

# Physico-chemical and dispersive characterisation of magnesium oxides precipitated from the $\text{Mg}(\text{NO}_3)_2$ and $\text{MgSO}_4$ solutions

Agnieszka Pilarska, Dominik Paukszta, Filip Ciesielczyk, Teofil Jesionowski\*

Poznan University of Technology, Institute of Chemical Technology and Engineering, M. Skłodowskiej-Curie 2 Sq., 60-965 Poznań, Poland

\*corresponding author: e-mail address: teofil.jesionowski@put.poznan.pl

An attempt was made to synthesise magnesium oxide of a high degree of dispersion permitting its use as adsorbent or catalyst. The synthesis method proposed was precipitation with the use of magnesium nitrate or magnesium sulfate. The influence of temperature, the mode and the rate of dosing, the concentration and the ratio of the reagents on the properties of the final product was analysed. Magnesium oxides were obtained by thermal decomposition of magnesium hydroxides and subjected to thorough analysis. The results permitted selection of the reaction systems ensuring synthesis of the final products of the desired properties.

**Keywords:** Magnesium oxide; Magnesium hydroxide; Precipitation; Particle size distribution and surface morphology; Adsorptive properties.

## INTRODUCTION

The main aim of producing materials on the nano- and microscale is to permit thorough assessment of their morphological and microstructural properties. The results of extensive research work permitted the production of ordered microstructural systems of particles of well-defined shapes and sizes. It has been shown that morphology and microstructure influencing the chemical and physical properties of the compounds, also determine their future use<sup>1</sup>.

Magnesium oxide is highly homogenous and has particles of spherical shape. It is non-toxic, inflammable, shows high electric resistance and great mechanical strength that makes it desirable for a wide range of applications. Besides the use in heterogeneous catalysis<sup>2</sup>, MgO is an interesting insulating and construction material or pharmaceutical compounds. Literature provides a number of methods developed for the synthesis of magnesium oxide, among them the sol-gel method<sup>3</sup>, methods based on chemical precipitation<sup>4</sup>, hydrothermal<sup>5</sup>, solvothermal<sup>6</sup>, electrochemical methods<sup>7</sup> and the method based on the use of microwaves<sup>8,9</sup>. The microwave method has been widely used in synthetic organic chemistry and in synthesis of other metal oxides by direct heating of hydrated precursors<sup>10</sup>. When applied to synthesise MgO it gives particles of different surface morphology. The influence of the parameters of the process (temperature, substrate concentrations) on the properties of the product has been studied. However, this technology is time-consuming and hence expensive and little promising if applied on a large scale.

Not many authors have been interested in the synthesis of metal oxides by precipitation methods. In this paper we propose a method of magnesium oxide preparation by precipitation with the use of magnesium sulfate or magnesium nitrate and sodium hydroxide. The influence of the parameters of the process on the dispersion and morphology of the product was analysed to provide the background for the selection of the experimental conditions that would ensure getting a product of specific target properties.

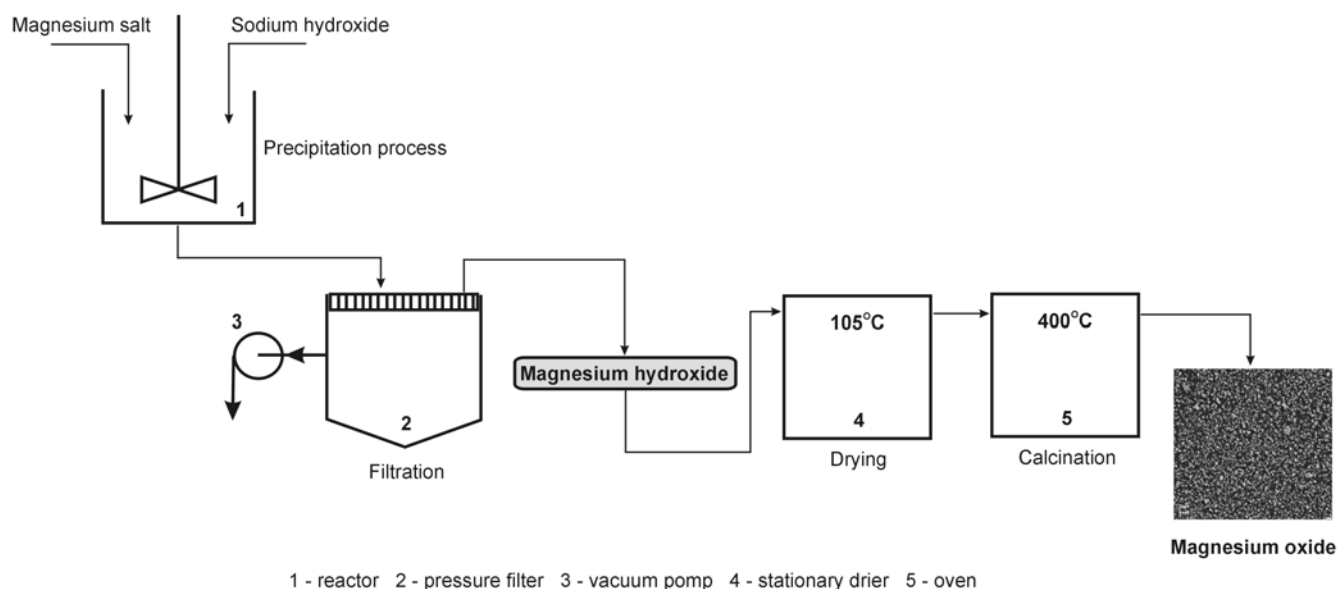
## EXPERIMENTAL

The precipitation reaction was performed with the use of solutions of hydrated magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ , of analytical grade, purchased from POCh SA) or magnesium sulfate ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , of analytical grade purchased from POCh SA) and sodium hydroxide (NaOH, of analytical grade, POCh SA). The substrates at the stoichiometric ratio or with excess of the magnesium salt were dosed simultaneously at the rate of 2.3 cm<sup>3</sup>/min to the water system. The magnesium salts were used at the concentrations of 5, 10 or 15% and at the temperatures of 40°C or 80°C, optimum for the use of magnesium nitrate and magnesium sulfate, respectively. Magnesium hydroxide precipitated was dried at 105°C and then calcined at 400°C for 2 hours till getting the final product of magnesium oxide. At first bulk density was measured for all the samples.

Then the samples were subjected to the measurements of particle size distributions with the help of Zetasizer Nano ZS (NIBS method). The surface of the selected samples was observed under an electron scanning microscope Zeiss VO40. The specific surface area BET as well as pore volumes and diameters were measured also for the selected samples (ASAP 2020 made by Micromeritics Instruments Co.). The crystalline structure of the selected samples was determined by X-ray diffraction method using a horizontal diffractometer, working with a HZG-3 type goniometer. Structural identification was performed using X-RAYAN software<sup>12</sup>. The samples were also subjected to the experiments aimed at the determination of their wettability and sedimentation profiles in water systems by a K100 tensiometer made by Krüss.

## RESULTS AND DISCUSSION

Table 1 gives the bulk densities and results of the dispersion measurements of MgO obtained by precipitation with the use of magnesium nitrate at different concentrations at 40°C. Samples 1, 2, 3 were obtained in the reaction with the stoichiometric rate of the reagents, while sample 4 was obtained at the excess of magnesium salt. The temperature of the reaction is the optimum for the



**Figure 1.** Technological scheme of the process of precipitation of magnesium hydroxide from a magnesium salt

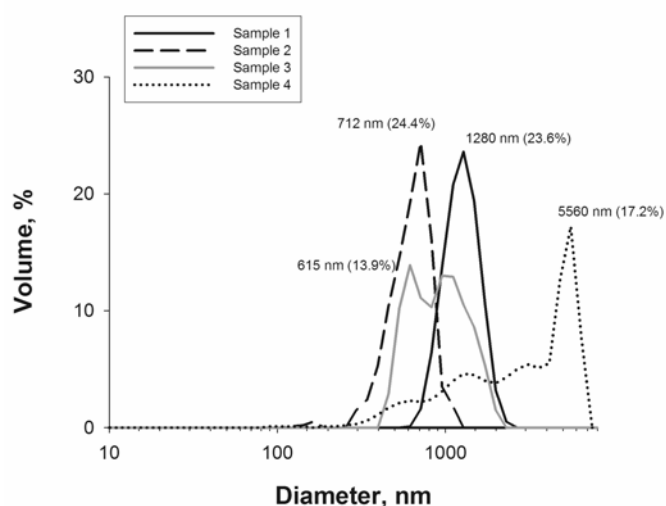
**Table 1.** Physico-chemical properties of MgO precipitated at 40°C, with the use of magnesium nitrate at different concentrations

| Sample No. | Mg(NO <sub>3</sub> ) <sub>2</sub> concentration, % | Salt/NaOH stoichiometric ratio | Bulk density, g/dm <sup>3</sup> | Diameter, nm             |
|------------|--|--------------------------------|---------------------------------|--------------------------|
| 1          | 5  | 1:1                            | 100                             | 615 ÷ 2300               |
| 2          | 10   |                                | 133                             | 122 ÷ 142;<br>459 ÷ 1110 |
| 3          | 15   |                                | 141                             | 459 ÷ 1990               |
| 4          | 10   | 1.5:1                          | 148                             | 91 ÷ 142;<br>164 ÷ 5560  |

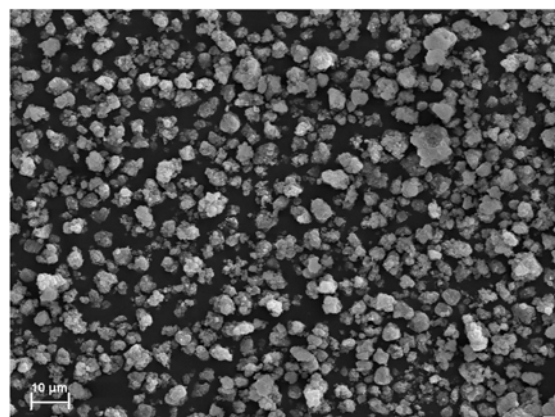
reaction systems with magnesium nitrate. The lowest bulk density of 100 g/dm<sup>3</sup> was found for sample 1 precipitated with the use of 5% solution of magnesium nitrate. The bulk density of magnesium oxide (sample 2) obtained with the use of a 10% solution of magnesium nitrate was slightly higher – 133 g/dm<sup>3</sup>. The values obtained for samples 1 ÷ 4 confirm the observation that bulk density increases with increasing the concentration of magnesium salt used. In the particles size distributions recorded for these samples the bands in nanometric range are relatively broad. The greatest diameters reaching as much as 5560

nm were found for the particles from sample 4. The narrowest band in this range of 122 ÷ 1110 nm was obtained for sample 2.

The particle size distributions obtained for samples 1 ÷ 4 shown in Fig. 2a permits the analysis of the effects of the reagents ratios and concentrations on the dispersion properties of MgO. The particle distribution curve of sample 2, (precipitated with 10% solution of magnesium nitrate) confirms the smallest scatter of particles diameters and their lowest values. The narrow band is shifted towards lower values of particles diameters and the maxi-



(a)



(b)

**Figure 2.** (a) Particle size distributions (Zetasizer Nano ZS) of magnesium oxides precipitated with the use of magnesium nitrate at different concentrations at 40°C, (b) SEM image of MgO sample 2

**Table 2.** Physico-chemical properties of MgO precipitated at 80°C with the use of magnesium sulfate at different concentrations

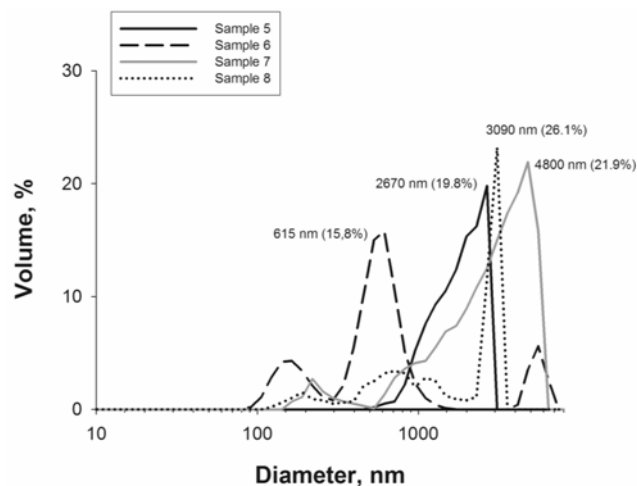
| Sample No. | MgSO <sub>4</sub> concentration, % | Salt/NaOH stoichiometric ratio | Bulk density, g/dm <sup>3</sup> | Diameter, nm |
|------------|------------------------------------|--------------------------------|---------------------------------|--------------|
| 5          | 5                                  | 1:1                            | 49                              | 531 ÷ 2670   |
| 6          | 10                                 |                                | 112                             | 91 ÷ 5560    |
| 7          | 15                                 |                                | 148                             | 164 ÷ 5560   |
| 8          | 5                                  | 1.5:1                          | 110                             | 122 ÷ 3090   |

imum volume contribution is brought by the particles of 712 nm in diameter. A single band covering the diameters from the range 615 ÷ 2300 nm was also recorded for sample 1, testifying to the homogeneity of this sample. The poorest dispersive and morphological properties revealed sample 4 precipitated with the use of volume excess of magnesium salt of 10% solution. The wide band covering diameters of high values (the maximum volume contribution is brought by the particles of 5560 nm in diameter) proves the diversified morphology of the sample and tendency to agglomerate formation. For sample 2, the uniform dispersive character of magnesium oxide particles of spherical and regular shape is additionally confirmed by SEM image, (Fig. 2b). The above analysis of the effects of the precipitation conditions on the final product (obtained with the use of magnesium nitrate) permitted the determination of the optimum conditions ensuring preparation of magnesium oxide of the best dispersion and morphology. According to the results, the best final product was sample 2, because of high homogeneity and relatively high refinement.

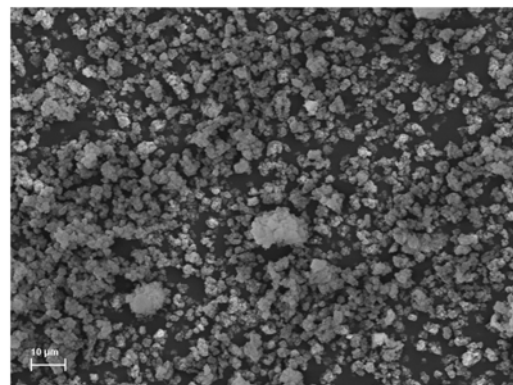
Table 2 presents the physico-chemical parameters of magnesium oxide samples precipitated with the use of magnesium sulfate at 80°C, which is the optimum temperature for the reaction system with this magnesium salt. Samples 5 ÷ 8 were subjected to measurements of bulk density and particle size distributions. Samples 5, 6, 7 of magnesium oxide were obtained at the stoichiometric ratio of the reagents, while sample 8 at the volume excess of magnesium sulfate. As follows from the data given in the table 2, the best properties were determined for sample 5, which has very low bulk density of 49 g/dm<sup>3</sup> and particles of diameters varying in a relatively narrow range up to 2670 nm. With increasing the concentration of the solution of magnesium sulfate the parameters of the final products get worse, their bulk density increases, the particle size distribution is scattered over a wide range, up to 5560 nm. The broad bands in the particle size distribution patterns obtained for samples 6 and 7 (Fig. 3) testify to the samples inhomogeneity and the tendency to agglomerate formation.

When the volume excess of the salt 5% solution was used, the final magnesium oxide (sample 8) the final product had higher bulk density than that obtained at the stoichiometric ratio of the reagents and contained particles of small and relatively large diameters. As follows from the particle size distribution pattern recorded for sample 8, the particles of small diameters bring a small volume contribution, while the volume contribution of larger ones is much greater (Fig. 3).

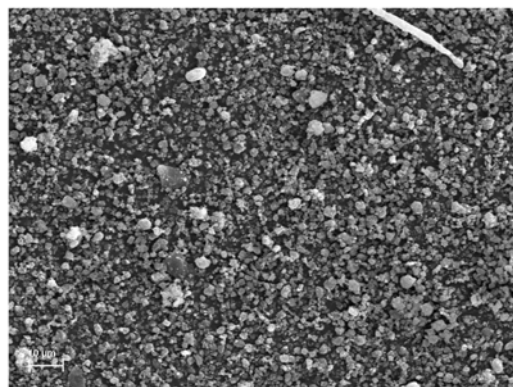
SEM photographs have shown that MgO samples 5 and 8 have surfaces of relatively homogeneous character and particles making agglomerates of intermediate size.



(a)



(b)



(c)

**Figure 3.** (a) Particle size distribution (Zeatasizer Nano ZS) of magnesium oxide samples precipitated with the use of magnesium sulfate solutions of different concentrations at 80°C; SEM images of (b) sample 5 (c) sample 8

At the subsequent stage of the study, the nitrogen adsorption/desorption isotherms were determined for samples 2, 5, 8. The shape of the isotherms (Fig. 4) points to

mesoporous structure of these samples. The volume of adsorbed nitrogen was found to systematically increase with increasing relative pressure up to a maximum value at  $p/p_0=1$ , of 180, 370 and 600  $\text{cm}^3/\text{g}$  for samples 2, 5 and 8, respectively. The specific surface area of sample 8 is 269  $\text{m}^2/\text{g}$ , which is rather great, that of sample 5 is smaller, of 146  $\text{m}^2/\text{g}$ , while that for sample 2, precipitated with the use of magnesium nitrate is 81  $\text{m}^2/\text{g}$ . The differences follow most probably from different microstructures of the samples. The greatest specific surface area was obtained for the sample precipitated at the volume excess of the magnesium salt at 80°C.

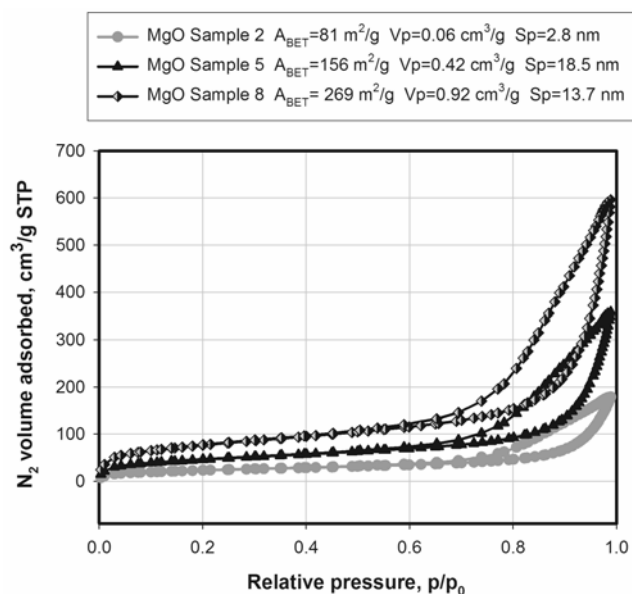


Figure 4.  $\text{N}_2$  adsorption/desorption isotherms for samples 2, 5, 8

The same samples, 2, 5 and 8 were then subjected to X-ray diffraction study to identify their structure with the help of X-RAYAN software. The XRD analysis proved that the samples contained synthetic magnesium oxide of the partially crystallized structure.

Fig. 5 a, b, c presents the diffraction peaks characteristic of the crystalline phase of MgO. The maximum at  $2\theta=37$  in the diffractograms informs about the partially-formed crystalline structure of the samples, most probably because of a too low temperature of calcination.

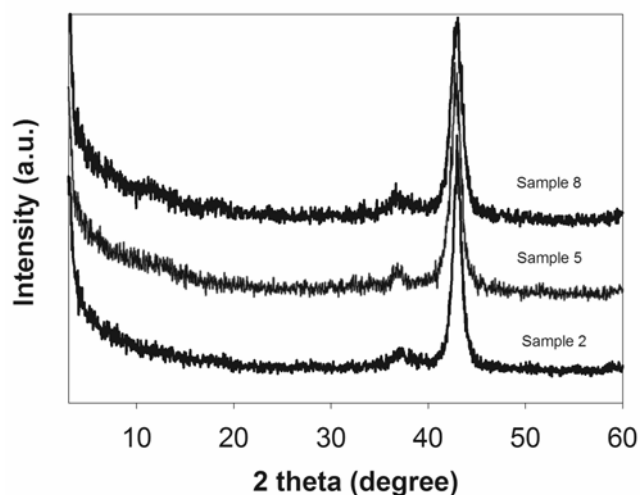
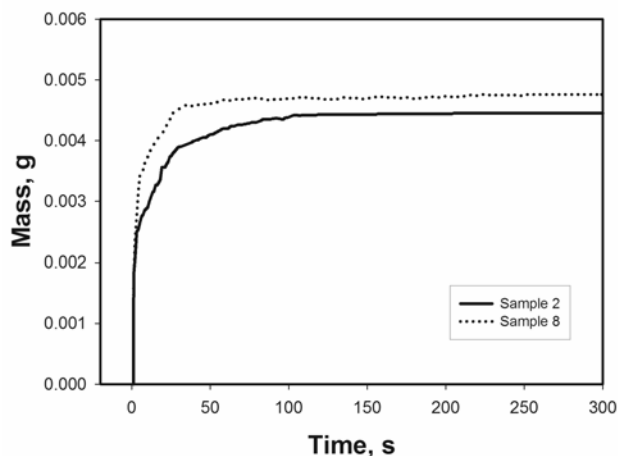


Figure 5. X-Ray diffraction patterns of samples 2, 5, 8

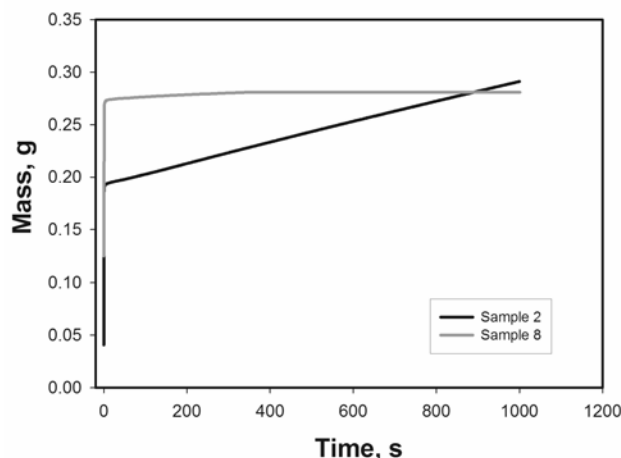
Samples 2 and 8, representing magnesium oxides obtained with two types of magnesium salts, were then subjected to measurements of sedimentation profiles and wettability with water (Fig. 6). The process of sedimentation provides the information on the microstructure of the substances studied, while wettability – defined as the ease of bounding water – determines the suitability of the material studied for certain applications, e.g. as a filler or adsorbent.

For sample 8 the mass increase was a bit greater (0.0048 g) in the same time than for sample 2 (Fig. 6a). The reason was a greater tendency towards agglomerates formations of this sample than that of sample 2, despite the lower bulk density of the former sample.

The amount of water adsorbed in the same time by sample 2 precipitated with the use of magnesium nitrate was comparable to that adsorbed by sample 8 precipitated with the use of magnesium sulfate, the corresponding values were 0.27 g and 0.29 g. However, the courses of the wettability curves (fig. 6b) reveal the difference in the character of the samples. The rapid mass increase of sample 2 proves its considerable tendency to bound water, sample 8 in a very short time reaches stabilisation. Therefore, the magnesium oxide obtained with the use of magnesium sulfate shows more hydrophobic nature than that precipitated with the use of magnesium nitrate.



(a)



(b)

Figure 6. Comparison of (a) sedimentation profiles and (b) wettability in water systems obtained for samples 2 and 8

## CONCLUSIONS

Synthesis of magnesium oxide with the use of sodium hydroxide and a magnesium salt in the optimum conditions permits getting the final products of well defined dispersive, morphological and adsorptive properties. When the precipitation is carried out with the use of 10% solution of  $\text{Mg}(\text{NO}_3)_2$  at  $40^\circ\text{C}$ , the final product is characterised by high dispersion (the maximum volume contribution is brought by particles of 712 nm in diameter) and uniform morphology.

The use of 10% solution of  $\text{MgSO}_4$ , at the volume ratio of the reagents of 1.5:1 at  $80^\circ\text{C}$  gives the final magnesium oxide of large specific surface area BET; the largest obtained was  $269 \text{ m}^2/\text{g}$ . XRD analysis of selected samples has proved that the final magnesium oxides obtained by calcination of magnesium hydroxides had not fully developed crystalline structure.

## Acknowledgements

This work was supported by the Poznan University of Technology research grant no. 32-125/2010-DS.

## LITERATURE CITED

1. Yan, Y., Zhou, L. & Zhang, Y. (2008). Synthesis of MgO hierarchical nanostructures controlled by the supersaturation ratio, *J. Phys. Chem.* 112, 19831 – 19835. DOI: 10.1021/jp806639x.
2. Choudhary, V.R. & Dumbre, D.K. (2009). Magnesium oxide supported nano-gold: A highly active catalyst for solvent-free oxidation of benzyl alcohol to benzaldehyde by TBHP, *Catal. Communications* 10, 1738 – 1742. DOI: 10.1016/j.catcom.2009.05.020.
3. Ouraipryvan, P., Sreethawong, T. & Chavadej, S. (2009). Synthesis of crystalline MgO nanoparticle with mesoporous-assembled structure via a surfactant-modified sol-gel process, *Mater. Lett.* 63, 1862 – 1865. DOI: 10.1016/j.matlet.2009.05.068.
4. Wang, W., Qiao, X. & Chen, J. (2008). The role of acetic acid in magnesium oxide preparation via chemical precipitation, *J. Am. Ceram. Soc.* 91, 1697 – 1699. DOI: 10.1111/j.1551-2916.2008.02326.x.
5. Byrappa, K. & Adschiri, T. (2007). Hydrothermal technology for nanotechnology, *Prog. Cryst. Growth Charac. Mater.* 53, 117 – 166. DOI: 10.1016/j.pcrysgrow.2007.04.001.
6. Fan, W., Sun, S., You, L., Cao, G., Song, X., Zhang, G. & Yu, H. (2003). Solvothermal synthesis of  $\text{Mg}(\text{OH})_2$  nanotubes using  $\text{Mg}_{10}(\text{OH})_{18}\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  nanowires as precursors, *Mater. Chem.* 13, 3062 – 3065. DOI: 10.1039/b307619a.
7. Zou, G., Chen, W., Liu, R. & Xu, Z. (2008). Morphology-tunable synthesis and characterizations of  $\text{Mg}(\text{OH})_2$  films via a cathodic electrochemical process, *Mater. Chem. Phys.* 107, 85 – 90. DOI: 10.1016/j.matchemphys.2007.06.046.
8. Wu, H., Shao, M., Gu, J. & Wei, X. (2004). Microwave-assisted synthesis of fibre-like  $\text{Mg}(\text{OH})_2$  nanoparticles in aqueous solution at room temperature, *Mater. Lett.* 58, 2166 – 2169. DOI: 10.1016/j.matlet.2004.01.010.
9. Polshettiwar, V., Baruwati, B. & Varma, R.S. (2009). Self-assembly of metal oxides into three-dimensional nanostructures: Synthesis and application in catalysis, *ACS NANO* 3, 728 – 736. DOI: 10.1021/nn800903p.
10. Marciniak, H. & Diduszko, R. (2004). X-Rayan – software for structure analysis and identification using WAXS technique (in Polish).