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PROBLEMS OF EXPLOITATIONS OF MICROWAVE REACTORS FOR NANOPARTICLES SYNTHESIS

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Key words: microwave, synthesis, high pressure, chemical reaction, reactor design, nanoparticles.

Abstract: The advantages of microwave reactors in chemistry have been exploited in many fields, but the proper reactor design still make a challenge. Areas where microwave technology is applied are drying, chemical decomposition, powder synthesis, sintering, and chemical process control. This article goes through the measurement and construction material's problems, especially in chemical synthesis of various nanoparticles. Issues of reactor's operation modes, materials used for microwave devices, and solvents are discussed. Examples of nanoparticles reactor's synthesis are given. The article describes typical problems encountered in research laboratories when preparing nanostructured powders.

Problemy przy eksploatacji reaktorów mikrofalowych do syntezy nanocząstek

Słowa kluczowe: mikrofale, synteza, wysokie ciśnienie, reakcje chemiczne, nanocząstki, reaktory.

Streszczenie: Zalety technologii ogrzewania mikrofalowego są wykorzystane w wielu dziedzinach, między innymi w mineralizacji, syntezie proszków, syntezach organicznych, spiekaniu oraz w suszeniu. W artykule omówiono zagadnienia związane z pomiarami parametrów reakcji oraz konstrukcji reaktorów dedykowanych do syntez chemicznych. Główną uwagę poświęcono trybom pracy reaktorów, materiałom konstrukcyjnym, a także problemom eksploatacji w urządzeniach mikrofalowych dedykowanych do otrzymywania nanoproszków różnego typu i przeznaczenia. Artykuł pokazuje możliwe problemy, które mogą wystąpić w laboratorium badawczym w którym używa się reaktorów mikrofalowych, szczególnie w syntezach nanocząstek.

Introduction

Microwave heating has a number of advantages, e.g., rapid heating, and direct delivery of energy to the heating object. Because of these advantages, microwaves have been used in many technological sectors, e.g., food processing, medical waste treatment, power synthesis, and sintering [1]. When microwave (MW) heating is applied in wet chemistry, the solution/suspension is heated first, and the vessel walls are heated afterwards due to contact with hot liquid. In conventional heating, it is in the opposite way, first the vessel walls are heated and then the solution.

Reaction times are reported to be shorter by using MW than using conventional heating [1–6]. Additionally, in microwave ovens, chemical reactions are reported to be more reproducible, because the heating process is uniform and highly controlled [1–3].

The main structural materials used to confine electromagnetic fields in the "cavity," where the electromagnetic energy transported by microwaves are metals, especially steels with high chemical resistance. The tight fit of all metal parts and their grounding determines the safety of use, effectiveness, and durability of microwave cavities as well as the entire devices [4–5].

In chemistry, the unusual course of reactions (e.g., fast reactions, selectivity) during microwave activation is called the "MW effect" and discussions on its reason are as old as chemical use of MW heating. Kappe [7] and Bana et al. [8] classified MW effects as thermal effects (differences of temperature), specific microwave effects (temperature based changes are not connected to MW heating and cannot be demonstrated by conventional heating), and non-thermal MW effects (changes cannot be rationalized by specific and thermal effects). One of the specific microwave effects is the superheating of solvents at atmospheric pressure [9].

However, when using microwave radiation, the challenges are to control of energy distribution in the reaction vessel, the interaction of microwaves with reactor materials, and the measurement of reaction temperatures. The synthesis of high quality chemical products and, in particular, nanoparticles depends on solving such problems. The use of microwave techniques requires solving a number of problems discussed in this article.

1. Challenges with microwave wet chemical synthesis

1.1. Typical designs of microwave laboratory devices

The chemical reactor for microwave synthesis has to be positioned in a metallic chamber, defined above as the cavity, where the microwave energy is confined. There are several cavity geometries, e.g., in the form of cylindrical, rectangular, or hexagonal chambers. The microwave irradiation and its interaction with matter are characterized by absorption, transmission, and reflection.

The reactor vessel can be made of MW transparent material, such as alumina, quartz, Pyrex® glass, and so on. In this case, the microwave energy goes directly to the sample across the container's walls. The size of the reactor vessel is very important for dielectric heating, since the microwave energy is absorbed by the specimen volume till a certain "penetration depth" [10]. It is essential to remember that even a very powerful 2.45 GHz source will not heat water evenly throughout a section greater than twice the penetration depth, i.e. 6 cm in each side in pure water. Unfortunately, when irradiating aqueous solutions of the precursors, the penetration depth is reduced.

1.2. Local heating, "hot spots" and measurements problems

The limited microwave penetration depth into different media constitutes an important limitation to the dimensions of a reactor [10–12]. Interference of the electromagnetic waves may lead to local "hot spots." Local overheating may lead to high reaction rates even though the mean temperature appears to be low [1].

The accurate temperature measurement in MW reactors for synthesis in liquid phase is a challenge, since metallic thermocouples couple with the electromagnetic field disturb its distribution, and they can lead to sparking and electromagnetic discharges in the reaction vessel. Measuring instruments connected with sensors exposed to microwave irradiation might be damaged as a result of the strong over-voltage generated by electromagnetic power. Strongly absorbing materials inside the reactor can cause unrepresentative temperatures. It is recommended to use fibre-optic sensors, which do not include metallic parts. However, the temperature range they can withstand is limited, and also their insertion in the reaction vessel is problematic [9, 13, 14]. More than one type of temperature measurements is recommended.

1.3. Burning of construction elements in the microwave reactor

During the exploitation of microwave reactors, the elements made of polymers (e.g., elements made of Teflon®, PTFE) may burn, especially in "hot spot" areas (Figs. 1–2). Hot spots can be also caused by segregation of MW absorbing reaction products at the reactor walls. Figure 1 shows the burnt out reaction cup and Teflon®

Fig. 1. Burnt out reaction chamber and Teflon® cover with antenna during ZnO NPs mineralization
Source: IHPP PAS.

Fig. 2. Burnt out Teflon® cover from burning on the antenna during the ZnO NPs synthesis
Source: IHPP PAS.

cover, including the inside, the antenna, and the inductor. Burning took place during mineralization of zinc oxide (ZnO) nanoparticles (NPs) with HNO_3, and the flame from the bottom of the chamber propagated inside to the rest of the system. Figure 2 shows a burned Teflon® cover during ZnO NPs synthesis. A rapid increase in pressure was noticed, the Teflon® cover was deformed upward, and the protective membranes over the reaction cup were damaged. To avoid burn outs, the operator should carefully clean all Teflon® surfaces inside and outside before the reaction.

1.4. Precipitation of synthesis materials on reactor walls

The important problem during MW synthesis is the deposition of powders on reactor surfaces and pitting of these walls. This causes changes in product concentration and also a risk of destroying the reactor vessel. Figure 3 shows an example of the sticking of hydroxyapatite to the reactor damper during a reaction.

Figure 4 shows cobalt doped ZnO NPs [15] deposited onto the Teflon® chamber of the reactor

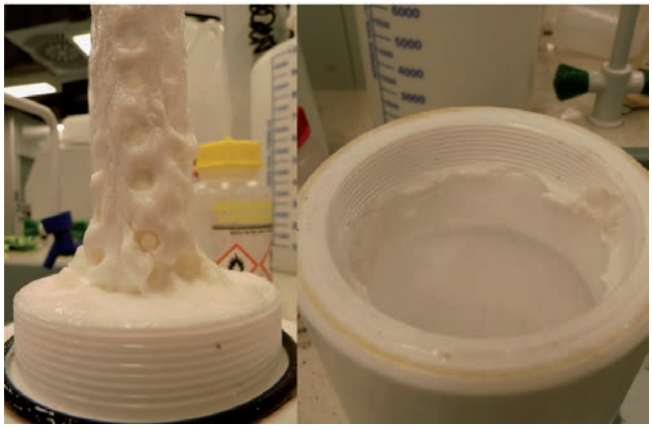

Fig. 3. Hydroxyapatite deposited on the damper during stop-flow reactions
Source: IHPP PAS.

Fig. 4. Cobalt doped ZnO NPs embedded in the reaction chamber during a few stop-flow reactions
Source: IHPP PAS.

with large pits. Visible precipitates are also seen in the cracks of the ceramic part of the reactor. The powdered sediment can absorb microwaves and produce hot spots on the Al_2O_3 ceramics surface. Every element of the reactor should be at good quality and purity. In the reaction chamber, defects can cause burnings during the MW reactions.

1.5. Challenges for construction materials, corrosion leaks, scratches

Microwave reactors in most cases are constructed in such a way that a polymer container is enclosed in a steel pressure vessel. A waveguide is connected to the vessel, and, at this place, the polymer vessel is not supported by steel. High temperature created during synthesis causes deformation of PTFE. Figure 5 shows a PTFE chamber in the microwave window and its bending at the waveguide contact points.

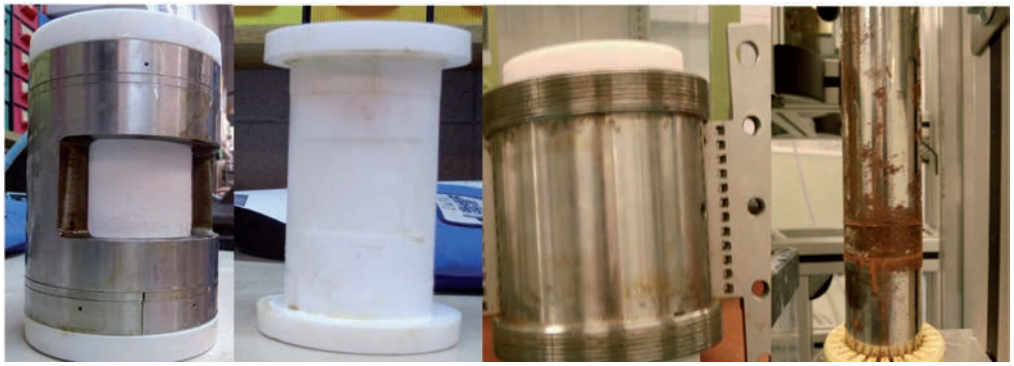

Fig. 5. Problems with PTFE deformations and steel elements, during synthesis in enhanced pressure
Source: IHPP PAS.

2. Examples of synthesis of nanoparticles in microwave reactors

Microwave reactions, as any chemical reactions, can take place in several modes: stop-flow, continuous, or batch. Each type of device has advantages but also operational limitations. It is important to adapt the type of device to a specific synthesis and specific final product.

In this section, examples will be given of the use of microwave reactors for the synthesis of HAP [16], ZnO [17–20], and ZrO_2 [21–24] nanopowders.

Hydroxyapatite (HAP) is a form of calcium phosphate with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$. This nanopowder is synthesized via a basic precipitation method in the acid/base neutralization process [16]. Microwave energy was used to regulate the size of the produced nanoparticles. Hydroxyapatite is an abrasive material and may lead to rapid erosion of valves and pumps. Moreover, the vessel's walls need regular cleaning, since hydroxyapatite sticks to them. In continuous reaction mode, sticking of nanoparticles to the reactor walls and pitting into the PTFE lining takes place. Cleaning should be planned every few processes, and it requires heating of acid solutions inside the reactor.

In ZnO NPs synthesis using the microwave solvothermal synthesis (MSS) technique, the reaction precursor is a solution of zinc acetate in ethylene glycol with the addition of water [15, 17–20]. Tests of ZnO NPs synthesis were performed in the MSS-2 reactor [6, 25, 26] (Fig. 6). The MSS-2 reactor made by Institute of

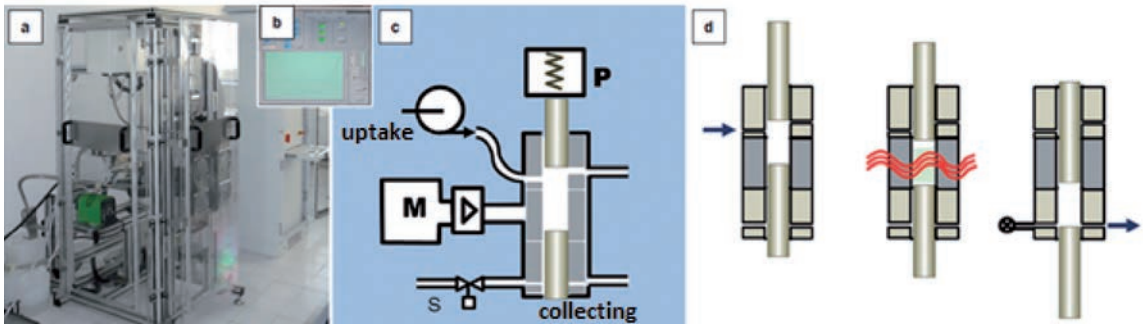

Fig. 6. The MSS2 reactor in stop-flow mode a), control panel b), working stop-flow scheme c), d) (M- magnetron, S- blow valve, P- pressure measuring converter)
Source [20].

High Pressure Physics PAS, Warsaw, and the Institute for Sustainable Technologies NRI, Radom, Poland, permits a rapid, uniform heating and make a synthesis under high purity conditions in a close vessel mode (batch) and stop-flow mode with precise control of the reaction time and obtained pressure. The MSS2 stop-flow reactor is a reactor with a 470 ml vessel. The design of this reactor ensures an easy and quick replacement of the reaction chambers. In the stop-flow mode, the products of the synthesis are emptied under pressure with rapid interruption of the reaction. Such operation provides the following: (i) a rapid cooling with no-agglomeration; (ii) easy control of the particle size, aggregation size; and, (iii) leads to a narrow size distribution in the final product [15-19]. For batch mode, it is easier to keep the walls clean from reaction products; however, this mode takes more time to synthesize the same amount of product, i.e. a volume of 270 ml. Moreover, mineralization ZnO can lead to the burning of the walls of the reactor, because of the enhanced absorption of microwaves by ZnO NPs attached to the reactor walls with the consequent appearance of the typical hot spots [4]. For Mn^{2+} or Co^{2+} doped ZnO NPs [15,27], contamination of the reactor walls is easy to be observed, because of the different colour on the white PTFE.

For batch mode compared to continuous reactor modes, the yield per unit time is lower, since the cooling rate should also be taken into account, because the reactor should be opened at a safe temperature and pressure level. On the other hand, filling the reaction cup with a new suspension or solution allows one to check the cleanliness and technical condition of the device, which reduces burn-out or hot spots.

3. Discussion

During the microwave driven chemical syntheses, an important aspect is the understanding of the behaviour of the precursors and synthesis material in the microwave field. Such knowledge helps in determining the parameters of the synthesis itself as well as the microwave device needed in this reaction.

Important questions are the following:

- Do metallic particles take part in the reaction? Can they strongly interact with the microwave field and cause bursts of burn?
- Is the substrate homogenous or heterogeneous? Is it a solution or a suspension?
- What is the penetration depth of MW into the suspension?
- Is it a better to use the continuous, stop-flow, or batch mode?
- Is the product easy to rinse, pump, or does it need mixing just before the microwave reaction?
- What is the risk of explosion? If reaction cup in batch mode is hermetically closed in a high pressure vessel, it is necessary to leave an empty space in the reaction cup (about 20% of volume without precursor for thermal expansion), and the reactor must have safety valves.
- Due to rapid reaction, the process should be digitally recorded and controlled, is it?
- Is the reaction toxic and requires additional air extracts and precautions? (This includes flammability and corrosiveness.)
- Will the material interact with reactor materials? Should it use stronger elements of supports, chambers, or special reaction chamber/vessel?

For nanoparticles synthesis new challenges arise. Since their toxicity is unknown, there is a tendency to consider them as potentially toxic. For this reason, it is particularly important to ensure they are always suspended as dispersion in a solvent and are not spread in air.

Summary

This article shows the typical problems of temperature measurements, construction problems, and synthesis problems during microwave wet chemical synthesis, with particular emphasis on nanoparticles synthesis. Equipment failures can be divided into general operational problems and specific microwaves problems. General samples are abrasion and sedimentation of suspensions/solutions and settling them on the elements of the reactor, or the problem of cleaning the system components between synthesis. Sedimentation of nanoparticles to the walls of the reaction vessels causes particular challenges during microwave reactions. Specific microwave challenges are how to measure temperature and pressure inside the system, hot spots, system/antenna sparking, and interaction of nanoparticles sedimented to vessel walls with electromagnetic waves. Despite problems during microwave synthesis, microwave energy is well suited in the synthesis of nanomaterials, because fast heating and high pressures lead to high quality nanoparticles.

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References

1. Sun J., Wang W.: Review on Microwave-Matter Interaction Fundamentals and Efficient Microwave-Associated Heating Strategies. Materials, 2016, 9(4), p. 231. DOI: 10.3390/ma9040231
2. Bogdal D.: Microwave-assisted Organic Synthesis, One Hundred Reaction Procedures. Amsterdam: Elsevier, 2005.
3. Schanche J.S.: Microwave synthesis solutions from personal chemistry. Molecular Diversity, 2003, 7(2-4), pp. 291–298. DOI:10.1023/B:MODI.0000006866.38392.f7
4. Cravotto G., Carnaroglio D. (eds.): Microwave Chemistry. Berlin: De Gruyter, 2017.
5. Leadbeater N.E., McGowan C.B.: Laboratory experiments using microwave heating. CRC Press, 2013.
6. Łojkowski W., Leonelli C., Chudoba T., Wojnarowicz J., Majcher A., Mazurkiewicz A.: High--Energy-Low-Temperature Technologies for the Synthesis of Nanoparticles: Microwaves and High Pressure. Inorganics, 2014, 2(4), pp. 606–619. DOI: 10.3390/inorganics2040606
7. Kappe C.O.: Controlled microwave heating in modern organic synthesis. Angewandte Chemie International Edition, 2004, 43(46), pp. 6250–6284. DOI: 10.1002/anie.200400655
8. Bana P., Greiner I.: Interpretation of the Effects of Microwaves. In: Keglevich G. (ed.): Milestones in Microwave Chemistry. Switzerland: Springer, 2016. DOI: 10.1007/978-3-319-30632-2_4
9. Fang Z., Smith Jr. R.L., Qi X.: Production of Biofuels and Chemicals with Microwave. Netherlands: Springer, 2015. DOI:10.1007/978-94-017-9612-5
10. Leonelli C., Veronesi P.: Microwave Reactors for Chemical Synthesis and Biofuels Preparation. In: Fang Z., Smith Jr. R.L., Qi X. ed.: Production of Biofuels and Chemicals with Microwave. Netherlands: Springer, 2015. DOI: 10.1007/978-94-017-9612-5_2
11. Balint E., Keglevich G.: The spread of the application of the microwave technique in organic synthesis. In: Keglevich G. (ed.): Milestones in Microwave Chemistry. Switzerland: Springer, 2016. DOI: 10.1007/978-3-319-30632-2_1
12. Horikoshi S., Schiffmann R.F., Fukushima J.: Serpone N.: Microwave Chemical and Materials Processing. Singapore: Springer, 2018. DOI: 10.1007/978-981-10-6466-1
13. Bogdal D., Bednarz S., Lukasiewicz M.: Microwave induced thermal gradients in solventless reaction systems. Tetrahedron, 2006, 62(40), pp. 9449–-9445. DOI: 10.1016/j.tet.2006.07.038
14. Kappe C.O.: How to measure reaction temperature in microwave-heated transformations. Chemical Society Reviews, 2013, 42, pp. 4977–4990. DOI: 10.1039/c3cs00010a
15. Wojnarowicz J., Chudoba T., Gierlotka S., Sobczak K., Lojkowski W.: Size Control of Cobalt-Doped ZnO Nanoparticles Obtained in Microwave Solvothermal Synthesis. Crystals, 2018, 8(4), p. 179. DOI: 10.3390/cryst8040179
16. Kuśnieruk S., Wojnarowicz J., Chodara A., Chudoba T., Gierlotka S., Łojkowski W.: Influence of hydrothermal synthesis parameters on the properties of hydroxyapatite nanoparticles. Beilstein Journal of Nanotechnology, 2016, 7, pp. 1586–1601. DOI: 10.3762/bjnano.7.153
17. Wojnarowicz J., Opalinska A., Chudoba T., Gierlotka S., Mukhovskyi R., Pietrzykowska E., Sobczak K., Lojkowski W.: Effect of Water Content in Ethylene Glycol Solvent on the Size of ZnO Nanoparticles Prepared Using Microwave Solvothermal Synthesis. Journal of Nanomaterials, 2016, 2789871. DOI: 10.1155/2016/2789871
18. Wojnarowicz J., Chudoba T., Koltsov I., Gierlotka S., Dworakowska S., Lojkowski W.: Size control mechanism of ZnO nanoparticles obtained in microwave solvothermal synthesis. Nanotechnology, 2018, 29(6), 065601. DOI: 10.1088/1361-6528/aaa0ef
19. Wojnarowicz J., Chudoba T., Gierlotka S., Lojkowski, W.: Effect of Microwave Radiation Power on the Size of Aggregates of ZnO NPs Prepared Using Microwave Solvothermal Synthesis. Nanomaterials, 2018, 8(5), p. 343. DOI: 10.3390/nano8050343
20. Wojnarowicz J., Chudoba T., Smoleń D., Łojkowski W., Majcher A., Mazurkiewicz A.: Przykłady otrzymywania nanocząstek z wykorzystaniem mikrofalowej solwotermalnej syntezy MSS. Szkło i Ceramika, 2014, 6, pp. 8–11 (in Polish).
21. Opalinska A., Leonelli C., Lojkowski W., Pielaszek R., Grzanka E., Chudoba T., Matysiak H., Wejrzanowski T., Kurzydlowski K.J.: Effect of pressure on synthesis of Pr-doped zirconia powders produced by microwave-driven hydrothermal reaction. Journal of Nanomaterials, 2006, 98769. DOI: 10.1155/JNM/2006/98769
22. Opalinska A., Malka I., Dzwolak W., Chudoba T., Presz A., Lojkowski W.: Size-dependent density of zirconia nanoparticles. Beilstein Journal of Nanotechnology, 2015, 6, pp. 27–35. DOI: 10.3762/bjnano.6.4
23. Kaszewski J., Łojkowski W., Narkiewicz, U.: Preparation of ZrO2:Tb via microwave hydrothermal method. Optica Applicata, 2009, 39(4), pp. 773–779.

24. Bondioli F., Ferrari A.M., Braccini S., Leonelli C., Pellacani G.V., Opalińska, A., Chudoba T., Grzanka E., Palosz B.F., Łojkowski W.: Microwave – Hydrothermal Synthesis of Nanocrystalline Pr - Doped Zirconia Powders at Pressures up to 8 MPa. Solid State Phenomena, 2003, 94, pp. 193–196. DOI: 10.4028/www.scientific.net/SSP.94.193
25. Majcher A., Wiejak J., Przybylski J., Chudoba T., Wojnarowicz J.: A Novel Reactor for Microwave Hydrothermal Scale-up Nanopowder Synthesis. International Journal of Chemical Reactor Engineering, 2013, 11(1), pp. 361–368. DOI: 10.1515/ijcre-2012-0009
26. Majcher A.: Batch Control of Microwave Hydrothermal Synthesis of Nanopowders Processs. Problemy Eksploatacji. Maintenance Problems, 2015, 98(3), pp 5–16.
27. Wojnarowicz J., Mukhovskyi R., Pietrzykowska E., Kusnieruk S., Mizeracki J., Lojkowski W.: Microwave solvothermal synthesis and characterization of manganese-doped ZnO nanoparticles. Beilstein Journal of Nanotechnology, 2016, 7, pp. 721–732. DOI: 10.3762/bjnano.7.64