



Supercritical deposition: Current status and perspectives for the preparation of supported metal nanostructures



Selmi Erim Bozbağ^{a,b}, Can Erkey^{c,d,*}

^a Paul Scherrer Institute, Laboratory for Catalysis and Sustainable Chemistry, CH-5232 Villigen PSI, Switzerland

^b ETH Zürich, Institute for Chemistry and Bioengineering, Zurich CH-8093, Switzerland

^c Department of Chemical and Biological Engineering, Koç University, 34450 Sariyer, Istanbul, Turkey

^d Koç University TÜPRAŞ Energy Center (KUTEM), Koç University, 34450 Sariyer, Istanbul, Turkey

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ABSTRACT

Supercritical deposition is an alternative technique to incorporate metals on supports. It has been used to deposit a wide variety of single or multi-metallic morphologies such as highly dispersed species, nanoparticles, nanorods and conformal films on high surface area supports, polymers and crystalline substrates. Preparation consists of three main stages which are the dissolution of a metal complex in a supercritical fluid, adsorption or sorption of the metal complex onto support and the conversion of the adsorbed complex to metal species. Studies associated with each of these stages were described along with a thorough summary of recent studies on the preparation of the aforementioned materials. Perspectives for future studies were presented at the end of each section.

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1. Introduction

Supported metals, metal oxides and sulfides are frequently used in catalysis, electronics and optics. Such supported materials can exist in different morphologies such as atomically dispersed metals, nanoparticles, nanorods and thin films. Nanostructured materials are highly interesting scientifically and hold potential for a wide range of technological applications due to their higher surface-to-volume ratios. In nanoparticles with very small particle size, a significant fraction of the nanostructure is composed of interfaces/grain boundaries and hence a large fraction of the atoms resides in grain boundaries. In this size range, phenomena associated with atomic and molecular interactions strongly influence the macroscopic properties of materials and give rise to the unique electronic, optical, electro-optical, magnetic and catalytic properties which are often superior to the properties of their conventional coarse-grained polycrystalline counterparts [1].

* Corresponding author at: Department of Chemical and Biological Engineering, Koç University, 34450 Sariyer, Istanbul, Turkey. Tel.: +90 212 3381866; fax: +90 212 3381548.

E-mail address: cerkey@ku.edu.tr (C. Erkey).

Supported metals are extensively used in catalysis. They are generally metals or metal oxides which are dispersed atomically or as nanoparticles on the internal surface of a support material. It is difficult to control metal distribution, nanoparticle size, size distribution, metal loading and nanocrystal orientation with conventional routes. For example, in liquid phase impregnation techniques, the control of catalyst properties such as metal distribution, nanoparticle size and single/binary metal loading is extremely challenging due to the complex chemistry of transition metal ions in solution-support medium along with the slow diffusion through liquids [2]. Moreover, in wet impregnation a tedious post-deposition filtration step is involved and agglomeration of particles during the evaporation of the solvent is quite common. The technique is also not suitable for materials such as aerogels because of the high surface tension of the liquid which can cause the collapse of the nanosized pores of the aerogels due to very high capillary pressure. In the co-precipitation method, controlling the homogeneity and the pH of the solution are the major problems. Sol-gel routes are advantageous since they enable one-pot synthesis of supported nanoparticles but they may suffer from the interference of the precursors with the polymerization chemistry leading to undesired properties. Vapor phase depositions are limited by vapor pressure of metal precursors and may require sequential deposition steps to reach the desired metal loading [3].

Furthermore, none of these methods are easily applicable to polymers [1,4].

Currently, in processor fabrication, the general strategy is to integrate a maximum number of transistors onto a limited space to increase processing speed. This is achieved by decreasing the size of the transistors and thus the interconnects. In interconnect technology, microprocessor interconnect requirements are lower than 32 nm as of 2014 [5] and aspect ratios higher than 6 are necessary. Other requirements include good uniformity with low impurity and lower growth temperatures [6]. Good material properties with minimum damage to the substrate materials are also needed. Furthermore, environmental regulations are becoming stricter in the coating industry [7]. For production of thin films for electronics and optics, the chemical vapor deposition (CVD) is considered as the most established technique. Using CVD, it is possible to produce dense and relatively pure films with controllable surface morphology. However, large thermal gradient characteristics of CVD units lead to a wide variety of flow patterns that affect film thickness, compositional uniformity and impurity levels [8]. Furthermore, highly volatile metal complexes (which are usually toxic) and relatively high processing temperatures are required. Another drawback of CVD is the mass transfer limited growth kinetics [9]. Aqueous plating techniques on the other hand suffer from drawbacks such as generation of large volumes of wastewater and poor control of the deposition process.

Using supercritical fluids (SCFs) to deposit metals and metal oxides on surfaces has been attracting increased attention due to the attractive properties of supercritical fluids. The advantages of using SCFs especially supercritical carbon dioxide ($scCO_2$) as deposition medium can be summarized as:

1. solvent power can be adjusted with changes in pressure and temperature,
2. no liquid waste is generated,
3. no solvent residue is left on the substrate,
4. mass transfer rates are fast compared to liquids which may enable fast rates of deposition,
5. low surface tension and
6. complete miscibility with reacting gases such as hydrogen or oxygen

Furthermore, $scCO_2$ can sorb into many polymers and the exposure to $scCO_2$ causes these polymers to swell which makes it possible to impregnate various polymers with metal complexes.

In this article, the physical and chemical fundamentals of SCD process for the preparation of supported nanostructures are described and recent developments in the area are reviewed. Perspectives are given at the end of sections.

2. Supercritical deposition

Highly dispersed metal or metal oxide nanoparticles or thin films can be deposited on a variety of organic or inorganic substrates using SCD. This process was first reported by the Watkins group [10] and includes three major steps shown in Fig. 1:

1. The dissolution of the metal precursor in SCF,
2. The sorption or the adsorption of the metal complex from SCF phase to the substrate,
3. The conversion of the adsorbed metal complex to its metal or metal oxide form,

Using SCD, nanoparticles or films of metals and oxides including Cu, Co Ni, Mo, Pt, Pd, Ru, Ag, Au, Rh, HfO_2 , ZrO_2 , yttria stabilized zirconia, ceria, titania, tantalum, niobium and bismuth oxide have

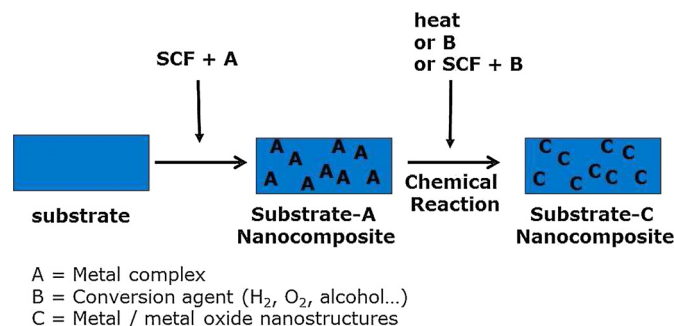


Fig. 1. Schematic representation of the SCD.

been deposited on a wide variety of supports such as polymers, carbon nanotubes, graphene, carbon blacks, aerogels, alumina, silica and silicon. In SCD, the most widely studied metal so far has been Pt, a commonly used catalyst in fuel cells or in hydrogenation since it stands out with its high catalytic activity. Carbon supported Pt electrocatalysts prepared using SCD were found to be highly active for oxygen reduction and hydrogen oxidation reactions [11–17]. Studies on SCD were reviewed over the last decade [4,18–22]. There is quite an increase in the number of studies appeared in this field over the last few years and review of the current status is necessary. Therefore, a summary of SCD studies published since 2008 are presented here. Summary of the studies on supported nanostructures are presented in Table 1 and on supported conformal films are given in Table 2.

2.1. Dissolution of metal complexes in $scCO_2$

As previously mentioned, the first step in SCD technique is the dissolution of a metal complex in a SCF. Along this line, the knowledge on thermodynamics of metal complexes and their mixtures in SCFs is very important. There are very few sets of data for the Solid–Liquid–Gas behavior of metal complexes in CO_2 . Türk group measured the melting point depression curves for $Pt(cod)me_2$ [62,105] and $Cu(thd)_2$ [105] from 0.1 to 25.7 MPa. Melting point of $Pt(cod)me_2$ decreased from 105 °C at 0.1 MPa to 87 °C at 25.7 MPa whereas for $Cu(thd)_2$ the melting point decreased from 199 °C at 0.1 MPa to 126 °C at 19.7 MPa.

In the case of preparation of supported nanoparticles, the adsorption isotherm of the metal complex-support system in the presence of SCF is an important parameter for the control of metal loading on the support. In the adsorption isotherm, the metal complex concentration in the fluid terminates at a particular concentration which is the solubility of the metal complex in SCF. The knowledge of variation of the solubility with temperature and pressure is equally important. Fluid phase concentration is also important for mass transport issues since higher concentrations lead to higher mass fluxes.

Metal precursors usually used in SCD are metal chelates including β -ketonates, fluorinated β -ketonates and organometallic complexes. The solubility of the metal complexes with ligand types including diketones, dithiocarbamates, macrocycles, organophosphorous ligands, hydroxamic acids in $scCO_2$ are available in the literature [106–110]. Complexes with fluorinated ligands have substantially higher solubilities as compared to their non-fluorinated analogues [108]. Carbonyl ligands also increase solubility of a metal complex due to its specific intermolecular interactions with CO_2 [111,112]. The incorporation of more non-polar methyl or *tert*-butyl groups in the complexes also allows for the enhanced solubility [106,113]. Prediction of the solubility of metal complexes in $scCO_2$ is also possible using semi-empirical correlations or Equation of State based methods [109,114].

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