Scientific Report

Regarding the Project Implementation during October-december 2011

Phase I. The developing of the conceptual models and theories regarding the synthesis methods for the preparation of doped TiO_2 nanostructured compounds.

1. ***Tehnical analysis of the laser pyrolysis systems design for the obtaining of titania with a major anatase content; The state-of-the-art of laser pyrolysis installations.***

From the point of view of IR photochemistry, basic principles of the laser pyrolysis rely on i) the resonant absorption of photons by the IR-active vibrational modes of molecules in the ground electronic state; ii) collision-aided vibrational energy transfer towards the translation-rotation degrees of freedom and iii) the heating of the reactant gases and their dissociation, followed by nucleation and growth of aggregates.

The system is based on a cross-flow configuration. The reactant flow emerges in the reactor through a nozzle system where it is orthogonally intersected by the focused IR radiation beam.

Standard experiments for TiO_2 nanoparticles pyrolysis use as precursors $TiCl_4$ and air / N_2O and ethylene as an energy transfer agent - sensitizer. Iron pentacarbonyl $Fe(CO)_5$ is another precursor used in doping of TiO_2 with Fe. The installation includes the following components: i) the reaction chamber; ii) collection chamber / filter; iii) the focused laser beam; iv) gas supply, with independent control of flows admitted in the reaction chamber through a system of concentric nozzles (multitubular injector); v) Ar flows are employed for the confinement of reactant gases/nucleated particles towards the flow axis and for flushing the windows, respectively; vi) cw CO_2 laser with max power. 1 kW and emitting at a wavelength $\lambda = 10.6$ μm (944 cm^{-1}).

Installation and irradiation geometry adapts to new nanoparticle architecture - both in terms of chemical composition and morphology and crystallography.

Criteria for selection of synthesis parameters for IR laser pyrolysis of TiO_2 nanocomposites and TiO_2-Fe and TiO_2-Fe-Si or TiO_2-Fe-silicone-derived polymer as well TiO_2-FeOx oxide mixtures is based on concurrent processes of decomposition, induced in the gas phase by laser radiation. These are: i) decomposition of Ti tetrachloride and ii) a concurrent decomposition of other precursors: a) $Fe(CO)_5$-like Fe precursor; b) hexamethyl disiloxane siloxane polymer (HMDSO) or silicon tetra isopropoxide (TEOS)-like Si precursor. In the first case follow Fe core-shell nanocomposites; in the following cases will be obtained (and select) variants that lead to nanocomposites with iron core and Ti /TiO_2 doped siloxane with shell.

C_2H_4 and SF_6 will be used as sensitisers.

The process allows the obtaining of high reaction temperatures and can be maintained continuously, allowing relatively high production yields. Adjusting the gas streams is performed electronically (via electronic flow meterd - mass flow controllers). These features allow the preparation of nanostructures/nanoparticles with high specific surface and dispersing reduced diameters.

2. *The development of the required specific components for the synthesis installations in order to obtain the new titanium oxide-based nanoparticles.*

2a. Design and manufacturing of injection systems for gaseous precursors

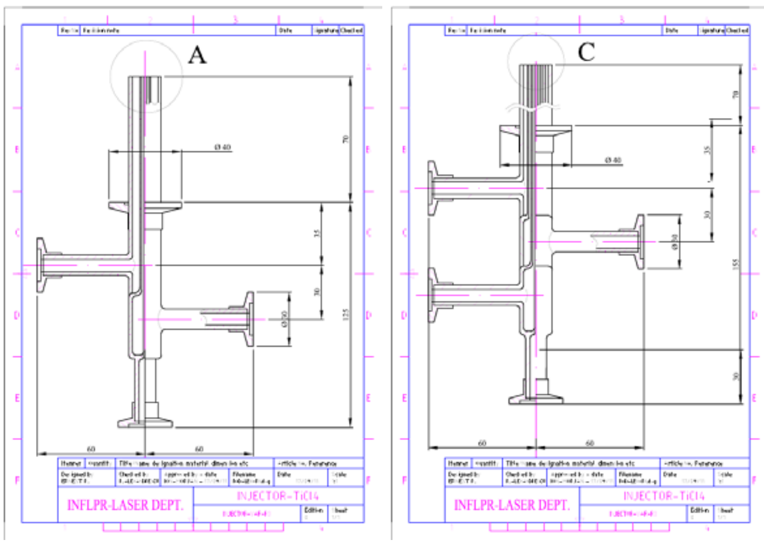

Fig.5. Injectors with 3 and 4 concentric nozzles

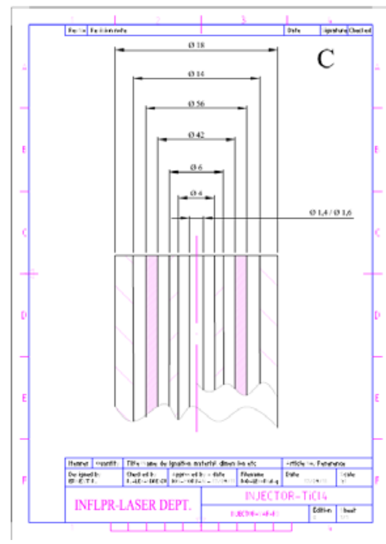

Fig. 6. Cross section of injector with 4 concentric nozzles

2b. Reaction chamber, the general and specific conditions.

It was designed and conducted a "cross" reaction chamber which has the following characteristics: i) reaction zone is well defined: these delimitation is done by coordinating cross-section of the laser beam, the size of the gas injection nozzles cross-section in the reaction chamber, the flow and consequently the speed of these gases; ii) no chemical contamination: the nature the material resulted from the reaction zone is well controlled both in quantity and quality; iii) there is no physical contact between the reaction chamber walls and materials that react or those resulting from pyrolysis reactions. All variants contain outer nozzle for confinement of reaction induced by the reaction center through a stream of argon.

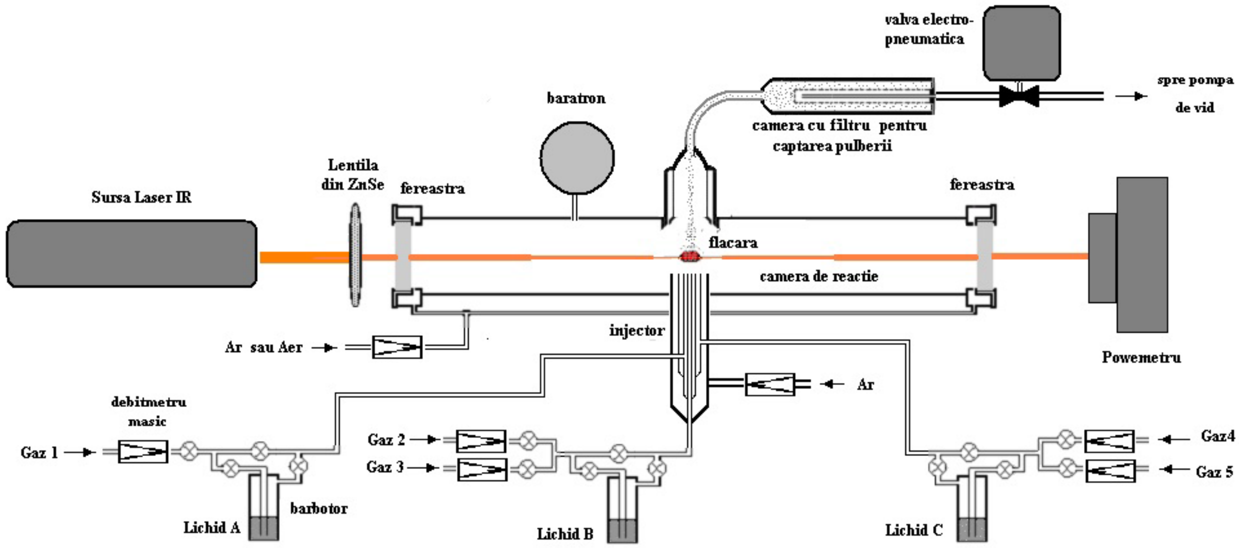

Fig.8. Laser pyrolysis instalation with 4 nozzles injector and 3 different sources of volatile liquid vapor by bubbling

In the case of the system with *three nozzles*: a) $TiCl_4$ vapors were combined with those of Fe $(CO)_5$ will be circulated through the median nozzle and an oxidant to the central nozzle (there will be obtained the magnetic material doped TiO_2 composite), and b) $Fe(CO)_5$ vapor will run through the central nozzle and $TiCl_4$ through the median nozzle, yielding magnetic core and Ti-based shell composites, Ti coating will oxidize, by passivating, when nanocompounds are taken out in the air under the action of the atmospheric oxygen.

If system has *4 nozzles*: a) introduction of $Fe(CO)_5$ vapors will be performed on the central nozzle; b) Si-containing vapor precursor (expected optimization experience using TEOS with lower volatility and siloxane monomers that are liquid HMDSO with higher volatility) will run on the nozzle median and c) $TiCl_4$ precursor will be placed on the nozzle side (aiming to be obtain a Ti-based layer either by the doping the polymer with TiO_2 nanoparticles - or getting two effects simultaneously (one surface and another volume). It should be mentioned that the introduction on the installation's structure of the three bubblers for separate and independent handling/controlling of different liquid precursors allows a homogeneous mixture with the carrier gas (either inert gas, such as argon or gas sensitivity as ethylene) and if necessary, with the oxidizer.

MULTINANEF project aims to develop a multifunctional magnetic nanocomposite, based on TiO_2, prepared by a single-stage method, laser pyrolysis, for use in the effective treatment of pollutants in water, while demonstrating skills for recovery/recycling. In this first stage of the project components required for synthesis installation were specifically designed and developed in order to obtain new nanoparticles/nanocomposites based on titanium oxide. They consist mainly of: i) injection systems for gaseous precursors, ii) reaction chamber suitable for new nozzle systems but also equipped with functionality for handling optical adjustments of the laser beam; iii) additional bubblers (3 in total) to ensure adducts precursor vapor as expected particle architecture. Our knowledge the reaction chamber equipped with injector 4 concentric nozzles would be reporting for the first time of such implemented device on a laser pyrolysis installation.

Project Director,