Catalytic materials prepared by chemical vapor deposition

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Abstract. In the 1980’s appeared the first several scientific papers dealing with chemical vapor deposition (CVD) of nanostructured catalytic materials. Since then, the tremendous increase in the number of related publications indicates the significant importance of CVD for the preparation of catalysts. CVD has the capability to generate various types of catalytically attractive nano-scale structures by modifying the surface properties of massive or even nano-divided substrates. Relatively new CVD processes such as catalytic CVD, fluidized-bed CVD, rotary CVD, two-step CVD and large spot laser CVD allow the formation of nanoparticles, nanotubes, nanofibers, nanocomposites and porous or oriented films. Intensive research is being performed on the production of CNTs and the preparation of supported catalysts by CVD. This paper provides an overview of the relatively new CVD processes involved in the preparation of catalytic materials and some representative examples reported in the open literature.

1. Introduction

Chemical vapor deposition (CVD) is an important technique for the production of catalytic materials as it has the capability to generate various types of nanostructures by modifying the surface properties of massive or even nano-divided substrates. The necessity to improve the performance and cost-benefit of catalytic materials has motivated the search of alternatives of synthesis to enhance efficiently their textural and morphological properties. Notably, although CVD has been generally used in materials processing technology for the synthesis of dense and continuous films over more than hundred years, it has been extensively investigated to produce catalytically important structures such as nanoparticles \cite{1}, nanotubes \cite{2}, nanofibers \cite{3}, nanocomposites \cite{4} and porous \cite{5} or highly oriented films \cite{6} of valuable support, promoter or active materials. Various CVD processes developed during the last three decades allow the formation of nano-scale structures. The relatively new processes include catalytic CVD \cite{7}, fluidized-bed CVD \cite{8}, rotary CVD \cite{9}, two-step (precursor vapor adsorption-decomposition) CVD \cite{10} and large spot laser CVD \cite{11}. To fabricate supported catalysts, the incorporation of active nanoparticles on high surface area porous supports is performed industrially by wet chemical methods including ion-exchange, co-precipitation, sol-gel, and wet impregnation. However, CVD has received increasing attention as an alternative for the preparation of supported catalysts because of its significant advantages over the traditional methods. Several of the new CVD processes allow the incorporation of active nanoparticles on fine-divided porous supports in a gaseous phase, i.e. without the need of liquid solvents and their drying and reduction steps, which may promote undesirable changes of the active particle size. Moreover, the higher dispersions and...
more uniform size distributions of the active phase in catalysts prepared by CVD have been reported to influence positively the catalytic activity. Fluidized-bed chemical vapor deposition (FBCVD) is frequently employed for the incorporation of particles on the surface of sub-micron particles [12]. In addition, catalytic CVD (CCVD) and rotary reactor CVD are considered as the most suitable techniques for the large scale and low-cost production of single- or multi-walled carbon nanotubes (CNTs) [9, 12-13]. More recently, FBCVD is also being employed for the preparation of CNTs on active metal particles [14-17]. CNTs and carbon nanofibers (CNFs) are being employed as catalytic supports [18]. Two-step CVD may produce highly dispersed metal active nanoparticles on the surface of CNFs and titania nanotubes (TNTs) even at high metallic loads [19-20]. Conventional CVD may produce catalytically active films [21], composites [22], CNTs [23] and particles at the micro- or nano-scale levels [1] by an adequate control of the deposition conditions. Enhanced CVD techniques such as plasma or laser CVD are being used to prepare porous and favorable oriented catalytic films.

The first several attempts at CVD of nanostructured catalytic materials were published in the 1980’s. Since then, there is a sharp increase in the total number of scientific papers dealing with CVD of supported catalysts, CNTs, CNFs, nanocomposites, porous films and oriented films. It reveals the increasingly importance of CVD in the field. The tremendous increase is mainly due to the intensive research on CNTs production and the preparation of supported catalysts by CVD. In this paper, the relatively new CVD processes involved in the preparation of catalytic materials and some representative examples are reviewed.

2. Catalytic materials prepared by conventional CVD

Ni powders are a typical example of catalytic materials produced by conventional CVD, particularly for fuel cell electrodes. Gas-phase particle formation occurs in CVD at high reactant concentration and substrate temperature. By carefully controlling the homogeneous gas-phase reaction conditions, nanometer-scale particles can be produced by conventional CVD. Figure 1 shows quasi-spherical Ni powder-600 nm mean particle size prepared by thermal decomposition of nickel carbonyl gas using conventional CVD [1].

![Figure 1. Quasi-spherical Ni powder-600 nm mean particle size prepared by thermal decomposition of nickel carbonyl gas using conventional CVD [1].](image)

The use of metal organic precursors in CVD is an alternative to prepare nano-scale noble metal particles. The impurity carbon arising from the thermal decomposition of the metal organic precursors could hinder the growth of continuous films, thereby producing porous films consisting in nano-scale metal particles surrounded by carbon. Nanocomposite porous films such as Pt-C, Ir-C, Ru-C, Pt-YSZ
and IrO$_2$-YSZ prepared by conventional metal organic CVD have been applied as catalytic electrodes for solid YSZ electrolytes [5, 22, 24-26]. Figure 2 depicts the a.c. impedance spectra of several nanocomposites films applied on the surface of YSZ solid electrolyte pellets by metal organic CVD [5]. The smaller the semicircle, the easier the charge transfer associated. The large semicircles (right-hand side of figure) are associated to charge transfer at the YSZ/electrode/O$_2$ gas triple phase boundary, TPB. The extremely small semicircle for Ir-C (magnified in the inset) indicates that this electrode, in particular, is highly reversible and catalytic for the charge transfer at the TPB. The interface conductivity resolved from a.c. impedance spectra for the Ir-C cluster film electrodes was about 100 times greater than that of pure Pt and Ir electrodes.

The flexibility of CVD to modify porous surfaces is strongly influenced by the chemical nature of the precursor. Pt nanoparticles (1-5 nm) with high degree of non-agglomeration and uniform distribution onto the microporous side of a commercial gas-diffusion layer using liquid injection metal organic CVD were contained in a penetration depth of 14 μm [27]. The catalytic performance of the CVD Pt electrode (104-225 μg Pt cm$^{-2}$) in a proton-exchange membrane H$_2$/O$_2$ fuel cell was shown to be better than a commercial electrode containing 500 μg Pt cm$^{-2}$. Single-phase Ru$_x$Ir$_{1-x}$O$_2$ catalytic films prepared by metal organic CVD showed to be very promising for the oxygen evolution reaction due to a synergistic effect [21]. Conventional CVD has also allowed the preparation of Pt-Ir/TNTs, Ru/MgO and Ru/SiO$_2$ catalysts [28-29]. Despite a uniform distribution of Pt-Ir particles, catalyst prepared by metal organic CVD was found to be less active in the cyclohexene disproportion reaction than a wet impregnated Pt-Ir/TNTs catalyst. Figure 3 shows a TEM image of Pt-Ir particles on the surface of TNTs prepared by metal organic CVD. The low activity was associated to the higher particle size of Pt-Ir particles than those obtained by wet impregnation. However, CVD Pt-Ir/TNTs catalyst showed a high selectivity to benzene at temperatures higher than 150 °C [28].

3. Supported catalysts prepared by FBCVD

FBCVD was first applied to the synthesis of silicon for microelectronic applications, and currently employed for the preparation of supported catalysts and the growth of CNTs. Basically the FBCVD
system consist of a vertical reactor in which an upward flow of precursor and carrier gas mixture fluidizes the solid support particles. The operational temperature is kept by an electrical furnace around the reactor. Compared with conventional methods (wet impregnation, ion exchange and co-precipitation), the production of supported catalysts by FBCVD has significant advantages [12]. In the absence of liquid solvents, the drying and subsequent calcination and reduction steps can be eliminated preventing the aggregation of active particles which would significantly lead to the detriment of catalytic activity. The dispersion of the catalytic particles is a key parameter in supported catalysts. In FBCVD, the surface area available for the deposition becomes extremely high in particular by using porous powders as supports with a specific surface area of about 160 m$^2$/g. The gaseous precursor would be totally consumed within a few centimeters after introducing into the fluidized-bed reactor. However, convenient FBCVD allows the homogeneous distribution of the precursor gas compensating the potential heterogeneity. The quality of fluidization strongly depends on the properties of the support particles, such as size, size distribution and density. Fortunately, the usual oxide particles ($\text{Al}_2\text{O}_3$, $\text{SiO}_2$, $\text{TiO}_2$, $\text{MgO}$ and aluminosilicates) employed for the preparation of supported catalysts are, in general, easy to fluidize belonging to Geldart-A classification (ideal for fluidization) of powders with a small mean size (20-150 $\mu$m) and low density [30]. Noble metal particles including Rh, Pd, and Pt have been deposited on $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, and activated carbon (AC) support particles by FBCVD [31-32]. Figure 4 shows the TEM image of 1 mass% Rh/$\text{SiO}_2$ catalyst prepared by FBCVD. The activity of this catalyst in hydrogenation of 1-octane was shown to be higher than that of a 1 mass% Rh/$\text{SiO}_2$ catalyst prepared by impregnation [8]. The high activities of FBCVD Pt/AC and Rh/AC catalysts in acetic acid hydrocarbonylation and benzene hydrogenation have been attributed to the higher purity of Rh and better dispersion of Pt compared with similar catalysts prepared by impregnation [31]. Not only noble metal but also Cu/$\text{Al}_2\text{O}_3$, Fe/$\text{Al}_2\text{O}_3$, Mo/$\text{Al}_2\text{O}_3$, and Fe-Mo/$\text{Al}_2\text{O}_3$ catalysts have been prepared by FBCVD [33-34].

![Figure 3. TEM image of Pt-Ir particles on the surface of TNTs prepared by metal organic CVD [28].](image1)

![Figure 4. TEM image of 1 mass% Rh/$\text{SiO}_2$ catalyst prepared by FBCVD [8].](image2)

4. Carbon nanotubes (CNTs) prepared by CCVD, FBCVD and rotary CVD

Multi- or single-walled CNTs are produced by CCVD, FBCVD and rotary CVD. Particularly, FBCVD and rotary CVD are highly attractive for the growth of CNTs due to the lower cost, high purity and high potential for large-scale production [9, 12-17]. The growth of CNTs by CCVD involves the decomposition of a carbon-containing gas source on catalyst particles such as Fe, Co and Ni and the subsequent CNT growth from the particles. In a typical horizontal fixed-bed CCVD system, the catalyst particles remain stationary in boats inside the reactor and the carbon gaseous source is
introduced when the required temperature is attained. Due to the system configuration, the efficiency of the CNTs growth is significantly affected by an inhomogeneous gas-solid contact. As CNTs grow on the catalyst particle surfaces, the contact between the particles and the gas carbon source is reduced in CCVD. Comparatively FBCVD and rotary CVD provide homogeneous and larger gas-solid contact since the continuous movement of catalyst particles allows the entire surface of each particle in contact with the gas source during deposition. Consequently, FBCVD and rotary CVD processes are more efficient for the growth of large quantities of CNTs. As compiled by Iyuke, rotary CVD has superior rate of production of CNTs (0.050 kg/h) followed by FBCVD (0.042 kg/h) and then horizontal fixed-bed CCVD (0.020 kg/h) [15]. A pilot mass production of agglomerated multi-walled CNTs by FBCVD was reported to yield a rate of 2.08 kg/h [17]. In addition, a production of CNTs as high as 3.0 kg/h was reported when high surface area lamellar Fe/Mo/vermiculite is employed as catalyst in FBCVD [16]. Figure 5 presents a TEM image of a bundle of SWCNT obtained at 1050 °C by FBCVD [14].

![Figure 5. TEM image of a bundle of SWCNT obtained at 1050 °C by FBCVD [14].](image)

CNTs and CNFs are of interest as catalysts or catalyst supports for heterogeneous catalysis as well as for electrocatalysis [18]. Various industrial catalytic or electrocatalytic reactions such as hydrogenation and dehydrogenation, hydroformylation and electro-oxidation reactions have been investigated using catalysts supported on CNTs. The unique structural and physical properties of CNTs and the particular interactions metal/support have been associated to the superior catalytic activity and selectivity of supported catalysts on CNTs. The catalytic performance of CNFs-supported Pt, Pd and Ru nanoparticles was investigated in the liquid-phase thermal decarboxylation of formic acid. The Pd/CNFs catalysts exhibited the highest activity [3].

5. Supported catalysts prepared by two-step CVD
The preparation of supported catalysts by two-step CVD consists in a first step of precursor vapor absorption on the support particles followed by a thermal treatment to obtain the active particles. Two-step CVD is also called vapor-phase impregnation-decomposition method. For a continuous process, the precursor vapors are simultaneously adsorbed and decomposed on the heated support. Two-step
CVD has been widely used to prepare catalysts supported on oxide particles generally in a micro-scale size (20-150 μm). Several catalysts were prepared by two-step CVD including Rh-Sn/SiO₂, Rh/AC, Co/SiO₂ and MoC/Al₂O₃ [35-38]. The two-step MOCVD of Pd(allyl)Cp in a fluidized-bed reactor was considered a highly suitable method for preparing hydrogenation catalysts with very high Pd dispersion [32]. Recently two-step CVD has also been applied for the preparation of catalysts on nanoscale size supports such as CNTs, titania nanotubes (TNTs) or Al₂O₃ nanoparticles [20, 34]. This is specially highlighted, since one important constraint of FBCVD is the difficulty to attain appropriate fluidization of support particles belonging to group C (difficult to fluidization) of the Geldart classification (typically less than 20 μm) [30]. Pt nanoparticles (2.1 mean in size) were prepared on TNTs (several hundred nm in length and 7-10 nm in diameter) by two-step CVD using a different strategy of precursor vapor impregnation [20]. TNTs and precursor powders were mechanically mixed before impregnation. The mixed powders were heated at 453 K for vapor impregnation. Then, the impregnated TNTs were moved to a higher temperature zone (673 K) to obtain the Pt nanoparticles. Figure 6 shows a TEM image of the Pt particles uniformly distributed on TNTs even at a high Pt load of 14 mass% by using this strategy. A large amount of Pt nanoparticles was in the reduced oxidation state (Pt⁰/Pt²⁺ atomic ratio of 3.9). Pt/TNTs catalyst prepared by two-step CVD had 10 times more active for naphthalene hydrogenation than a conventionally wet impregnated Pt/TNTs catalyst with the same metallic load.

![Figure 6. TEM image of the Pt particles uniformly distributed on TNTs prepared by two-step CVD [20].](image)

6. Catalytic films prepared by plasma enhanced CVD and laser CVD

Catalytic films containing Co₃O₄ nanoclusters (4-6 nm) prepared by plasma-enhanced CVD could be promising in the oxidation of n-hexane [39]. Ru-C and C-Ru-RuO₂ nanocomposite films prepared by plasma-enhanced CVD showed attractive interfacial electric conductivity when used as catalytic electrodes for YSZ solid electrolyte [40]. CeO₂ films grown by a particular large spot (20 mm in diameter) laser CVD combine catalytically desirable features such as a highly (100)-orientation and a columnar structure with considerable amount of nano-scale voids [41]. The (100) plane of the fluorite structure of CeO₂ is unstable as compared with the (110) or (111) planes and potentially more reactive. Figures 7 (a)-(b) show the cross-sectional TEM images at the top-ending of the columnar grains of the highly (100)-oriented CeO₂ films prepared by laser CVD at a laser power of \( P_L = 100 \) W. The SAD
pattern (figure 7c) indicated that the axes of the columns and lateral slopes were aligned in the (100) and (111) directions of the cubic CeO$_2$ structure, respectively. The nano-scale void structure (figure 7d) generated a favorable high surface area and highly dispersed and accessible catalytic sites.

Figure 7. Cross-sectional TEM images at the top-ending of the columnar grains of the highly (100)-oriented CeO$_2$ films prepared by laser CVD [41].

7. Conclusions
CVD is a viable alternative for the preparation of catalytic and electrocatalytic materials. Particularly, FBCVD, CCVD and two-step CVD processes have a high potential for the efficient production of high quality supported catalysts. Not only noble but also Cu, Fe and Mo metal catalysts can be successfully prepared by these processes. FBCVD and rotary CVD are useful in preparing CNTs at a large scale and low-cost production. Conventional CVD can be used for the preparation of nano-scale powders of Ni and composites. Large spot laser CVD has potential for the preparation of highly oriented catalytic films.

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