur simultaneously on the surface of the support particles, through the intermediary role of function groups (usually hydroxyls) which can be adjusted in density by appropriate means. Such a process is inherently continuous, and therefore offers excellent control over the structure of the active metal phase (Binder, Heel, & Kasper, 2007; Heel & Kasper, 2005), but has a minimal product yield on the order of mg per hour and at a substantial loss of unused precursor material, which tends to decompose mostly on the internal reactor walls.

The other route is via a fluidized bed (FB-CVD). Hierso et al. (Hierso, Serp, Feurer, & Kalck, 1998; Hierso, Feurer, Poujardieu, Kihn, & Kalck, 1998; Hierso, Satto, Feurer, & Kalck, 1996; Hierso, Feurer, & Kalck, 2000; Hierso, Feurer, & Kalck, 1998) were among the first groups to combine the well-established fluidized bed processes with CVD coating technologies. Other research groups followed and successfully synthesized a variety of materials including highly dispersed supported noble metal catalysts (Mu et al., 200; Naumann d’Alnoncourt, Becker, Sekulic, Fischer, & Muhler, 2007; Li, Liang, King, Jiang, & Weimer, 2010). As described in these studies, FB-CVD is essentially a batch process operated in one or more steps at substantially sub-atmospheric pressures around 60–130 mbar. The precursor sublimates in a separate vessel (“sublimator”) under low pressure and elevated temperature. The vapor is then injected into the bottom of the FB through a porous frit that also supports the bed of particles. The fluidization flow (which is often used to supply additional educts such as oxygen to the reaction) is also delivered through the frit, together with the precursor. The bed may be heated during precursor delivery for concurrent decomposition, or one may first let the precursor adsorb and then induce decomposition in a second step by heat or/and a reactive gas.

Two major technical challenges associated with FB-CVD are the generation of sufficient precursor vapor and its delivery to the reaction zone (the bed) wherein the support particles are to be coated (Maury, 1996; Vahlas et al., 2007). CVD precursors are often expensive, have low volatility, and may become unstable chemically in a temperature range where the vapor pressure is high enough to achieve sufficient concentrations. Precursor losses in the frit may exceed the amount available for coating. Although FB-CVD has been widely studied for the production of supported noble metal catalysts, these difficulties are one reason why the technology is often found unsuitable for industrial scale applications. Nevertheless FB-CVD is a relevant technology in various other industrial fields (Bye & Ceccaroli, 2014; Filtvedt et al., 2010; See & Harris, 2007).

This work describes a simple, low-cost FB-CVD process at atmospheric pressure based on aerosol assisted precursor delivery (Xu & Hampden-Smith, 1994; Lim, Huang, Lim, & Mazhar, 2014; Wang, Xia, Meng, & Peng, 2000). The precursor is first converted into an aerosol of fine, sub-micron particles in an inert carrier gas, e.g. by atomization of a solvent-precursor mixture. This aerosol is then sublimated completely and delivered directly into the fluidized bed from above via a compactly built temperature controlled tube (Fig. 1). The implementation of delivery from above has the potential for avoiding massive precursor losses by premature decomposition in the frit that plague many FB-CVD reactors. This point was therefore investigated specifically.

Aerosol assisted precursor delivery as such is not a new concept (Xu & Hampden-Smith, 1994; Choy, 2006; Hong, Kim, & Choi,

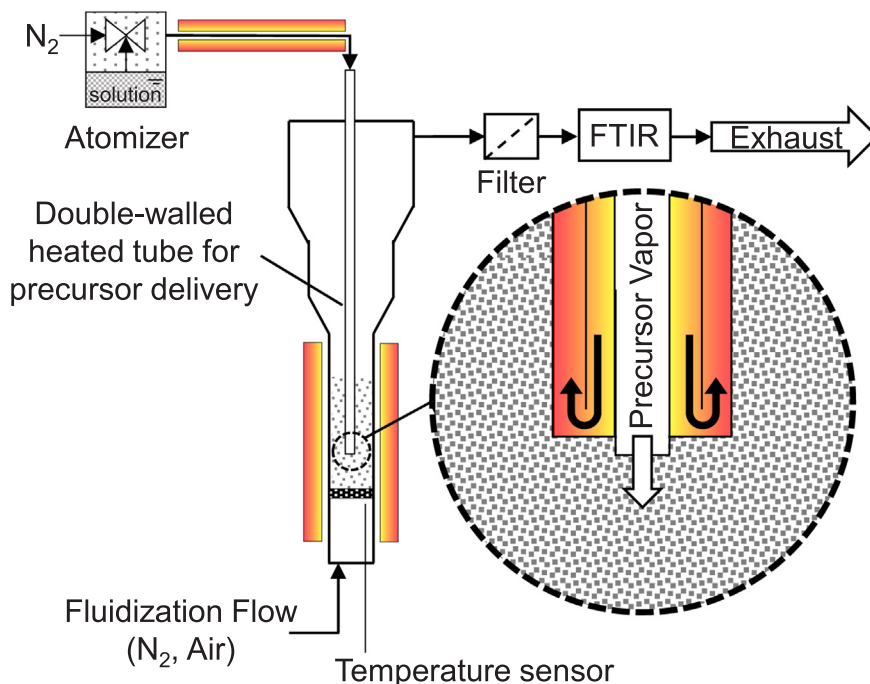


Fig. 1. Schematic of the FB-CVD with the aerosol assisted precursor delivery system.

Download English Version:

<https://daneshyari.com/en/article/11032640>

Download Persian Version:

<https://daneshyari.com/article/11032640>

[Daneshyari.com](https://daneshyari.com)