The Role of Microwave Irradiation and Solvent Distillation on the Synthesis of TiO_2 Nanoparticle-Based Photocatalytic Materials Within the Framework of SIMPLIFY European Project

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Abstract

In the framework of the SIMPLIFY European project (No° 820716), our research groups are involved in the development of a microwave-assisted synthetic method for the preparation of photocatalytic TiO_2 nanoparticles to substitute the current industrial procedure, for process intensification purposes. The reaction was firstly studied using MW vessel reactors, where promising preliminary results were obtained, then we switched to a three-necked flask reactor, which allows better reaction control due to the possibility of contemporaneous heating, stirring and solvent distillation. In this way we succeeded in producing nanoparticles with low size and excellent long-term stability in suspension. The material can also be fully dried, and the resulting powders, easier to handle and ship, show comparable photocatalytic activity to the corresponding industrial product. Preliminary viscosity tests carried out on the reaction mixture reveal the crucial importance of stirring for a future continuous flow procedure, since without stirring the mixture's viscosity increases considerably.

1 Introduction

SIMPLIFY (Sonication and Microwave Processing of Material Feedstocks) is an EU Horizon 2020 (call **SPIRE-02-2018)** funded project under the grant agreement No° 820716 [1]. The aim of the project is to bring technical innovation in the processing of many kinds of materials according to the process intensification principles, especially by the use of ultrasound and microwaves (MW) as effective tools for energy supply.

This allows to save time, energy and money with respect to previous conventional processes, with the use of greener and smarter dedicated technologies. Eleven academic and industrial partners are involved in this project. Each of them is devoted to the development of process intensification of one of the three main cases of studies, project management, or to Life Cycle Assessment of newly developed processes. The three main case studies are:

1) The HEUR (polyurethane) continuous production activated by microwaves and ultrasound;
2) Microparticle crystallization by microwaves and ultrasound in COBRs (Continuous Oscillatory Baffled Reactor);
3) TiO_2 nanoparticle syntheses by microwaves and ultrasound in PFR (Plug Flow Reactor).

While other partners are developing the first two cases of study, the authors of the present paper are involved in the development of the third one. Photocatalytic TiO_2 nanoparticles are used widespread as functional components due to the ability of TiO_2 nanoparticles to catalyze pollutants decomposition under UV irradiation [2], and most recently also under visible light [3], upon catalyst modification. For example, coating for self-cleaning applications in buildings [4, 5], pigments [6], air purifying filters [7] and so on exploit this technology for air cleaning indoors and outdoors [8]. Colorobbia group [9] is one of the main manufacturers of these products in Italy, with a tradition of successful research and development in advanced ceramics and a global market currently estimated to be 6 tons/y sales for their main product as principal ingredient for smart coatings. In order

to increase production and improve process eco-compatibility, the company became interested in the development of a hybrid ultrasound/microwave technology for their heating steps and for this reason became involved in the SIMPLIFY project. The research group of Prof. Cristina Leonelli [10], at the University of Modena and Reggio Emilia, is interested in the development of new processes assisted by microwaves and, therefore, these two partners are working in close collaboration for the research on the third case of study within the SIMPLIFY project. The present paper is an update of the results achieved in the last two years on this part of the project summarizing the results published so far [11] or about to be published on the topic.

2 Results and discussion

Low nanoparticles size and long-lasting suspension stability are the two key parameters to ensure quality and reliability of the commercial product. These two key features are classically obtained with a conventionally heated synthesis of TiO_2 using $Ti(O\text{-}iPr)_4$ as precursor in a hydrolytic sol-gel reaction carried out in acidic conditions [12]. For the attainment of the desired product features heating the mixture to 50 °C for 24 h is required, followed by a distillation of isopropanol, the co-product of the reaction, which is also necessary.

First, technology transfer tests to microwave heating were carried out on an ETHOS one (Milestone, Bergamo, Italy) system equipped with vessels (**Figure 1a**). It is of course unreasonable to prolong the reaction time in a microwave synthesis to 24 h, as in a conventional cycle, so in a microwave synthesis we selected 30 min as the reaction time. Delightfully, promising results were obtained concerning crystallinity and nanoparticles size, the latter being very low after a few days of aging at room temperature. Unfortunately, not all the batches were found stable over time and some of them showed an irreversible particles size enlargement in 30 days (e.g. the dotted red line in **Figure 2**). We noticed that the reactions carried out at higher temperatures gave more stable batches and, confirmed also by a literature survey [13] and by the industrial procedure [12], we decided to distill isopropanol at the end of reaction (**Figure 1a**). In this way, we obtained stable batches over time (**Figure 2**, solid red line).

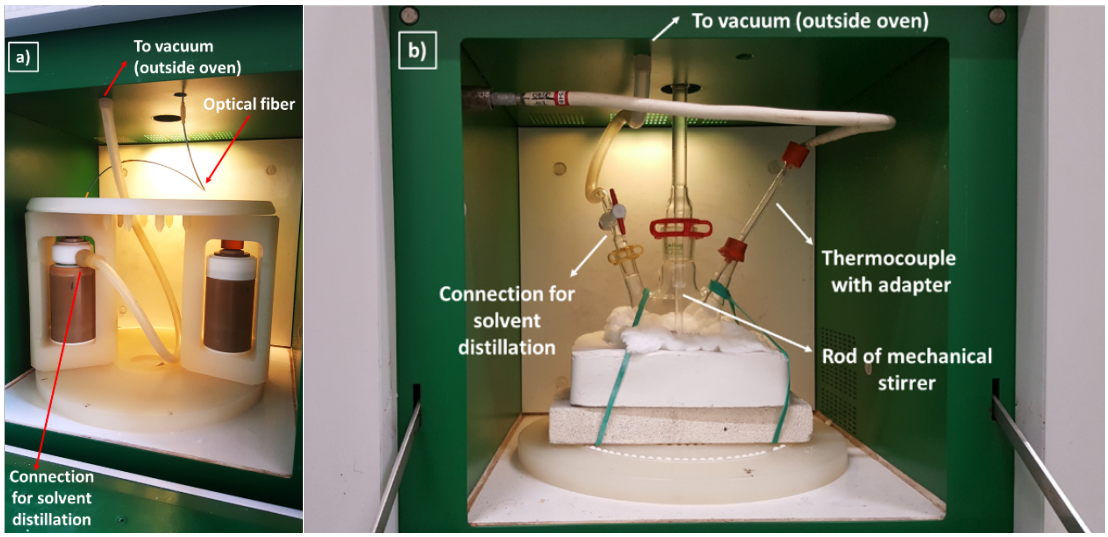

Figure 1. a) MW apparatus modified to distill solvent from a vessel. b) MW apparatus modified to distill solvent from a flask.

The procedure using vessels, anyway, was very tedious and impossible to scale up: for this reason, we switched to a system that closely mimics the industrial apparatus used for this reaction and carried out our tests in a three-necked flask (**Figure 1b**). This system offers the possibility of a scale up in a stop-and-flow process, and introduces a way to stir the reaction (mechanically) that gives further benefits to the process control. Moreover, distillation of isopropanol under microwave irradiation is possible. We were glad to find that, also in this system, after isopropanol distillation batches showed high crystallinity and a low nanoparticles size, even without ageing, and were

very stable over a long time, with the best results obtained when working at 60-70 °C (the example of reaction carried out at 60 °C is given in **Figure 2**, solid green line).

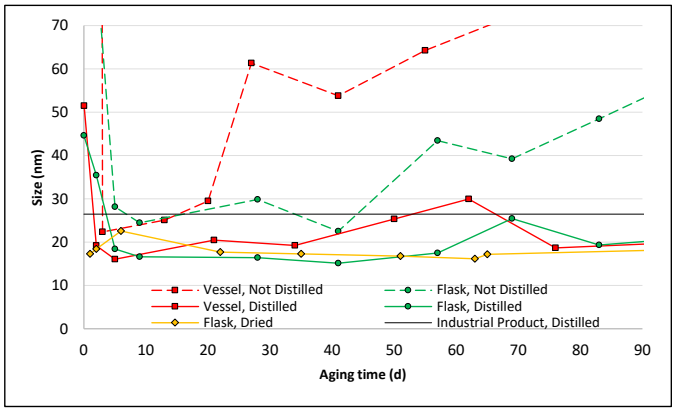

Figure 2. Selected examples of MW TiO_2 synthesis: reactions were carried out in vessels (red lines) or flasks (green lines) at 60 °C for 30 min, and then isopropanol was distilled (solid lines) or not distilled (dotted lines). In one case (yellow line) also water was distilled along with isopropanol, giving a powdered product. Nanoparticle size was determined via dynamic light scattering (DLS). With this technique the error is about 1-10%.

A distillation apparatus attached to the microwave system gave us the opportunity to perform the reaction directly under vacuum: reaction and distillation can therefore be carried out at the same time, saving even more time and energy, without compromising the result, at least when working at 70 °C (not shown).

The system arranged in this way allows us to remove the solvent completely and finally get a powder. The attainment of a powder can be advantageous for a future industrial scale up, since powders are stored and handled in an easier way and in bigger amounts with respect to suspensions. A test carried out at 60 °C, where solvent was removed completely (**Figure 2**, yellow line) finally gave a yellowish powdered product in quantitative yields that meets all quality standards of the industrial product: the resulting powders are very small in size, and show remarkable long-term stability if re-suspended in water. Importantly, the reaction is fully reproducible, giving three batches of the same stability and size (not shown). Moreover, the photocatalytic activity of this product following a nitrogen oxide depletion test was found equal to the corresponding industrial product (**Table 1**). It is interesting to note that the reaction time in our case is just 30 minutes, and also isopropanol distillation takes only 30 minutes, so processing times are dramatically reduced with respect to the industrial procedure.

Table 1. The photocatalytic activity in NO depletion of the industrial product and of nanosized TiO_2 sample synthesized in our lab under microwave and distilled to complete dryness.

Experiment time (min)	NO Depletion (%)	
	Industrial product	Flask dried product
5	0	0
25	20.4	31.7
45	35.6	41.8
65	48.6	52.1
85	63.0	63.4
105	77.4	73.7

We have already mentioned that it is unrealistic to carry out a MW reaction for 24 h, but we were very surprised by the good results obtained in such a short time. In order to investigate a possible MW effect on this reaction, we performed the syntheses in the same conditions, but using conventional heating in place of microwave, and compared also with the industrial procedure (re-created in our lab) that lasts for 24 hours and performs distillation at this time. The temperature selected for these tests was 70 °C for a better temperature control during conventionally heated reactions. The results found were intriguing since it's possible to see in **Figure 3a** that a very steep nanoparticles size decrease is observed during distillation, regardless of the moment at which it is performed. In both 30 minutes long reactions (MW and conventional heating, yellow and blue line respectively), the size of nanoparticles drops after 30 min, when distillation is performed. In the 24 h reaction (green line), nanoparticles size is initially very large and decreases to 220-230 nm over 8 hours, but then the size is stable until the 24th hour.

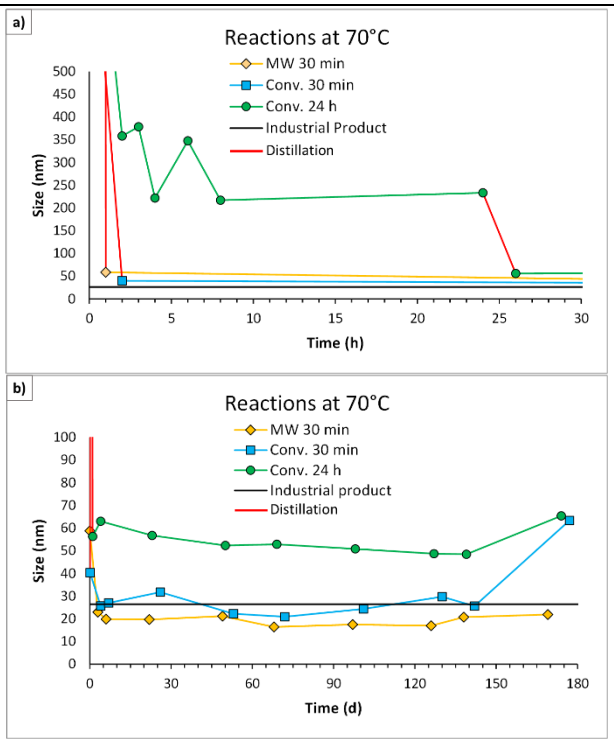

Figure 3. a) size of TiO_2 nanoparticles during the considered reactions and first hours of ageing shown to emphasize the crucial role of distillation in size lowering. Distillation is highlighted in red. b) the long-term ageing of the same reactions.

Only when distillation was performed, we observed further particle size decrease to low values (50-60 nm). In this last case, size is stable at 50-60 nm over long ageing (140 days, **Figure 3b**, green line), while both the 30 min reactions show a further decrease in size to 20-30 nm after 4 days of aging, and then they are stable up to 140 days (**Figure 3b**, yellow and blue lines). Interestingly, the microwave reaction batch (**Figure 3b**, yellow line) is stable up to 180 days (when ageing data collection was stopped) while the conventionally heated reactions encounter particle growth at that time (**Figure 3b**, blue line). It's interesting also to note that the MW batch tests show slightly an overall lower nanoparticles size with ageing time (**Figure 3b**, yellow line). Anyway, these results prove that the main parameter that influences nanoparticles size is the removal of isopropanol from the reaction media, that prompts shrinking of nanoparticles regardless of the moment or the heating mode used, and it's rather better using a short reaction time in both heating modes. A specific microwave effect is reasonably excluded: the very slightly better stability and lower size of the batch produced via microwave could also be due to a better temperature control of the reaction performed with this heating mode, especially during distillation.

Since the ultimate goal of the project is to develop a microwave synthesis in a plug flow reactor, the viscosity of the reaction mixture must be evaluated, especially considering that the reaction mixture is a gel.

Since in the flask synthesis the stirring is constant and helps to decrease the viscosity, it seemed interesting to us to test viscosity in the vessel case, where viscosity is higher due to the lack of stirring. We reasoned that it is also possible to compare viscosity measurements of the unmodified reaction mixture and after a stirring that can be applied separately, out of MW oven. Applying many cycles of MW heating and then separate stirrings, it is possible to monitor the viscosity of the mixture over time. In this way we would obtain viscosity of both the stirred and unstirred mixtures at different reaction times and have useful data both in the case of normal flow in coils and in the case that some problem stops the flow, and the reaction is left stationary under heating for some time.

The "fall time" method was applied for viscosity measurement tests: first, a linear correlation was found between the reported viscosity and the fall time of four standard fluids, so that measurements on reaction mixtures can be taken and the obtained data just interpolated on this straight line. Then, the measures on viscosity were taken with the very same method. Final results of viscosity measurements are interesting firstly because there is a lot of difference in viscosity between the measurements taken before and after stirring (compare **Figures 4a** and **4b**): whereas before stirring viscosities are very high, after stirring viscosity is much lower and always constant (**Figure 5b**). On the opposite, the viscosity before stirring reaches a maximum after 15 min and then drops again to values recorded at the beginning of the treatment (**Figure 5a**).

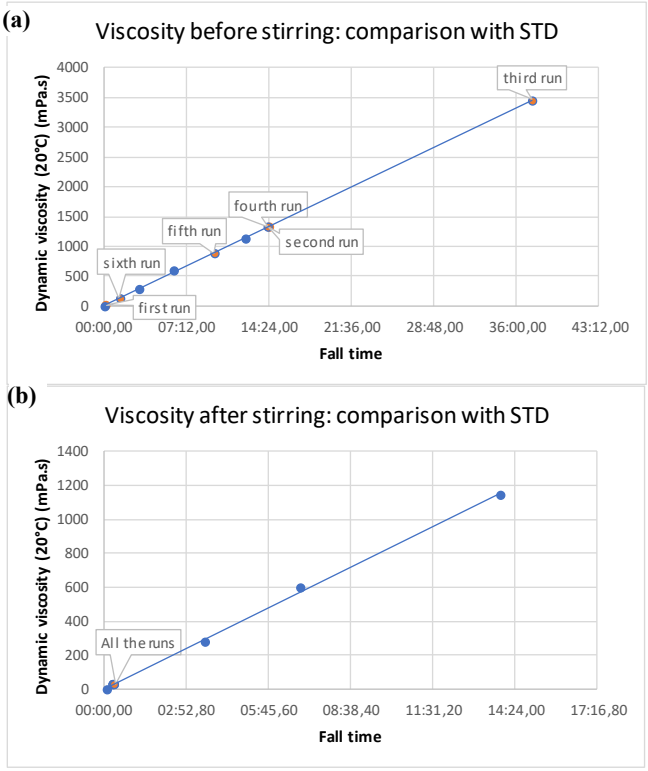

Figure 4. Viscosities of reaction mixture before (a) and after (b) stirring after each run (orange) compared with standards (blue).

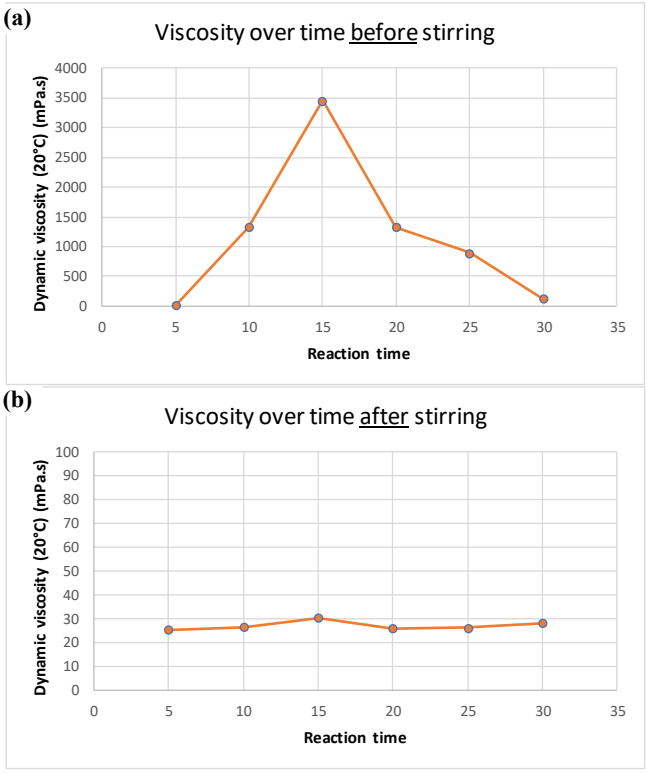

Figure 5. viscosities of reaction mixture before (a) and after (b) stirring after each run.

This means that, during the reaction, a chemical transformation which increases viscosity really occurs, but then, apparently, after 30 minutes of microwave treatment reaction is complete and the mixture's viscosity goes back to the initial value. This data also implies that, in a future flow equipment, care must be taken if the flow is stopped for some reason, because without flow the viscosity of the gel will increase considerably.

3 Conclusions

In summary, a fast and efficient procedure for microwave synthesis and solvent distillation was found for the preparation of a nanosized TiO_2 photocatalyst. The final product can be obtained both as a suspension, for an immediate use, or as powders, for better storage and shipping, that can later give a suspension for *in situ* coatings production without any loss in product quality and photocatalytic performance.

Comparison of the results obtained using microwave vs conventional heating revealed that, apart from heating rate, a specific microwave effect can reasonably be excluded, but that distillation has a deep impact on the reaction outcome.

Moreover, viscosity measurements useful for the next continuous flow optimization step were collected, and stirring was found crucial to keep low values of viscosity.

These findings can be considered milestones in the development of a highly efficient industrial microwave synthesis of TiO_2 nanoparticles that represent the third case of study in the SIMPLIFY project.

For further reading

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Enrico Paradisi is a post-doctotral researcher at the Department of Engineering "Enzo Ferrari" of the University of Modena and Reggio Emilia for the past three years. His research interest lies on the synthesis of nanometric TiO_2 for photocatalytic application of industrial interest. As a chemist, his background is principally in synthetic organic chemistry: his work was mainly focused on the total synthesis of biologically active compounds (M.Sc and postdoc) and asymmetric organocatalysis (Ph.D).

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Cristina Leonelli is Full Professor in Principles of Chemistry for Applied Technologies at the University of Modena and Reggio Emilia. Her field of interest is in solid state chemistry with particular interest in the reactivity of ceramic powders and transition from amorphous to crystalline state. She has a personal experience in designing new composition, preparation and characterization of different inorganic powders and bulk ceramic materials as well as application developments. She has also been active in the field of several innovative preparation techniques and microwave heating applied to materials processing and synthesis.

Valentina Dami is emloyed as a chemist at Colorobbia Consulting s.r.l. since several years. She is involved in the synthesis of photocatalytic nanoparticles and their technology applications, as well as polymeric glass for vitreous coatings.

Giovanni Baldi is currently Head of Research at CERICOL Research Centre, Colorobbia Consulting s.r.l. (Florence, Italy), where he spent most of his professional career. With a demonstrated history of working in the nanotechnology industry, he is skilled in Thin Films, Nanomedicine, Materials Science, Nanomaterials, and Spectroscopy, as well as a strong consulting professional. He is Professor for Industrial Nanotechnologies contracted at the University of Pisa. He holds a PhD in Industrial Engineering focused in Photo Chemistry from Università degli Studi di Firenze.