Silicon Chemical Vapor Deposition on macro and submicron powders in a fluidized bed

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A B S T R A C T

Titanium oxide (TiO2) submicron powders have been treated by Chemical Vapor Deposition (CVD) in a vibrofluidized bed in order to deposit silicon layers of nanometer scale on each individual grain from silane (SiH4). Experimental results show that for the conditions tested, the original granular structure of the powders is preserved for 90% of the initial bed weight while the remaining 10% consists of agglomerates in millimetre range found near the distributor of the reactor. A comparison between experimental and modelling results using the MFIX code shows that for Geldart’s Group B alumina particles (Al2O3), the model represents both the bed hydrodynamics and silane conversion rates quite well. The future objective is to extend the simulation capability to cohesive submicron powders in order to achieve better predictability of the phenomena governing ultrafine particles.

1. Introduction

The Fluidized Bed Chemical Vapor Deposition (FBCVD) process represents one of the most efficient ways to modify the surface properties of micro- or nano-powders. The most important applications concern the coating of powders against corrosion and oxidation or the synthesis of supported catalysts.

When coating powders using FBCVD, one major consideration is the fluidizability of the particles. Micronic powders belonging to Geldart’s group C [1] are difficult to fluidize because the interparticle cohesive forces are often much greater than the drag force exerted by the fluid. Consequently when subjected to fluidization, they tend to agglomerate and often lead to gas-bypass due to channelling and slugging. King et al. [2] showed that the agglomerates form, break and reform and their size (up to 500 µm) and shape change with time.

To overcome this problem, activation of the fluidization process becomes necessary. Some authors [3–5] proposed to improve the fluidization by using mechanical stirrers inside the bed or introducing a small amount of large particles into the fine powders. More recently, Alavi and Caussat [6] and Xu and Zhu [7] showed that mechanical vibration increases the forces acting on particles and tends to break up agglomerates, leading to a reduction of both the average size and the segregation of agglomerates in the bed.

Only a few reports in the literature deal with CVD on micronic or submicron powders. Morooka et al. [8] have deposited TiN either on 50 µm agglomerates of Si3N4 nanoparticles (mean diameter equal to 130 nm), or on 300 µm agglomerates of Al2O3 nanoparticles of diameter 390 nm. King et al. [2] and references therein report that Atomic Layer Deposition (ALD) can be performed in FB under reduced pressure, to coat micro- and nanometer particles by alumina (Al2O3). To improve fluidization, they used column vibrations, mechanical stirring, or injection gas pulsations. They claim that films can be deposited with monolayer control on individual particles, but did not analyse the particle size distribution after treatment and the deposition uniformity along the bed height.

Silicon CVD using silane (SiH4) is a well known process to treat easy-to-fluidize particles [9–12] at atmospheric pressure, but to the best of our knowledge it has never been used to treat Geldart’s Group C particles. It is particularly interesting to study the deposition of this CVD precursor as it is the sole precursor for which the homogeneous as well as heterogeneous chemical reaction pathways and associated kinetics are well known [9, 11,12]. This allows one to perform a simulation of the FBCVD process, which can help us to understand the physical and chemical phenomena involved in the deposition. If applied to the conditions of treatment of Group C powders, this understanding could be valuable to find the optimal hydrodynamics and CVD parameters to uniformly coat submicronic powders by silicon.

Indeed, due to its high complexity, the understanding and the prediction of Fluidized Bed (FB) dynamics is essential to design an optimal fluidization and coating strategy. Due to the rapid advances in...
computational capabilities, computational fluid dynamics (CFD) appears to be a promising design tool. Due to the complex behaviour of fluidized gas–solid systems as compared to traditional fluid flow, the development of such multiphase flow simulation tools is still a topic of current research. For example, there is still no general agreement on the appropriate closure models [13], and terms such as the solid phase stresses or the interphase momentum transfer.

Most of the works on simulation of gas–solids FB were carried out with particles of Geldart’s Group B [14–16]. Due to the cohesive behaviour of Geldart’s Group C powders, the incorporation of cohesion into continuum models seems to have been rarely attempted [17]. Thus to correctly reproduce a cohesive FB, Weber [18] proposed to use a Lagrangian representation in which the interparticle forces are considered via a square-well or Hamaker model, but the current computing capabilities limit the applicability of this representation to millions of particles in a real FB.

If we wish to exploit CFD models in our study, as previously explained, it is essential to have accurate implementation of the chemical kinetic models dictating the CVD processes. Indeed, chemistry plays an important role in the reactive flow simulations due to the wide range of temporal and spatial scales encountered in these flows. The first step is to establish a grid-independent solution to be sure that the bed hydrodynamics is accurately predicted before the reaction kinetic schemes can be implemented. At the present time, only Guenther et al. [19] simulated the dynamics of silicon CVD on a FB of Group B alumina particles.

In this framework, the present study deals with silicon FBCVD on macro- and submicron powders. The first part goes into the study of silicon deposition from silane on submicronic powders (TiO₂ particles) in a vibrated fluidized bed. The objective is to form nanometer scale continuous layers around each individual grain and thus preserve the original size distribution. In the second part, we present results about silicon deposition on Geldart’s group B powders of non-porous alumina Al₂O₃. These experimental results provide a validation database for the simulations of the FB hydrodynamics coupled with the CVD process. Bed heights and the silane conversion rates from the simulations are compared to the experimental data.

2. Experimental

Fig. 1 shows the schematic of the experimental setup. The cylindrical column was made of stainless steel with an internal diameter of 0.05 m and a height of 1 m. The reactor was heated externally by a three-zone electrical furnace and the wall temperatures were monitored using three thermocouples. Several thermocouples were also bundled into a 6 mm diameter tube and placed inside the reactor as shown in Fig. 1. An Inconel™ porous plate is used for the gas distribution. Silane and nitrogen were supplied to the bottom of the bed through ball rotameters associated to manometers. A differential fast response pressure sensor with taps under the distributor and top of the column was used to measure the total pressure drop across the bed. The vibrated fluidization experiments were performed by fixing the reactor on a vibrating table as shown on Fig. 1. Two vibro-motors were mounted on the opposite sides of the table to achieve the horizontal vibration of the column. The vibration frequency could be varied from 15 to 50 Hz and the vibration amplitude, from 0.5 to 6 mm. The forces on the column due to the vibration were measured using an accelerometer. Hydrogen concentration in the outlet gas stream was measured using a hydrogen detector (catharometer). A DasyLab® system enabled the on-line acquisition of the differential pressure, FB temperatures and H₂ outlet concentration. In addition, observations of the hydrodynamics of the bed were made in an equivalent transparent glass column using a video camera (Panasonic Tri CCD NV-GS400).

Alumina (Al₂O₃) particles of Geldart’s Group B and titanium dioxide (TiO₂) Group C powder were used in this study. Their main characteristics are summarized in Table 1. The cohesivity and the Hausner Ratio (HR) of the Geldart’s Group C particles indicate that these powders are not fluidizable [20]; indeed we have verified that they form channels and slugs when fluidized resulting in a very poor gas–solids contact.

The fluidization hydrodynamics has been studied by plotting the bed pressure drop and expansion versus decreasing gas velocity. In addition, for TiO₂ powders, the mean diameter of the agglomerates was deduced from the video images. A normalized bed pressure drop ΔP⁎ has been calculated by dividing the bed pressure drop measured experimentally by the theoretical bed pressure drop (equal to the bed weight per column surface area) [21]. A normalized bed expansion H⁎ has also been measured as the ratio between the expanded bed height and the fixed bed height.

In the CVD experiments, a theoretical coating thickness was deduced from the deposited silicon mass assuming uniform coating on spherical particles. The silane conversion rate was deduced from the hydrogen concentration at the outlet. The initial and final size distributions of the powders were measured by a laser granulometer (MasterSizer2000). The deposition morphology was analysed by scanning electron microscopy (SEM, LEO 435 VP). Some Raman spectroscopy measurements have been performed at the “Service de Spectroscopies Vibrationalles” of the Paul Sabatier University (Toulouse) on a Labram HR800 from Jobin Yvon equipped with a

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>d₅₀ (nm)</th>
<th>d₃₂ (nm)</th>
<th>Density (kg/m³)</th>
<th>Geldart’s group</th>
<th>HR (%)</th>
<th>Cohesivity (%)</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>342</td>
<td>329</td>
<td>3900</td>
<td>B</td>
<td>1.14</td>
<td>12.5</td>
<td>Broken solids</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.49</td>
<td>0.48</td>
<td>4000</td>
<td>C</td>
<td>1.75</td>
<td>43</td>
<td>Sphere</td>
</tr>
</tbody>
</table>

Fig. 1. Experimental set up.
laser He/Ne (ex: 632.8 nm). Some transmission electron microscopy (TEM), Infra Red (IR) spectroscopy and X-ray Diffraction (XRD) analyses have been performed respectively on a Philips CM20, a spectrometer (Perkin Elmer Series 100) and on a diffractometer (SEIFERT 3000TT) at CEMES.

3. Vibro-FB CVD of silicon on TiO2 powders of 0.5 μm

Before performing the CVD experiments, a hydrodynamic study has been conducted at the ambient temperature in a glass column in order to identify the fluidization conditions that provide the best gas–solids contact. The influences of the initial powder compaction state, the distributor porosity, the initial bed weight, the initial gas velocity, (i.e. the maximum velocity applied to build the pressure drop curves), and the direction of vibration were investigated. The qualitative results obtained are detailed in Cadoret [22]. We found that the most efficient direction of vibration was the horizontal one; the distributor porosity was of main importance as well as the initial state of powder compaction. Moreover, we found improved fluidization for a certain range of vibration intensities [22]. As illustrated in Fig. 2, corresponding to optimized vibration conditions, the initial gas velocity also influences the bed hydrodynamics. A fluidization plateau can be observed for all initial gas velocities except for 0.66 cm/s and a suitable fluidization expansion is obtained for the two highest velocities tested. For these conditions, the measured minimum fluidization velocity ($U_{mf}$) is close to 3 cm/s. So, TiO2 particles can be fluidized, but only under the form of dynamic agglomerates and not as “single” particles. Without vibration, segregation took place in the bed: stagnant agglomerates with an approximate diameter of 2 mm were present near the distributor whereas smaller ones were observed in the top part of the bed (600–700 μm). We selected optimal conditions of vibro fluidization that obtain the minimum agglomerate size while maintaining maximum interphase contact all along the bed. With these optimal vibration conditions, segregation was far less significant with the mean agglomerate size varying from 300 μm at the top to 600 μm at the bottom of the bed.

These hydrodynamic results allowed us to perform first experiments of vibro–FB-CVD on TiO2 powders as detailed in Table 2. The objective was to form nanometer scale continuous layers of silicon around each individual grain and to avoid particle agglomeration due to CVD. We have then chosen to work in a deposition regime highly limited by the reaction, i.e. with low inlet percentages of silane in nitrogen (<4 vol%) and at relatively low temperature. The initial weight of powders was always 450 g corresponding to a ratio of initial fixed bed height to the reactor diameter ($H_0/D$) close to 5. Run T7 has been performed with a higher silane inlet mass fraction because the silicon depositions with thickness lower than 5 nm were difficult to characterize by TEM.

Due to the small SiH4 inlet concentration and to the large specific surface area of powders, the silane conversion rate was always 100%. It is well known that silane begins to decompose around 370 °C [9] and as a consequence, it is necessary to cool the zone below the distributor to prevent plugging by undesirable silicon deposition. This cooling is responsible for significant thermal gradients along the FB (from 40 °C to 80 °C) as detailed in Table 2 and this has been also mentioned in previous studies [9–12]. Fortunately, they are not too detrimental to the uniform deposition as the particles circulate axially inside the bed.

During experiments, according to pressure drop measurements, no de-fluidization occurred for all the conditions tested. As mentioned earlier, the main challenge was to conserve the original powder size distribution. The results showed that only few stable and hard agglomerates larger than 1 mm were formed, representing less than 10% of the bed weight. These agglomerates have always been found at the bottom of the bed, near the distributor where fresh silane is injected. Before measurements by laser granulometry, those “big” agglomerates were easily separated by sieving. Fig. 3(a) shows that the volume size distributions of particles after CVD measured by laser granulometry remained quite similar to the initial one, despite small peaks detected in the 1–10 μm range. This shows that some small micronic hard agglomerates remained after sieving. Thus, no clear influence of the CVD conditions can be found on the final size distribution of powders. For the conditions tested, based on these observations, we infer that the formation of agglomerates is probably controlled by the fluidization conditions with the likely source being the very poorly fluidized zone near the bottom of the bed. Fig. 3(b) presents size distributions based on number of particles. The small hard agglomerates are not visible anymore indicating that they represent a very small proportion of the total number of particles.

![Fig. 2. Bed (a) normalized pressure drop and (b) expansion versus gas velocity for various initial gas velocities, for optimized vibration conditions (not given for confidentiality reasons).](image)

Table 2

Operating conditions and experimental results for silicon deposition on TiO2 powders

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperatures (°C)</th>
<th>Weight of injected Si (g)</th>
<th>Run duration (min)</th>
<th>Calculated thickness of Si deposits (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>550</td>
<td>605</td>
<td>3.7</td>
<td>72</td>
</tr>
<tr>
<td>T2</td>
<td>550</td>
<td>610</td>
<td>7.8</td>
<td>61</td>
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<tr>
<td>T3</td>
<td>550</td>
<td>610</td>
<td>3.8</td>
<td>72</td>
</tr>
<tr>
<td>T4</td>
<td>560</td>
<td>600</td>
<td>1.4</td>
<td>63</td>
</tr>
<tr>
<td>T5</td>
<td>585</td>
<td>585</td>
<td>1.7</td>
<td>64</td>
</tr>
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<td>T6</td>
<td>565</td>
<td>600</td>
<td>2.7</td>
<td>116</td>
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<tr>
<td>T7</td>
<td>560</td>
<td>610</td>
<td>31</td>
<td>60</td>
</tr>
</tbody>
</table>
612 cm\(^{-1}\) can be attributed to rutile phase of TiO\(_2\) and the peaks at 154 cm\(^{-1}\) and 400 cm\(^{-1}\) are attributed, respectively to the anatase and rutile phases, although they are broadened and shifted relative to the corresponding features in bulk TiO\(_2\) [23,24]. It has been demonstrated [25] that these shifting and broadening could be related to some oxygen vacancies, maybe due to a partial reduction of the material. A new peak appeared at 500 cm\(^{-1}\) characteristic of the presence of amorphous silicon [26].

Fig. 4(b) and (c) present TEM views of TiO\(_2\) particles before and after CVD for run T7. In Fig. 4(b) grains appear aggregated due to interparticles cohesive forces. In Fig. 4(c) blobs of amorphous silicon can be observed and the film does not seem to be fully continuous. For this particle, the film thickness is approximately 10 nm which is in good agreement with the calculated value of Table 2.

The uniformity of the deposition along the bed height has been studied by sampling powders at various levels in the bed after each run. Fig. 5 presents TEM results obtained after run T7 for the whole bed and for powders taken at the middle and at the top of the bed. These results show that there is no perceptible difference between the deposition at two different axial locations and thus indicates that the CVD treatment is uniform along the bed. We attribute this to the optimization of the fluidization conditions and the favourable axial mixing of powders. This result is characteristic of all the runs performed with more than 5 nm thick Si deposits [22], although only the 10 nm case is presented here.

4. FBCVD of silicon on alumina powders of 330 μm

4.1. Experimental study

The operating conditions tested and the corresponding results are listed in Table 3. The inlet volumetric percentage of silane in nitrogen has been varied from 0.5 to 10. The aim of the study was to create a validation database for the numerical simulations of the FBCVD process that are presented in the next section. The operating conditions have been chosen so that the silane conversion rates were less than 100%, to ensure that the data can be used to validate the model. The inlet silane percentage (comprised between 2.4 and 10.5%) was higher here than for TiO\(_2\) experiments, because these Geldart's group B particles are easy to fluidize and no agglomeration occurs for volumic percentage of silane in nitrogen lower than 15% [9–12]. In addition, working with weights of deposited silicon greater than 10 g allowed us to ascertain the mass balance by weighing the bed.

First, the reproducibility of the results has been verified through runs A10 and A11. Thermal gradients were still present for these runs but they can be lowered to around 15–20 °C by decreasing the mean bed temperature, which gave acceptable uniformity of deposition primarily due to the intense circulation of the particles inside the bed. The reason to increase the initial FB weight (run A12) was to decrease this gradient by taking advantage of better thermal transfers between the reactor walls and powders.

The deposition rate was varied between 30 and 120 nm/min. As previously observed in the literature [9–11], this parameter and the silane conversion increased with temperature. The silane conversion logically increased with the initial FB weight (runs A6 and A12). For runs A3 to A5 and A7 to A12, the weights of injected silicon were high. For these runs, some reversible disturbances of the thermal profile and pressure drop along the FB have been observed. They are due to a partial de-fluidization of the bed, probably related to the appearance of short-lived agglomerates; indeed silicon dangling bonds are probably formed on the surface of each particle during deposition, acting as glue for the surrounding particles [9]. Such disturbances have not been observed for TiO\(_2\) particles because of the low amount of SiH\(_4\) used.
For the conditions tested, the size distribution of powders has not been changed by the deposition indicating no agglomeration and SEM analyses revealed that deposition is uniform on powders. These are now well-established results for silicon FBCVD from silane on Geldart’s group B particles [9–12]. For the highest weights of silicon injected, coating thickness of several hundreds of nanometers was achieved. Some Raman and XRD measurements have shown that when the FB temperature was lower than 610 °C, silicon deposition was mainly amorphous whereas it was polycrystalline at higher temperature.

4.2. CFD modelling of the process

The CFD open-source code MFIX [27], a benchmark tool for the simulation of FB, was used for this study. 2-D axisymmetric and 3-D calculations were performed using the continuum model, the drag law of Syamlal–O’Brien [28], kinetic theory of granular materials with an algebraic form for granular temperature equation for the solid phase stress tensor in the viscous regime and the Schaeffer model [29] for the calculation of the solid phase stress tensor in the plastic regime. For the alumina powder, a mean Sauter diameter of 330 µm and an internal angle of friction of 40° were considered. The latter value corresponds to the repose angle (note that for non-cohesive powders, these two parameters are identical [30]). Since we did not find any data in the literature about the coefficients of restitution for the collisions of alumina particles, the default value of 0.8 was used.

Some preliminary calculations showed that using the Superbee method for spatial discretization scheme (order 2), grid independent results in terms of bed expansion and silane conversion rate were achieved by using 200 cells along the axial direction for a height of 0.4 m, 15 cells along the radial direction for the half diameter, and for 3-D calculations, 6 angular cells. This result is true over all the range of the operating conditions studied.

As a first step only the pure hydrodynamic behaviour of the bed has been modelled. In this study, experiments were performed using 800 g of powder fluidized with air at ambient temperature in the glass column, using average superficial gas velocities, $U_g$, between 5 and 40 cm/s. The fluidization plateau was reached at a minimum fluidization velocity ($U_{mf}$) of about 12.5 cm/s, the pressure drop across the bed being very close to the theoretical value of 4000 Pa. Then, the bed behaviour was more specifically studied for 3 gas velocities: 18, 25 and 30 cm/s, using the video camera. This allowed determining accurately minimum and maximum average heights of the fluctuating bed for each gas velocity.

The knowledge of $U_{mf}$ allowed adjusting the coefficients of the Syamlal–O’Brien drag correlation [28]. Then, 2-D axisymmetric and 3-D MFIX simulations were performed for the 3 gas velocities studied. Values of minimum, maximum and average bed expansions, $H/H_{mf}$, obtained from experiments and from calculations are compared in Fig. 6. All calculations overestimate bed expansions and fluctuations, but results obtained with 3-D simulations are much closer to experimental data than results obtained with 2-D calculations. It appears that the best prediction of 3-D calculations is obtained for the highest velocity ($U_g = 30$ cm/s) with overestimations of average bed heights and fluctuations of about 7%. Note that this gas velocity was used for experiments of Si CVD.

The second step aimed at modelling the silicon deposition process. The simulations considered the thermal profiles existing along the FB and the presence of the 6 mm diameter tube along the column axis. A chemical model was implemented in MFIX to simulate the deposition of silicon from SiH₄. The kinetic law of Furusawa et al. [12] was chosen because it has been well-established for the FBCVD process for our conditions. In the present version of the model, only the overall reaction of silicon deposition from silane is considered, leading to the

Table 3
Operating conditions and experimental results for silicon deposition on Al₂O₃ powders of Geldart’s group B

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperatures (°C)</th>
<th>$U_g/U_{mf}$</th>
<th>Initial weight of powders (g)</th>
<th>$H_{mf}/D$</th>
<th>Weight of injected Si (g)</th>
<th>Run duration (min)</th>
<th>Weight of deposited silicon (g)</th>
<th>Silane conversion rate (%)</th>
<th>Calculated thickness of deposited Si (µm)</th>
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<tr>
<td>A1</td>
<td>575</td>
<td>4.2</td>
<td>800</td>
<td>4</td>
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<td>800</td>
<td>4</td>
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<td>40</td>
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production of gaseous hydrogen:

\[ \text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2 \]

Runs A5 and A7 of Table 3 were then simulated in 3-D with an average bed temperature of 600 °C by considering an increase of the axial temperature during deposition of about 50 °C as measured along the bed. The fluidization ratio was close to 4.5.

The coefficients of the Syamlal–O’Brien drag correlation have been adjusted considering a value of \( U_{mf} \) equal to 7.5 cm/s at 600 °C. Note that a preliminary modelling study showed that discrepancies of about 10% on bed expansions and fluctuations had no effect on the final conversion rates of silane calculated.

Instantaneous fields of void fraction and normalized silane mass fraction calculated after 7.1 s of deposition for run A7 are presented in Fig. 7. Fig. 7(a) shows that a slug of gas occupies about 60% of the FB height. Some millimetre scale gas bubbles are present near the distributor but due to the high \( H_0/D \) ratio used the bed is clearly in the slugging regime, as observed experimentally. Although Fig. 7(b) shows complete conversion of silane in the exit gas, the average conversion is indeed much less than 100%. Note the low conversion in the gas at the center of the slug. When the slug erupts at the top, gases with low silane conversion will exit the reactor. The average silane conversion was found by time-averaging the instantaneous values.

Final conversion rates of silane measured and calculated for run A5 are of 81% and 79% respectively. For run A7, they are of 65.5% and 65% respectively. This agreement is quite good considering that only the heterogeneous phase reaction kinetics have been implemented in the model.

5. Conclusion

In order to individually and uniformly coat submicronic powders by CVD in a vibro-fluidized bed, the optimization of the bed hydrodynamics is of major importance. A study of the influence of the main fluidization parameters (the initial powder compaction state, the distributor porosity, the initial bed weight, the initial gas velocity, and the direction of vibration) has allowed us to determine the optimum conditions for fluidizing submicronic TiO\(_2\) powders, which, however, fluidize only in the form of agglomerates of hundreds of microns. These optimized parameters have been applied to perform silicon CVD on these powders.

The preliminary results show that the original granulometry can be preserved for all the particles except for those present near the distributor where fresh silane enters and causes agglomeration of particles. More than 90% in mass of the bed particles can be uniformly coated with silicon for the conditions tested. In order to increase this percentage, new experiments are under progress, in particular by improving the fluidized bed hydrodynamics and using a sequential feeding of silane.

3-D, transient CFD simulations of both fluidized bed hydrodynamics and of reactive mass transfers existing during silicon CVD (from silane) on Geldart’s Group B powders have been performed using the code MFIX [27]. The predicted conversions (79% and 65%) for two flow conditions are in good agreement with the experimental data (81% and 65.5%).

Our future work is to implement (i) the homogeneous reactions occurring during silicon pyrolysis, (ii) the column vibrations and (iii) at longer term extend this code to represent beds of cohesive particles, to better understand the physical and chemical phenomena involved when treating submicronic powders.

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