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Synthesis of supported nanoparticles in supercritical fluids by supercritical fluid reactive deposition: Current state, further perspectives and needs

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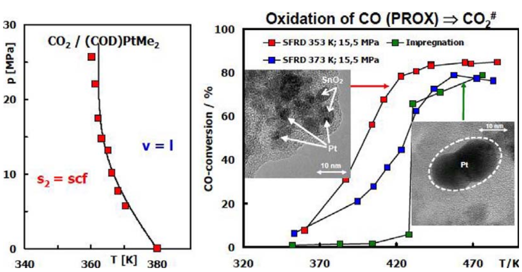
GRAPHICAL ABSTRACT



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ABSTRACT

Supercritical fluid reactive deposition is an environmentally friendly technique for the synthesis of supported mono- or bimetallic nanoparticles. Firstly, the present article gives a short introduction into the fundamental aspects of the particle formation process. A critical survey of published knowledge about synthesis of nanostructured materials and their deposition on different kind of supports is given and the underlying process basics i.e. dissolution of the precursor in the supercritical phase, adsorption or sorption of the precursor on the substrate and reduction of the precursor to its metal form are discussed. Examples for successful applications of these supported nanoparticles are highlighted. Based on a critical analysis and evaluation of the current status, strategies for overcoming the knowledge gaps, for essential future research directions are suggested. Throughout the manuscript, the challenges that need to be overcome for an improved understanding of the relationship between process conditions and obtained product properties are stated.

1. Introduction

Design, development and synthesis of nanostructured materials, such as supported metal nanoparticles (NPs), are of particular interest for both scientific and industrial communities [1–5]. NPs are characterized by unique properties such as high specific surface areas, leading to an enhanced energetic state and thus a higher reactivity. At this scale, optical, magnetic and electrical properties are dramatically sensitive to particle size and shape.

Particle formation with supercritical fluids (SCFs) is one of the early areas of application with SCFs such as $scCO_2$ or scH_2O (not considered in this contribution). The area is still very active with much academic and industrial interest as it offers an effective and environmental friendly pathway for the sustainable design and production of organic and inorganic materials without contamination or degradation.

In general, these SCF-based particle formation processes are often classified as physical (e.g. rapid decompression, anti-solvent effect) and chemical (e.g., hydrolysis, reduction) transformation processes and can be conveniently exploited for the preparation of nanostructured materials for application in a large number of technological important areas

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such as chemistry, energy, electronics, optics, pharmacology, and material science.

In particular, the synthesis of supported mono- or bimetallic nanoparticles by SCF-based particle formation processes is a broad field of promising applications. An interesting preparation route is the use of a SCF as a solvent, reaction, and separation media to achieve high dispersions of NPs on porous substrates by supercritical fluid reactive deposition (SFRD). In addition, SFRD provides an environmentally benign, efficient, and rapid alternative to conventional liquid-phase impregnation techniques as commonly used for the preparation of supported nanoparticles.

However, in order to improve both the technical and economical feasibility of these processes and their optimization, it is crucial to develop a deeper knowledge about the influence of the various operating parameters and processing conditions on the obtained product characteristics. The successful application of this challenging task requires more research and has to be closely connected to an intensive interdisciplinary cooperation between researchers from different but complementary disciplines as well as fundamental and experimental researchers.

Last but not least, the comparison of the performance of materials prepared via SFRD with materials prepared by conventional techniques and the ability to understand and explain the principle of cause and effect would be essential for the progress in SCF based particle formation processes. More details about the different concepts that are currently employed in the preparation of metallic NPs using SCFs are summarized in various overviews (e.g. see without any claim to completeness Refs. [1–5]).

2. Current state

2.1. Supercritical fluid based particle formation

Metal NPs such as platinum (Pt), palladium (Pd), gold (Au) or silver (Ag) are efficient catalysts for a wide variety of chemical reactions such as hydrogenation, hydration and oxidation. Usually the diameter of these catalytically active NPs is in the range from 2 to 10 nm and the particles are characterized by a high surface-to-volume ratio and high surface energy, which enable them to easily form agglomerates. In order to stabilize the NPs and to prevent agglomeration they are usually deposited on porous substrates with high surface areas.

The widespread conventional and established methods for the preparation of supported metal NPs, such as incipient wetness impregnation (IWI), co-precipitation, chemical vapor deposition (CVD) and flame spray pyrolysis (FSP) have some disadvantages and limitations. Supported metal NPs can be prepared by wet impregnation of a substrate, followed by a reductive treatment and an energy-intensive drying step. This method yields often to particles with broad particle size distributions (PSD) and to huge volumes of solvent. Furthermore, this technique is not suitable for aerogels due to the high surface tension of the used liquids, which can cause the collapse of the pores of the aerogels. Major problems associated with co-precipitation are to control the homogeneity of the PSD and the pH of the solution. Chemical vapor deposition requires relatively high temperatures and highly volatile metal precursors that are usually toxic. Furthermore, the mass transfer-limited growth kinetics is an additional disadvantage. Flame spray pyrolysis requires the use of liquid solutions and the high temperatures that are required to reduce the inorganic precursors can cause undesired byproducts. Another drawback of these techniques is the fact that they cannot easily be applied to polymeric substrates.

A promising alternative to these conventional preparation methods is the application of SCFs to design inorganic nanostructured materials by SFRD. Note, that this process is identical with the so-called chemical fluid deposition (CFD), supercritical fluid deposition (SCFD), supercritical deposition (SCD) and supercritical fluid chemical deposition (SFCD) method. Nevertheless the basic principle of the deposition and particle formation process remains the same [1–5].

Usually, SFRD based synthesis of nanostructured materials takes place in batch mode, which is a useful technique for the synthesis of highly crystalline products. However, the drawback of this approach is the relatively long processing time i.a. for reaching adsorption equilibrium, and the difficulty to control nucleation, particle growth and subsequent processing steps separately. However, a promising opportunity for the preparation of highly versatile nanostructures is the continuous processing. The control of the obtained material properties (size, morphology, structure, and composition) can be achieved by choosing specific process parameters such as solvent nature, pressure, temperature, nature of the precursor and its concentration, residence time and additive agents (e.g. co-solvent or surfactants). Nevertheless, both approaches can be used to create interesting and very versatile materials with desired properties that are applicable in numerous technologically important fields.

In the following, we are giving a short introduction into the batch-mode SFRD technology and its underlying process basics. In 1995 the Watkins group used this process for the first time as a new approach for the preparation of thin metal films and Pt nanoparticles on porous Al_2O_3 at low temperatures [6]. Thereafter, the groups of Cabanas [7,8], Erkey [1,4,5,9] and Türk [2,10–12] developed the thermodynamically controlled synthesis of supported mono and bimetallic or metal oxide NPs, while the group of Aymonier [3,13,14] introduced the kinetically controlled surface nano structuration as a fast and versatile concept of SFRD.

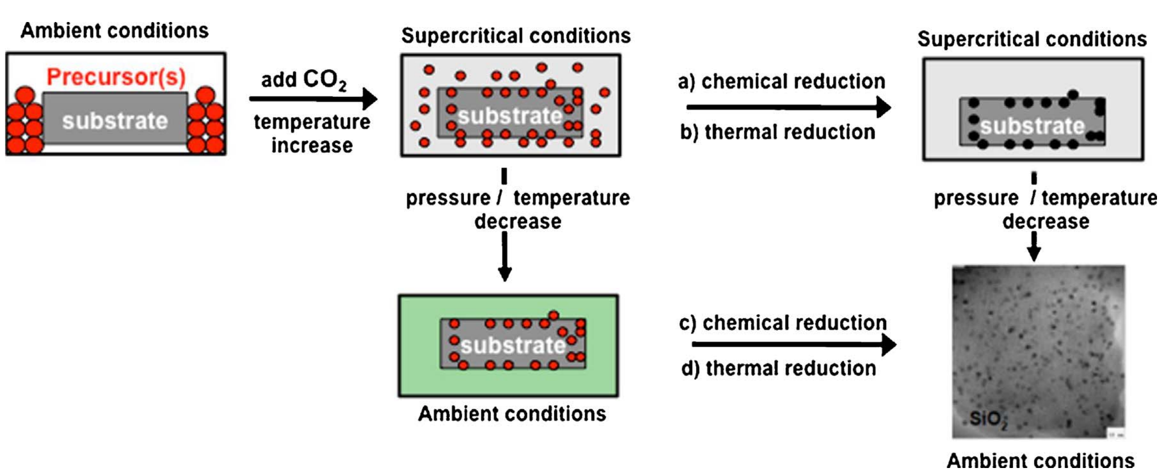

Fig. 1. Schematic representation of the SFRD process, more details about the experimental procedure are given in literature e.g. [1,2,12,16]. Precursor: e.g. $Pt(cod)Me_2$; $Pd(acac)_2$; Substrate: nano-powders of e.g. Al_2O_3,TiO_2, SiO_2 etc.