



Chemical vapor deposition of silicon nanodots on TiO₂ submicronic powders in vibrated fluidized bed

L. Cadoret^a, C. Rossignol^{b,1}, J. Dexpert-Ghys^b, B. Caussat^{a,*}

^a Laboratoire de Génie Chimique, UMR CNRS 5503, Université de Toulouse, ENSIACET/INPT, 4 allée Emile Monso, BP 74233, 31432 Toulouse Cedex 4, France

^b CEMES, UPR CNRS 8011, UPS-Toulouse, 29 rue Jean Marvig, 31055 Toulouse Cedex 4, France

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ABSTRACT

Silicon nanodots have been deposited on TiO₂ submicronic powders in a vibrated fluidized bed chemical vapor deposition (FBCVD) reactor from silane SiH₄. Deposition conditions involving very low deposition rates have been studied. After treatment, powders are under the form of micronic agglomerates. In the operating range tested, this agglomerates formation mainly depends on the fluidization conditions and not on the CVD parameters. The best results have been obtained for anatase TiO₂ powders for which the conditions of fluidization have been the most optimized. For these anatase powders, agglomerates are porous. SEM and TEM imaging prove that silicon nanodots (8–10 nm in size) have been deposited on the surface of particles and that this deposition is uniform on the whole powders and conformal around each grain, even if not fully continuous. Raman spectroscopy shows that the TiO₂ powders have been partially reduced into TiO_{2-x} during deposition. The TiO₂ stoichiometry can be recovered by annealing under air, and IR spectroscopy indicates that the deposited silicon nanodots have been at least partly oxidized into SiO₂ after this annealing.

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1. Introduction

The control of the surface properties of micro and nanoparticles is a great challenge since the performances of these particles for many applications could be thus highly enhanced [1,2]. One of the most efficient technologies to coat the outer surface of powders is the fluidized bed chemical vapor deposition (FBCVD) process. CVD offers several advantages compared to wet preparation routes, in particular the absence of solvent and of additional steps of calcination or separation [3]. The fluidized bed (FB) provides incentives for powders coating due to intense solid mixing, excellent heat and mass transfer and homogeneous temperatures [4–6].

However, most literature FBCVD studies concern Geldart's group A or B particles [7], of diameters comprised between 50 and 300 μm, because they are easy to fluidize. For micro and nanometric powders belonging to Geldart's group C, the interparticle cohesive forces are often much greater than the drag forces exerted by the fluid. Consequently, these particles tend to agglomerate, and when subjected to fluidization, they form channels and slugs and do not fluidize individually.

It is possible to partly overcome this problem by activating the fluidization process. Some authors [8–10] propose to improve fluidization by using mechanical stirrers inside the bed or introducing a small amount of large particles into the fine powders. Other groups of searchers [11–13] have shown that mechanical vibrations increase the forces acting on particles and tend to break up agglomerates: the average size of agglomerates is thus reduced and more convenient fluidization behaviors can be obtained.

Only a few works of the literature deal with FBCVD on micronic or submicronic powders. Morooka et al. [14] have deposited TiN on Si₃N₄ particles of mean diameter equal to 130 nm, fluidized under the form of agglomerates of 70–700 μm. No indication about the fluidization is given or about the deposition thickness and uniformity. SnO₂ from SnCl₄ and H₂O has been deposited by FBCVD on ultra fine alumina Al₂O₃ particles by Li and Hua [15]. According to these authors, this powder naturally fluidizes under the form of agglomerates. After CVD, SnO₂ coated Al₂O₃ composite agglomerates were av. 30 μm and were harder than those naturally formed in bed without CVD. But they were easily disintegrated by fingertips. Hakim et al. [16] claim to have conformally coated zirconia particles, 26 nm in diameter, by alumina nanolayers using atomic layer deposition (ALD) in a vibrated fluidized bed (FB) under reduced pressure. Due to their small size, these ZrO₂ nanoparticles have been fluidized as aggregates of several hundreds of microns in size. But according to the authors, a dynamic aggregation mechanism has been observed when interparticles forces were minimized in the vibrated FB. These dynamic aggregates partially break apart and

* Corresponding author. Tel.: +33 5 34 32 36 32; fax: +33 5 34 32 37 00.

E-mail address: Brigitte.Caussat@ensiacet.fr (B. Caussat).

¹ Permanent address: LEPMI, UJF Grenoble 1, LEPMI, 1130, rue de la Piscine BP 75 38402 – Saint-Martin d'Hères Cedex, France.

reform all along the deposition process, which allows the entire surface of the particles to be exposed to the reactive gases. The same group has deposited in a similar mode iron oxide on zirconia nanoparticles [2], and also alumina nanolayers on various nanopowders including BN platelets, carbon nanotubes, TiO₂ and polymeric particles, by ALD into a mechanically stirred FB under reduced pressure [2]. ALD is a self-limiting vapor phase chemisorption process that utilizes critical purge steps to prevent reactions between precursors [16]. CVD is clearly a simpler process.

In the present work, TiO₂ submicronic particles have been treated by CVD in a vibrated fluidized bed in order to individually coat each grain by nanometric silicon layers. The aim of such layers is to quench the photocatalytic activity of TiO₂ by an inert coating for applications related to pigments and UV blockers in sunscreens [17]. Silane SiH₄ has been used as silicon precursor. The influence of the operating conditions on the deposition features has been studied. In particular, the final diameter distribution of powders has been measured by sieving and by laser granulometry, the chemical composition of the deposition has been analyzed by Raman and Infra-red spectroscopy, and its localization on the surface of grains has been evaluated by SEM and TEM imaging.

2. Experimental

As detailed elsewhere [18], the FBCVD reactor was made of a vertical cylindrical column of stainless steel with an internal diameter of 0.052 m and a height of 0.8 m. It was externally heated by a three-zone electrical furnace and the wall temperatures were monitored by three thermocouples. Several thermocouples were also placed into a vertical tube of 6 mm in diameter inside the reactor. An Inconel™ porous plate was used for the gas distribution. Electronic grade silane and N50 nitrogen (from Air Liquide) were supplied to the bottom of the bed through ball rotameters connected to manometers. Uncertainties of ±5% could affect the flow rates measured and then the amounts of injected silane. In order to avoid any premature decomposition of silane, the region under the distributor was maintained below 350 °C. A differential fast response pressure sensor (Druck LPX5480) measured the total pressure drop across the bed. The hydrogen concentration of the outlet gases was measured by a catharometer (Hydros100, Rosemount). A DasyLab® system enabled the on-line acquisition of the differential pressure, hydrogen concentration and FB temperatures.

The granular materials used in this study were two groups of nonporous titanium oxide TiO₂ particles, one belonging to the anatase crystalline phase (purchased from Sigma–Aldrich), and the other to the rutile phase (from Produits Chimiques du Midi). These two materials have been studied in order to test the ability of our process to treat varied micronic powders; the choice of the crystalline phase was imposed by the purchaser. Their mean volume

diameters were respectively 1.6 and 0.52 μm for anatase and rutile TiO₂ (0.7 and 0.48 μm for the mean Sauter diameters) as measured by laser granulometry. Their grain density was measured by Helium pycnometry and was equal to 3800 kg/m³; their specific surface areas were equal to 10.07 and 16.3 m²/g respectively, as measured by BET. Their Hausner ratios were equal to 1.86 and 1.5 respectively, classifying both of them into the Geldart's group C.

Their fluidization without vibration was impossible: some gas channels or fixed paths appeared through the bed, which remained quasi-immobile for the whole range of velocities tested. Vibration was then mandatory to overcome the important interparticles forces existing in these beds. The hydrodynamic behavior of the vibrated FB was analyzed by classically measuring the pressure drop of the gas crossing the bed and the bed expansion, as a function of gas velocity [19]. After a long and rigorous study, some convenient fluidization conditions were found for the anatase TiO₂ particles, in terms of weight of powders treated per run, type of distributor, frequency and amplitude of vibrations and fluidization velocity, as detailed elsewhere [20]. These optimized conditions of fluidization were also used for the rutile powders.

The deposition conditions tested are detailed in Table 1. The inlet molar fractions of silane and the temperatures were chosen in order to work in conditions of high chemical limitation, i.e. in conditions for which the heterogeneous reaction rate is low in comparison with the gaseous species transport, in order to exalt gaseous species diffusion and to limit external densification of agglomerates due to silicon deposition. The aim was also to deposit very low amounts of Si to form nanometric layers around each grain. The inlet volume percentage of silane was always lower than 4%, and the mean FB temperature did not exceed 595 °C. Rutile TiO₂ runs were the first ones to be performed with very low inlet percentages of silane; however, as detailed later, the amount of Si deposited was too low to be detected by TEM. This is why higher silane percentages were used for the anatase runs. Two runs (A4 and A7) were performed using sequential injections of silane, involving a constant flow rate of nitrogen and a slightly variable total flow rate (+ or –2%) due to the SiH₄ sequential injections. The duration of each sequence was calculated to obtain a theoretical thickness of 0.5 nm on each grain at each sequence. The total number of sequences was determined in order to inject a total weight of silicon similar to that of runs A1 and A5. The aim was to limit the agglomeration phenomenon in decreasing the surface reactivity of powders during the purges with nitrogen. As a consequence, three modes of silane injection were tested for a similar total weight of silicon injected (runs A1, A4/A7 and A5): for run A1, silane has been injected continuously during 60 min; for run A5 the duration of the experiment was twice, and the inlet fraction of silane was divided per two, to analyze the influence of run duration and of the inlet silane percentage. The influence of deposition temperature was investigated through runs A1,

Table 1
Operating conditions tested.

Run	Temperature gradient before silane injection (°C/cm)	Mean temperature (°C)	Total gas flow rate (nl/h)	Inlet vol. % of SiH ₄	Mass of silicon injected (g)	Deposition duration (min)	Injection mode	Total run duration (min)
A1	2	593	660	2	16.5	60	Continuous	60
A2	2.1	593	669	3.36	28.1	60	Continuous	60
A3	1.8	593	642	0.44	3.5	60	Continuous	60
A4	0.85	594	657	2.01	16.5	60	Sequenced	120
A5	1.5	588	650	1	13.6	100	Continuous	100
A6	2.35	544	657	2.01	16.5	60	Continuous	60
A7	2.25	584	660	2	16.5	60	Sequenced	120
A8	0.85	501	657	2.01	16.5	60	Continuous	60
R1	1.95	580	609	0.4	3.58	70	Continuous	70
R2	3.7	588	595	0.43	3.75	70	Continuous	70
R3	2	586	620	0.17	1.32	60	Continuous	60
R4	5.6	564	627	0.18	1.43	60	Continuous	60
R5	2	588	623	0.18	2.77	120	Continuous	120

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