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Large Scale Production of Nanoparticles by Laser Pyrolysis

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Abstract

Laser pyrolysis is a very suitable method for the synthesis of a wide range of nanoparticles. A pilot unit based on this process has been recently developed at CEA. This paper reports results showing the possibility to produce SiC and TiO_2 nanoparticles at rates of respectively 1 and 0.2 kg/h and also the possibility to adjust the mean grain size of the particles and their structure by changing the laser intensity and reactants flow rates. First tests of liquid recovery have been also successfully performed to limit the risks of nanoparticles dissemination in the environement during their recovery.

Keywords : laser pyrolysis, nanoparticles, silicon carbide, titanium dioxide, liquid recovery

1. Introduction

Among all the methods used for the production of nanoparticles, laser pyrolysis is one of the most flexible.

This method is based on the CO_2 laser decomposition of flow of reactants constituted of gas and/or liquids followed by a quenching effect [1]. Laser pyrolysis has been successfully applied to the synthesis of a wide range of nanoparticles at lab-scale such as single carbides, nitrides oxides, metals and composite nanoparticles.

However, the demonstration of the mass production using this method is still required to develop nanostructured materials prototypes integrating nanoparticles in large quantities on one hand and on the other hand industrial plants. In order to fulfill this objective, a pilot unit based on the laser pyrolysis process has been designed and installed at the French Atomic Commission (CEA – France). It has been first tested on the synthesis of silicon carbide (SiC) and titanium dioxide (TiO_2) nanoparticles using differents reactants flow rates and laser intensities.

A liquid recovery system has also been designed and tested for the recovery of TiO_2 nanoparticles in water, directly at the exit of the reactor for safety purpose.

2. Experimental and Results

In a laser pyrolysis experiment, a part of the energy of a CO_2 laser beam is absorbed by a flow of reactants thus leading to their decomposition and to the homogeneous nucleation of particles in a flame, their growth being stopped by quenching (Fig. 1). In order to get high production rates by this process, it is necessary to ensure a large reaction volume at the intersection of the reactants with the laser beam and therefore: a large nozzle and a large laser beam with sufficient power density. Consequently, we have chosen a 5 kW CO_2 laser, five time more powerful than those used at lab-scale, coupled with a beam expander. Optionally, a cylindrical lens in ZnSe can be used to focus the beam in the vertical direction in order to reach high laser intensities.

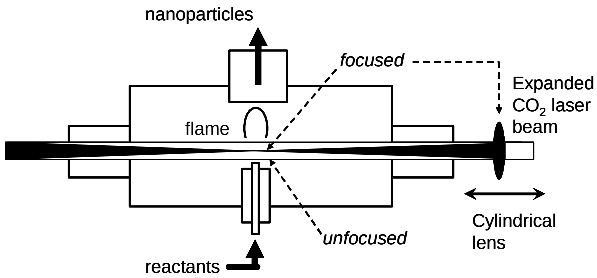

Fig. 1. Principle of the laser pyrolysis at pilot scale.

The table 1 presents the processing parameters used to produce SiC nanoparticles from gaseous mixtures of silane (SiH_4) and acetylene (C_2H_2) and the obtained results. The experiments were conducted with a defocused laser beam resulting in an elliptical beam shape having a height of 10 mm and a width of 30 mm at the intersection with the reactants flow rate.

Table 1. Parameters for SiC nanoparticles and results. The experiments were conducted at 900 mbar under argon

Ref.	Flow rate (lpm)		Las. Int.	Prod. Rate	Yield
	SiH_4	C_2H_2	(W/cm^2)	(g/h)	
SiC-06	6	3	1200	590	0.92
SiC-07	12	6	1200	1113	0.88
SiC-08	2	1	1200	190	0.91
SiC-11	6	3	400	530	0.83

The results show the possibility to produce more than 1 kg/h of SiC nanoparticles at moderate laser intensity with yields close to 0.9. Furthermore, the specific surface area (SSA) can be adjusted by changing the reactant flow rate as shown on figure 2. The increase of the flow rate provokes an increase of the SSA probably due to the decrease of the mean grain size induced by the decrease of the residence time of the particles in the flame. Moreover, low laser intensities seem favor large SSA and consequently low grain sizes.

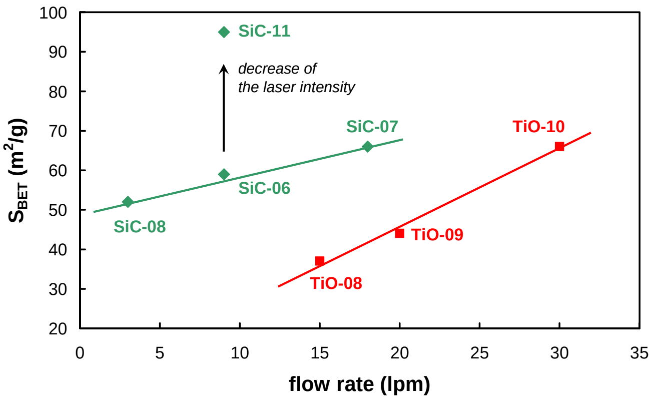

Fig. 2. SSA measured by the BET method as a function of total flow rates of reactants. For SiC, it corresponds to the sum of the reactants flow rates and for TiO_2/C to the carrier gas flow rate.

The variation of the SSA with flow rate is also observed for TiO_2/C nanoparticles synthesized from liquid titanium isopropoxide (Ti isop.) ($Ti(OCH(CH_3)_2)_4$) using a high flow rate ultrasonic aerosol generator. The experimental details are reported in table 2 with results. It is important to note that free carbon coming from the reactant has been detected in the nanoparticles by TGA.

Table 2. Parameters for TiO_2/C nanoparticles and results. The quantity of liquid injected is around 300 ml/h for 10 lpm of carrier gas.

Ref.	Flow rate of argon (lpm)	Las. Int. (W/cm^2)	Prod. Rate (g/h)
TiO-08	15	1600	95
TiO-09	20	1600	160
TiO-10	30	2000	140
TiO-11	25	1600	180

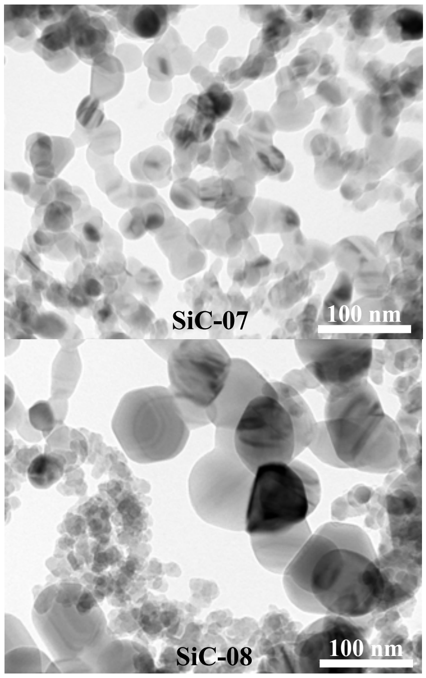

Fig. 3. TEM observations of SiC-07 and SiC-08.

The TEM observations (Fig. 3.) performed on SiC nanoparticles confirmed that large particles (up to 130 nm) are formed at low flow rate (SiC-08, 3 lpm), whereas at high flow rate (SiC-07, 18 lpm) smaller particles are obtained. The small particles observed in SiC-08 are probably formed at the border of the flame where temperature and residence time are reduced in comparison with the central region.

The TiO_2/C nanoparticles produced during the run TiO-11 have been recovered directly in the form of a water suspension (0.7 wt. %) using a liquid recovery system directly connected to the reactor and based on bubbling and pulverisation principles.

3. Summary

A pilot unit based on the laser pyrolysis has been designed and installed at CEA (France). The unit is able to produce SiC nanoparticles at a rate of more than 1 kg/h and TiO_2/C nanoparticles at a rate close to 200 g/h. A decrease of the SSA corresponding to an increase of the mean grain size has been observed with decreasing reactants flow rates. The liquid recovery connected to the laser pyrolysis reactor has been successfully tested on TiO_2/C nanoparticles produced by laser pyrolysis.

4. References

1. W.R. Cannon et al., J. of the Am. Ceram. Soc., **[65], 7**, p330 (1982).