Production of supported gold and gold–silver nanoparticles by supercritical fluid reactive deposition: Effect of substrate properties

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ABSTRACT

Supported monometallic gold and bimetallic gold–silver nanoparticles on different substrates are prepared by reactive deposition of $Au(acac)Me_2$ and $Ag(cod)(hfac)$ from supercritical carbon dioxide. Among others such supported metallic nanoparticles are suitable as catalysts for chemical reactions, e.g. CO oxidation. The influence of the substrate properties on the resulting mean particle size, distribution, particle structure and metal loading with focus on the provided surface area was investigated. The obtained mono- and bimetallic nanoparticles were characterized by transmission electron microscopy, electron dispersive X-ray spectroscopy, optical emission spectrometry with inductively coupled plasma and UV–Vis spectroscopy. The mean particle size varied between 2 and 26 nm for monometallic gold and between 4 and 28 nm for bimetallic gold–silver nanoparticles depending on the used substrate (mean particle size on BP2000 < γ-Al_2O_3 < TiO_2 < β-CD). EDXS line scans of single particles show both monometallic and bimetallic gold–silver core/shell particles consisting of a gold core which is surrounded by an intermetallic shell with an average composition of Ag_1Au_3.

1. Introduction

During the past decades supercritical processes using carbon dioxide (CO_2) as solvent and reaction medium have been extensively investigated with the aim of synthesizing functionalized materials for a wide range of applications including catalysis [1], biomedicine [2], spectroscopy [3] and microelectronics [4]. The application of supported metallic or metal oxide nanoparticles as catalysts in chemical reactions has become very important since more than 90% of all chemical processes involve catalytic reactions. Metal nanoparticles are characterized by high surface-to-volume ratio with high surface energy, which enables them to easily form agglomerates. To stabilize the nanoparticles and to prevent agglomeration the nanoparticles are deposited on substrates with high surface area [5–7].

Amongst supercritical processes, the supercritical fluid reactive deposition (SFRD) provides an easy method to produce metallic nanoparticles with defined particle size, distribution and metal loading [7–9]. In the SFRD process, supercritical carbon dioxide (sc-CO_2) is usually used to dissolve organometallic complexes, followed by molecular adsorption of the complexes onto a suitable substrate, and complex reduction with e.g. hydrogen to the metal form. Regarding the influence of the process conditions, supercritical deposition processes have already been well-examined over the past twenty years, since Watkins et al. established the method to deposit metal thin films on substrates in 1995 [10]. It has been discovered that the resulting particle size does not only depend on the process parameters, but also on the kinetics of the precursor transformation and on the chemical and physical properties of the substrate and the organometallic compounds [7,10–12].

Noble metals and metals of the platinum group which exhibit enhanced catalytic activity have been deposited on a large number of substrates with different surface properties including aerogels, carbon blacks, carbon nanotubes, ceramics, silica, silicon wafers and polymers [1–12]. The catalytic behavior of such metallic nanoparticles is directly related to the particle properties, the nature of particle bonding to the substrate surface, and hence directly related to the manufacturing process [13]. It has been shown that catalysts obtained from supercritical deposition processes exhibit some of the highest catalytic activities in chemical reactions [1,9].

In particular, supported gold nanoparticles show a remarkable catalytic behavior. Since the gold nanoparticles are bound to the surface of the substrate, the high catalytic activity may well originate at free sites at the gold-substrate interface [14]. It has been shown that gold nanoparticles interact with the substrate surface, enhancing the catalytic activity by an electron transfer from the

substrate to the metal nanoparticle surface [15–18]. Deposited on titanium, silica and other metal oxides, they can be used for, e.g. the hydrogenation of carbon dioxide for the methanol synthesis or the oxidation of CO [17,19]. Gold has a strong affinity toward CO, but is unable to bind O_2. Doping gold nanoparticles with another O_2 adsorbing metal may well lead to an enhanced activity. The metal, e.g. silver, can provide the O_2 that is necessary to oxidize the activated CO bound onto the gold surface [20].

2. State of the art

Several research groups have deposited monometallic silver and gold nanoparticles on various substrates using different precursors. Due to their high solubility in sc-CO_2, Ag(cod)(hfac) and Au(acac)Me$_2$ are often used in supercritical fluid based processes.

Monometallic deposition of silver from Ag(cod)(hfac) has been studied quite well. Casciato et al. obtained particle sizes between 20–200 nm from the supercritical deposition of Ag(cod)(hfac) on silicon and glass surfaces [21]. Yang et al. also used Ag(cod)(hfac) in sc-CO_2 to impregnate polymer substrates in order to create semiconducting materials [22]. They obtained particle sizes between 2 and 10 nm after an impregnation time of 1–24 h at 313 K and 10.3 MPa in sc-CO_2. The reduction was carried out after depressurization to ambient pressure and by adding hydrogen to the system. Rybaltovskii et al. impregnated VYCOR® glass and synthetic opal matrices with silver nanoparticles from Ag(cod)(hfac) at temperatures higher than 323 K and a pressure of 20 MPa, followed by thermal reduction in air [23]. The average silver particle size was 4–5 nm. Gittard et al. impregnated textiles with silver aggregates to form antibacterial fabrics [2]. Nazem et al. used the dimer of Ag(cod)(hfac) to synthesize reflective PEEK films with silver nanoparticles <10 nm [3].

Au(acac)Me$_2$ has rarely been used in supercritical deposition processes. Cabañas et al. deposited gold films on SiO_2 and TiN substrates in a H_2-assisted reduction applying temperatures ranging between 333 and 398 K and a process pressure of either 13.8 or 15 MPa [4]. They achieved highly reflective gold films with a thickness of 100–400 nm. Wong et al. synthesized gold nanoparticles impregnating silica or polymer substrates with a solution of Au(acac)Me$_2$ in sc-CO_2 at 313 K and 27.58 MPa [24]. After 24 h of impregnation the process pressure was released followed by the reduction at 353 K with a pressure of 10.34 MPa in continuous hydrogen flow for 24 h. For another 24 h the sample was purged with sc-CO_2 at 313 K and 27.58 MPa. The obtained average particle size ranged from 3.7 to 6.6 nm.

Until now, bimetallic gold–silver nanoparticles have been mainly synthesized in wet impregnation processes using water-soluble silver and gold salts, such as $AgNO_3$ or $HAuCl_4$, and strong reducing agents to form stable nanoparticle dispersions. To synthesize gold–silver nanoparticles, the substrates are added to the reaction solution prior to the reduction of the metal salt. Afterwards several steps, including filtration, washing, drying and calcination are necessary to obtain the metallic products [20]. Dispersions and materials such as binary alloys, core/shell nanoparticles and nanorods in varying concentrations and with different metal content have already been synthesized and documented [20,25–31]. Yet nanoparticle structures with a gold core and an alloyed gold–silver shell have not been synthesized. These gold core/gold–silver shell nanoparticle structures are expected to be catalytically very active and suitable for CO oxidation. In addition, no attempts to synthesize bimetallic gold–silver nanoparticles in a supercritical CO_2 based process have been published so far.

The objectives of this study are to prepare supported bimetallic gold–silver nanoparticles in a process using supercritical CO_2 and to investigate the influence of substrate properties on metal loading,
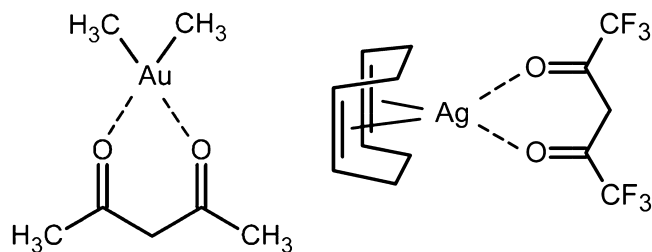

Fig. 1. Molecular structures of Au(acac)Me$_2$ (left) and Ag(cod)(hfac) (right).

particle size and distribution by applying different characterization methods.
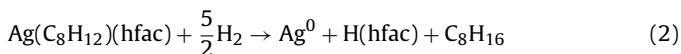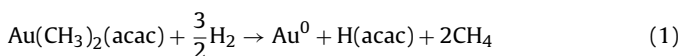
3. Experimental

3.1. Materials

The molecular structures of the organometallic precursors used in this investigation are depicted in Fig. 1 while some selected physical properties of the precursors, of CO_2 and of H_2 are summarized in Table 1. Dimethylacetylacetonato-gold(III) (Au(acac)Me$_2$) with a purity of 98% was obtained from STREM Chemicals Inc. 1,5-Cyclooctadienehexafluoroacetylacetonato-silver(I) (Ag(cod)(hfac)) with a purity of 99% was purchased from Sigma–Aldrich Chemie GmbH. Carbon dioxide (CO_2) with a purity of 99.995% and hydrogen (H_2) with a purity of 99.9990% were obtained from Linde AG. All substances were used without further purification.

Four different substrates were used for the deposition of metal nanoparticles. Titanium dioxide TiO_2 (AEROXIDE®P25) was purchased from Evonik Industries AG, aluminum oxide γ-Al_2O_3 from Sigma-Aldrich Chemie GmbH, β-cyclodextrin β-CD (CAVAMAX®W7) from WACKER Chemie AG and BlackPearls®2000 BP2000 (carbon black) was obtained from Cabot International. All substrates were used as received. TiO_2, γ-Al_2O_3 and BP2000 are nano powders with a mean particle size <50 nm, characterized by large and in case of BP2000 super high specific surface area S_{BET} (determined by Brunauer–Emmett–Teller theory). Selected properties of BP2000, γ-Al_2O_3, TiO_2 and β-CD are listed in Table 2. The TEM images in Fig. 2 show the pure substrates prior to metal deposition.

3.2. Reduction mechanisms

Au(acac)Me$_2$ and Ag(cod)(hfac) were chosen as precursors and their reduction pathways in reaction with hydrogen (cf. Eqs. (1) and (2)). All byproducts are gaseous and/or soluble in sc-CO_2 and can be easily transported out of the vessel during the depressurization.

The reduction of organometallic gold and silver complexes with hydrogen in supercritical carbon dioxide generally proceeds according to the following mechanisms:

$$Au(CH_3)_2(acac) + \frac{3}{2}H_2 \rightarrow Au^0 + H(acac) + 2CH_4 \tag{1}$$

$$Ag(C_8H_{12})(hfac) + \frac{5}{2}H_2 \rightarrow Ag^0 + H(hfac) + C_8H_{16} \tag{2}$$

In contrary to Au(acac)Me$_2$ and Ag(cod)(hfac), the reduction of Pt(cod)Me$_2$ by hydrogen has been studied quite well and its mechanism is known to be autocatalytic [33]. In earlier experiments it has been found that the reduction of Ag(cod)(hfac) is incomplete at temperatures below 373 K and a pressure of 15.5 MPa. However, in the presence of Pt or Au the reduction takes place and bimetallic particles are formed. Therefore it can be assumed that the reduction of Ag(cod)(hfac) might be catalyzed by elemental platinum or gold.