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# SYNTHESIS OF MgO IN MAGNESIUM HYDROXIDE CARBONATISATION PROCESS

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A method for synthesis of magnesium oxide by calcination of magnesium carbonate, obtained by carbonisation of magnesium hydroxide with carbon dioxide, is presented and the products obtained are characterised. The influence of the following experimental conditions on the final product properties was established: pH of the reaction medium, mode and rate of reagents supply. The final products were characterised by determination of their dispersion properties, wettability profiles (with water), specific surface area (BET), size and volume of pores. The products were identified by the X-ray diffraction method. The results proved a significant influence of the reaction conditions on the physicochemical parameters of the final magnesium oxide.

*keywords: MgO, precipitation, carbonisation process, particle size distribution, surface morphology, wettability, adsorptive properties*

## 1. INTRODUCTION

Due to its great mechanical resistance and thermal stability magnesium oxide is applied as catalyst or catalyst support (Choudhary, 1997; Ruckenstein, 1997; Xu, 2008). It is also a promising sorbent of pollutants of different types (Gulkowa, 2004). Thanks to its unique basic character magnesium oxide and its derivative make a specific class of substances of similar properties, similarly as the classes of acidic,

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neutral or amphoteric sorbents such as aluminium oxide, zeolites, silica and activated carbon.

The magnesium oxide features, highly desirable for the above applications, are mesoporosity and large specific surface area (Choudhary, 2004; Gulkova 2004). According to an interesting suggestion given by (Przepiórski, 2009) the control of porous structure in carbon materials appears as one of the most important aspects of adsorbents design. The adsorbing substances should be characterised by diversity of pores.

Many methods of obtaining microporous and mesoporous carbon materials have been described in literature. Mesoporous carbon materials can be obtained by thermal decomposition of a carbon precursor mixed with MgO or other magnesium-containing components like acetate or citrate.

Magnesium oxide is most often obtained by thermal decomposition of magnesium hydroxide (Green 1983), organic (Chhor, 1995; Thomas 1997) and inorganic salts (including hydrogencarbonate) (Botha, 2001), magnesium carbonate (Choudhary, 2004; Morozow, 2003) and containing it minerals (Yildirim, 2010). It has been proved that magnesium oxide obtained from magnesium carbonate is catalytically active. Morozow (2003) and other authors reported experimental studies on thermal decomposition of magnesium carbonate to magnesium oxide, including analysis of structural and textural characterisation of the intermediate and final products (XRD, BET). At particular stages of calcination conducted usually in the range 20÷800°C, the degree of decomposition was evaluated by DTA and TG methods. An important observation was that different DTA or TG curves were obtained for products synthesised from the same substrates but under different conditions, i.e. the time and temperature of calcination.

This paper presents a method for obtaining magnesium oxide by thermal decomposition of magnesium carbonate precipitated in our laboratory from magnesium hydroxide and carbon dioxide in a gas form. The influence of parameters of precipitation on the properties of the final product was analysed and the final product was characterised.

## 2. EXPERIMENTAL

Magnesium carbonate was obtained as a result of carbonisation of magnesium hydroxide ($Mg(OH)_2$, POCh SA) with $CO_2$ in the gas form (see Fig. 1). Precipitation was performed in a reactor of 500 $cm^3$ in capacity, equipped with a high-speed stirrer of Eurostar digital type made by IKA-Werke GmbH. Carbon dioxide was introduced to a suspension of magnesium hydroxide by a peristaltic pump ISM833A made by Ismatec, or in parallel with the suspension to the water system, at the rate of 1÷6 $dm^3$/min, for 3h, until getting pH=8 and stirred at 1800 rpm. The reaction was conducted at 20 or 40°C, using the suspension at the concentration of 5%. The precipitated magnesium carbonate was dried (105ºC, for ~8h) and then calcined at either 300, 600 or 950°C, for 1.5 h to get magnesium oxide as a final product using programmable oven (Controller P320 MB1, Nabertherm GmbH).

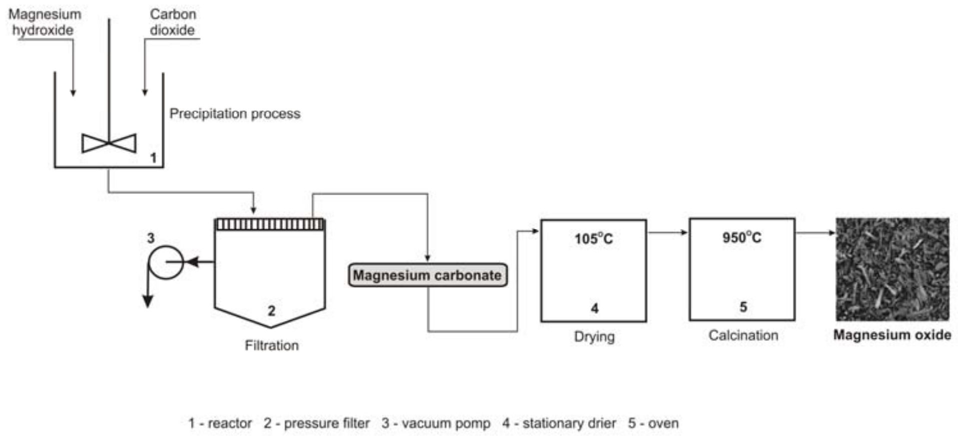


Fig. 1. Technological scheme of the process of precipitation of magnesium carbonate from magnesium hydroxide and carbon dioxide

The samples were characterised by determination of bulk density and particle size distributions using Zetasizer Nano ZS and Mastersizer 2000 made by Malvern Instruments Ltd, permitting measurements of particle diameters in the range from 0.6 to 6000 nm (NIBS method) and 0.2-2000 µm (diffraction laser scattering technique). Crystalline structures of selected magnesium oxides were studied by the WAXS method. The X-ray patterns were taken with the help of a computer-controlled horizontal diffractometer TUR M-62, equipped with a HZG-3 type goniometer. The wettability of magnesium oxide with water samples obtained was estimated by using a tensiometer K100 made by Krüss. To characterise the texture of selected MgO samples, the nitrogen adsorption-desorption isotherms were analysed to determine the specific surface area (BET), pore volume and pore diameter (calculated by the BJH method). The isotherms were taken by ASAP 2020 instrument made by Micromeritics Instruments Co.

## 3. RESULTS AND DISCUSSION

At the first stage of the experiment, samples of magnesium carbonate were precipitated according to the following procedure: $CO_2$ was introduced to a 5% suspension of magnesium hydroxide placed in the reactor at the rates in the range from 2 to 5 $dm^3$/min at 20 or 40°C. The intermediate products were subjected to calcination to get magnesium oxide samples. The final samples obtained are characterised in Table 1.

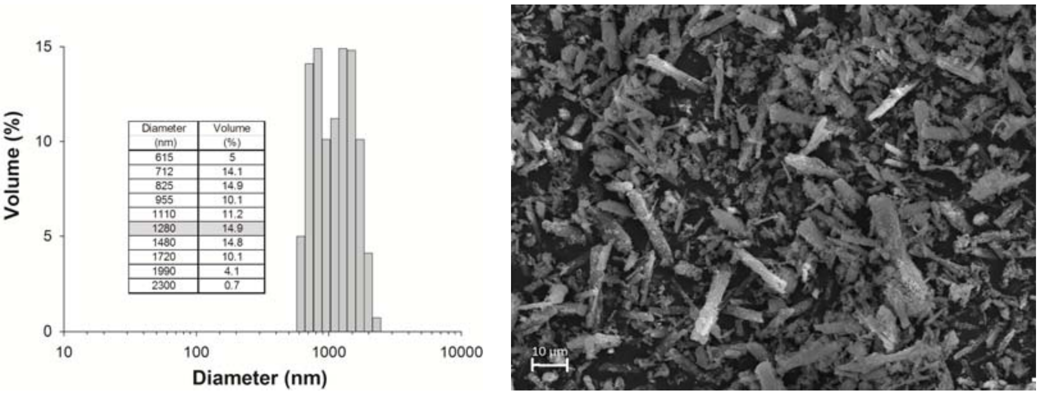
Table 1. Physicochemical and dispersive properties of magnesium oxide precipitated by introducing $CO_2$ to a 5% suspension of magnesium hydroxide

| Sample No. | Precipitation process conditions | | Physico-chemical and dispersive properties | | | | |
|---|---|---|---|---|---|---|---|
| | Flow rate ($dm^3$/min) | Temperature (°C) | Bulk density ($g/dm^3$) | Diameter (nm) from Zetasizer Nano ZS | Diameter (µm) from Mastersizer 2000 | | |
| | | | | | d(0.1) | d(0.5) | d(0.9) |
| 1 | 2 | 20 | 109 | 459÷2300 | 2.30 | 8.20 | 24.55 |
| 2 | | 40 | 138 | 122÷2300<br>4150÷5560 | 3.09 | 8.87 | 42.58 |
| 3 | 3 | 20 | 120 | 615÷2300 | 2.88 | 7.77 | 25.98 |
| 4 | | 40 | 125 | 122÷255<br>295÷2300<br>4150÷5560 | 3.25 | 9.67 | 32.83 |
| 5 | 4 | 20 | 160 | 91÷5560 | 2.78 | 16.01 | 46.03 |
| 6 | | 40 | 171 | 164÷531<br>615÷5560 | 2.93 | 17.02 | 47.03 |
| 7 | 5 | 20 | 167 | 91÷255;<br>295÷1720 | 2.78 | 16.32 | 46.82 |
| 8 | | 40 | 182 | 79÷342<br>459÷4150<br>4800÷5560 | 3.72 | 20.05 | 48.76 |

The physicochemical properties of magnesium oxide samples (1-8), obtained under conditions specified above, were found to be significantly depended on the rate of $CO_2$ supply and temperature of the process. The products obtained at relatively low rates of $CO_2$ supply (2 and 3 $dm^3$/min) were characterised by rather small bulk densities from 109 to 125 $g/dm^3$, and the lower values of densities were obtained when the process was run at 20°C. When the rate of $CO_2$ supply was increased to 4 and 5 $dm^3$/min, the product density increased to 182 $g/dm^3$ (aample 8, 5 $dm^3$/min, 40°C). A similar relation was observed for particle diameters. They were smaller for the low rates of $CO_2$ supply and at 20°C (samples 1 and 3). According to the results of measurements with Mastersizer 2000, in sample the contribution of particles of diameters not greater than 2.30 µm in the sample is 10%, the contribution of those of diameters below 8.20 µm is 50% and the contribution of those of diameters not greater than 24.55 µm is

90%. For the products obtained at 40°C a tendency to formation of particles of greater diameters was observed. For the rates of $CO_2$ supply of 4 and 5 dm$^3$/min, the process of particle agglomeration developed irrespective of the temperature applied. The magnesium oxide samples precipitated under such conditions (samples 5÷8) were characterised by relatively high values of *d*(0.9) up to 48.76 µm.

Figs 1 and 2 present the particle size distributions and SEM photographs of MgO samples 1 and 3, showing the most beneficial physico-chemical properties. The curves in Figs 1a and 2a display monomodal bands covering similar ranges of particle diameters, from 615 to 2300 nm and from 459 to 2300 nm, respectively. The similar dispersion, morphology and microstructure of the samples are confirmed by the SEM photograph, revealing the dominant presence of longitudinal crystallites of irregular form.



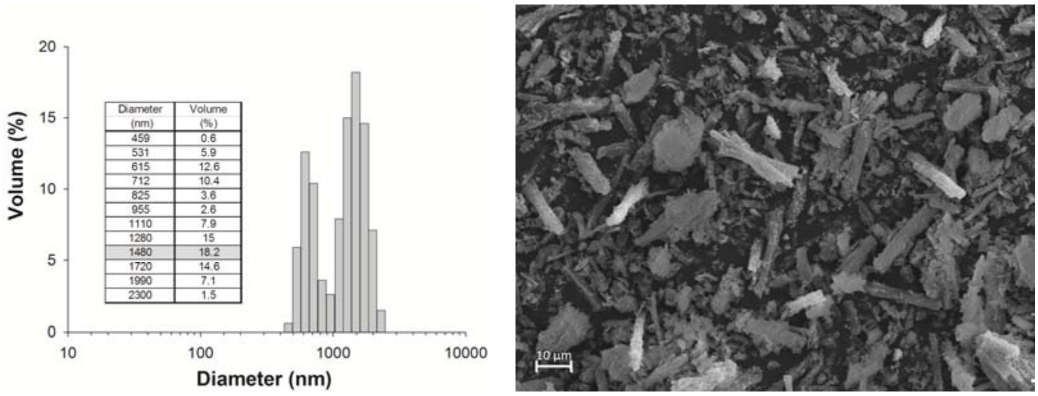
| Diameter (nm) | Volume (%) |
|---|---|
| 615 | 5 |
| 712 | 14.1 |
| 825 | 14.9 |
| 955 | 10.1 |
| 1110 | 11.2 |
| 1280 | 14.9 |
| 1480 | 14.8 |
| 1720 | 10.1 |
| 1990 | 4.1 |
| 2300 | 0.7 |

(a) (b)

Fig. 1. (a) Particle size distribution (Zetasier Nano ZS) and (b) SEM photograph of magnesium oxide (sample 1) precipitated when $CO_2$ was introduced to magnesium hydroxide suspension at the rate of 2 dm$^3$/min, at 20°C

Particle size distributions of samples 1, 2, 3 from the micrometric range are similar and vary from 1 to 79 µm. As to the particles bringing the maximum volume contributions, for sample 1 the maximum volume contribution of 6.3% is brought by the particles of 6.6 µm in diameter, whereas for samples 2 and 3 by particles of greater diameters. In sample 2 the maximum volume contribution of 6.7% comes from the particles of 11.5 µm in diameter. The character of the particle size distribution curve obtained for sample 4 proves its variable dispersion. Two maxima in the particle size distribution pattern imply the dominance of particles of diameters in the micrometric and nanometric ranges.

At the second stage of study the final samples were obtained when both substrates were simultaneously introduced into the water system.



| Diameter (nm) | Volume (%) |
|---|---|
| 459 | 0.6 |
| 531 | 5.9 |
| 615 | 12.6 |
| 712 | 10.4 |
| 825 | 3.6 |
| 955 | 2.6 |
| 1110 | 7.9 |
| 1280 | 15 |
| 1480 | 18.2 |
| 1720 | 14.6 |
| 1990 | 7.1 |
| 2300 | 1.5 |

(a) (b)

Fig. 2. (a) Particle size distribution (Zetasizer Nano ZS) and (b) SEM photograph of magnesium oxide (sample 3) precipitated when $CO_2$ was introduced to magnesium hydroxide suspension at the rate of 3 $dm^3$/min, at 20°C

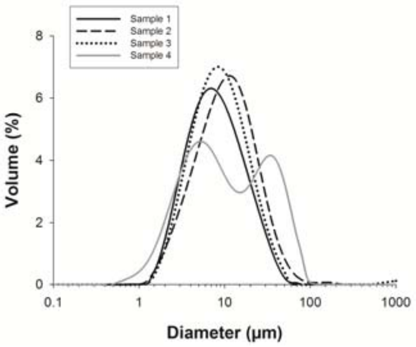


Fig. 3. Particle size distribution (Mastersizer 2000) of magnesium oxide samples 1, 2, 3 and 4 precipitated when $CO_2$ was introduced to magnesium hydroxide suspension at the rate of 2 and 3 $dm^3$/min, respectively

Bulk densities of samples 9-16 (Table 2) obtained when the two reagents were introduced simultaneously, are close to those of the samples obtained when $CO_2$ was introduced to magnesium hydroxide suspension and are higher for the process carried out at 40°C and for higher rates of the reagents supply. For example, the bulk density of sample 9 is 138 g/$cm^3$, while that of sample 16 is 171 g/$cm^3$. The diameters of particles from the nanometric range (measured with Zetasizer Nano ZS), irrespectively of the precipitation conditions, vary from 255 nm to 5560 nm. Some differences in the dispersion and morphology of the samples were revealed by the results of particle size diameters from the micrometric range (Mastersizer 2000). Analysis of $d(0.9)$ values indicated greater tendency towards formation of agglomerates for the samples precipitated at 40°C, similarly to the samples obtained in the first stage of the study.

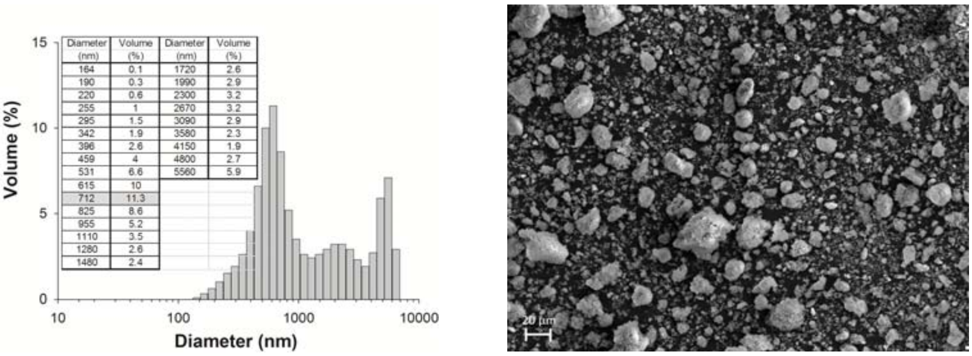
Smaller agglomerates are observed in the samples obtained in the process run at 20°C and at higher rates of the reagents supply. The latter observation is true only for the samples obtained at the second stage of the experiment, i.e. for simultaneous supply of reagents. Among all samples of magnesium oxide obtained in the first and in the second stages of the experiment, the particles of the smallest diameters were obtained for sample 15 (Mastersizer 2000). In this sample 10% volume was taken by the particles of diameters not greater than 1.58 μm, 50% volume was taken by those of diameters below 4.04 μm and 90% volume was taken by those of diameters below 13.59 μm.

Figures 4a and 5a show the particle size distributions of samples 13 and 15 corresponding to the diameters of particles from the nanometric range. For these two samples the ranges of particle diameters are comparable with maxima at 5560 nm. The SEM photographs in Figs. 4b and 5b reveal inhomogeneity of the samples and much greater diameters of agglomerates in sample 13.

Table 2. Physicochemical and dispersive properties of magnesium oxide obtained for simultaneous supply of $CO_2$ and 5% suspension of magnesium hydroxide

| Sample No. | Precipitation process conditions | | Physico-chemical and dispersive properties | | | | |
|---|---|---|---|---|---|---|---|
| | Flow rate ($dm^3$/min) | Temperature (°C) | Bulk density (g/$dm^3$) | Diameter (nm) from Zetasizer Nano ZS | Diameter (μm) from Mastersizer 2000 | | |
| | | | | | d(0.1) | d(0.5) | d(0.9) |
| 9 | 2 | 20 | 138 | 91-5560 | 2.27 | 9.47 | 36.61 |
| 10 | | 40 | 144 | 142-5560 | 2.63 | 16.11 | 50.08 |
| 11 | 3 | 20 | 141 | 164-5560 | 2.27 | 13.65 | 40.63 |
| 12 | | 40 | 146 | 122-5560 | 3.08 | 20.49 | 53.70 |
| 13 | 4 | 20 | 156 | 164-5560 | 2.39 | 9.48 | 29.54 |
| 14 | | 40 | 158 | 142-5560 | 2.55 | 9.93 | 44.51 |
| 15 | 5 | 20 | 161 | 91-5560 | 1.58 | 4.04 | 13.59 |
| 16 | | 40 | 171 | 255-5560 | 1.87 | 5.71 | 40.39 |

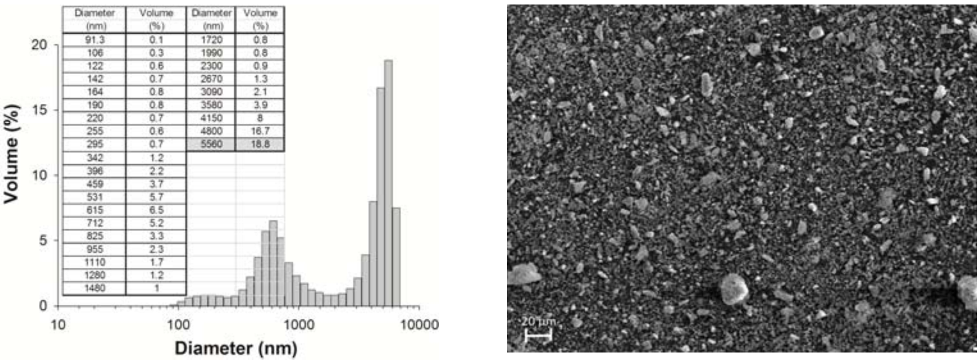
The particle size distribution profiles presented in Fig. 6 can be assigned to two groups according to dispersion. The first group includes samples 15 and 16 in which the maximum volume contribution of 7% and 5.6% is brought by the particles of diameter of 3.8 μm. The band obtained for sample 15 is relatively narrow, which means that this sample is relatively homogeneous (Fig. 5b). The bands corresponding to samples 13 and 14 are wider and the maximum volume contributions in them are brought by particles of greater diameters.



| Diameter (nm) | Volume (%) | Diameter (nm) | Volume (%) |
|---|---|---|---|
| 164 | 0.1 | 1720 | 2.6 |
| 190 | 0.3 | 1990 | 2.9 |
| 220 | 0.6 | 2300 | 3.2 |
| 255 | 1 | 2670 | 3.2 |
| 295 | 1.5 | 3090 | 2.9 |
| 342 | 1.9 | 3580 | 2.3 |
| 396 | 2.6 | 4150 | 1.9 |
| 459 | 4 | 4800 | 2.7 |
| 531 | 6.6 | 5560 | 5.9 |
| 615 | 10 | | |
| 712 | 11.3 | | |
| 825 | 8.6 | | |
| 955 | 5.2 | | |
| 1110 | 3.5 | | |
| 1280 | 2.6 | | |
| 1480 | 2.4 | | |

(a) (b)

Fig. 4. (a) Particle size distribution (Zetasizer Nano ZS) and (b) SEM photographs of sample 13 precipitated at simultaneous supply of the reagents at the rate of 4 dm$^3$/min at 20°C



| Diameter (nm) | Volume (%) | Diameter (nm) | Volume (%) |
|---|---|---|---|
| 91.3 | 0.1 | 1720 | 0.8 |
| 106 | 0.3 | 1990 | 0.8 |
| 122 | 0.6 | 2300 | 0.9 |
| 142 | 0.7 | 2670 | 1.3 |
| 164 | 0.8 | 3090 | 2.1 |
| 190 | 0.8 | 3580 | 3.9 |
| 220 | 0.7 | 4150 | 8 |
| 255 | 0.6 | 4800 | 16.7 |
| 295 | 0.7 | 5560 | 18.8 |
| 342 | 1.2 | | |
| 396 | 2.2 | | |
| 459 | 3.7 | | |
| 531 | 5.7 | | |
| 615 | 6.5 | | |
| 712 | 5.2 | | |
| 825 | 3.3 | | |
| 955 | 2.3 | | |
| 1110 | 1.7 | | |
| 1280 | 1.2 | | |
| 1480 | 1 | | |

(a) (b)

Fig. 5. (a) Particle size distribution (Zetasizer Nano ZS) and (b) SEM photograph of magnesium oxide sample 15, precipitated upon simultaneous introduction of reagents at the rate of 5 dm$^3$/min at 20°C

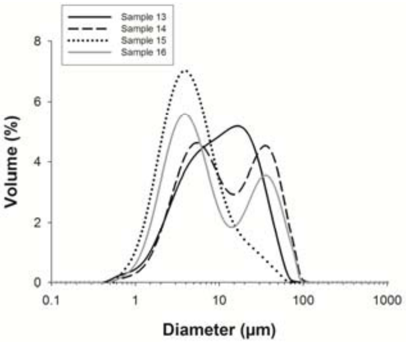


Fig. 6. Particle size distribution (Mastersizer 2000) for samples 13 and 14 precipitated upon simultaneous supply of the reagents at the rage 4 dm$^3$/min and for samples 15 and 16 precipiated in the same mode of reagents supply at the rate of 5 dm$^3$/min

According to WAXS results, undertaken to identify the samples with the X-RAYAN program, the samples obtained after calcination of magnesium carbonates (intermediate products) were synthetic magnesium oxides of crystalline structure. Figure 7 presents typical of the crystalline MgO phase diffraction maxima for samples 1 and 15.

Selected samples were also characterised as to the wettability with water. Figure 8 presents wettability profiles recorded for samples 1, 2, 15 and 16. The greatest tendency to absorb water (the highest hydrophilicity) was noted for sample 1, (0.95 g), precipitated upon introduction of $CO_2$ to magnesium hydroxide suspension. The lowest tendency to absorb water showed sample 15 (0.70 g), obtained upon simultaneous supply of reagents. All samples absorbed characteristic the amount of water during similar time (165-185 s) after which the mass of the samples got stabilized.

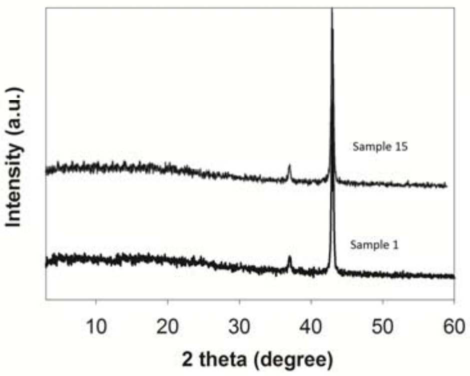


Fig. 7. X-ray diffraction patterns of selected magnesium oxides (samples 1, 15)

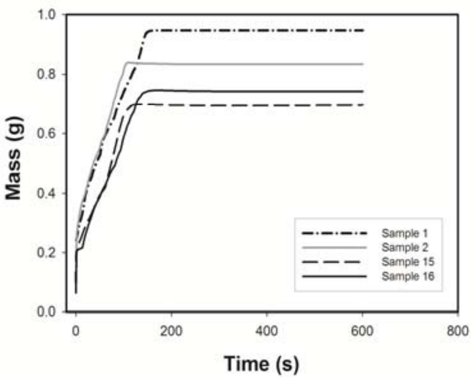


Fig. 8. Profile of wettability with water obtained for selected magnesium oxides (samples 1, 2, 15, 16)

Table 3. Adsorptive properties of selected magnesium oxide samples precipitated under different precipitation process conditions

| Sample No. | BET surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Pore size (nm) |
|---|---|---|---|
| 1 | 15.2 | 0.01 | 3.0 |
| 3 | 21.2 | 0.15 | 28.5 |
| 13 | 18.7 | 0.01 | 2.7 |
| 15 | 17.5 | 0.01 | 2.9 |

To check the potential use of the oxides as adsorbents and catalysts, their adsorption capacity was determined on the basis of nitrogen adsorption-desorption isotherms. Figure 9 presents the isotherms recorded for sample 3. With increasing relative pressure the volume of nitrogen adsorbed systematically increased to reach at $p/p_0=1$ a maximum value of 100 $cm^3/g$.

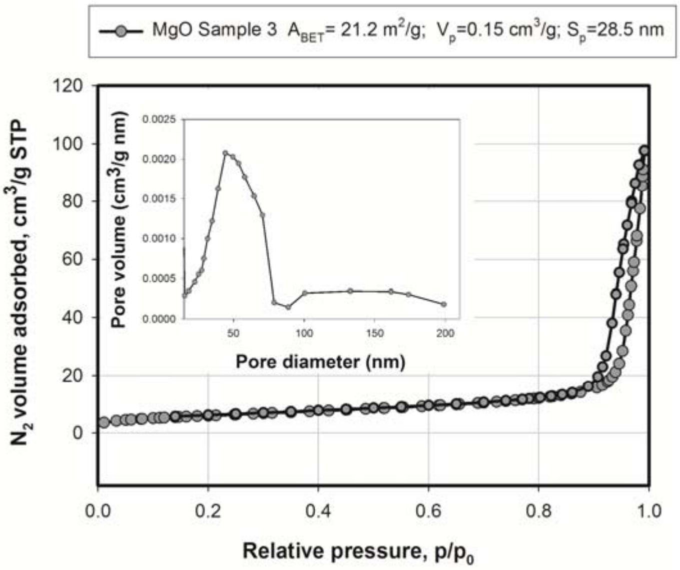


Fig. 9. Nitrogen adsorption-desorption isotherm and pore density distribution of sample 3

Analysis of the isotherms of nitrogen adsorption and desorption recorded for samples 1, 3, 13, 15 permitted determination of specific surface area, pore volume and pore diameters (table 3). All samples have relatively low specific surface area ranging from 15.2 to 21.2 $m^2/g$. The best adsorption properties were found for sample 3. According to the pore size of about 28.5 nm, this sample is classified as mesoporous.

## 3. CONCLUSION

The proposed method of obtaining MgO from $MgCO_3$ precipitate using magnesium hydroxide and carbon dioxide, permits getting magnesium oxide of desired dispersive, morphological and adsorption properties by controlling the conditions of synthesis. The magnesium oxide samples obtained revealed a significant tendency towards formation of secondary agglomerations. Sample 15 was found to have the particles from the micrometric range of the smallest diameter of 13.59 μm. This sample was precipitated at 20°C upon simultaneous supply of reagents at the rate of 5 $dm^3/min$. The same sample also showed the smallest tendency to absorb water. The samples obtained in the experiment, when $CO_2$ was supplied to magnesium hydroxide suspension, were characterised by better dispersion properties when lower rates of supply were applied. The optimum temperature of the process was found to be 20°C as the magnesium oxide samples, precipitated at that temperature, were generally lighter and less agglomerated. The majority of samples obtained were characterised by small adsorption activity. Sample 3, found to have the largest pore diameters of 28.5 nm, was obtained upon $CO_2$ introduction to magnesium hydroxide suspension at the rate of 3 $dm^3$/min at 20°C.

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Przedstawiono badania nad otrzymywaniem tlenku magnezu z użyciem wodorotlenku magnezu i ditlenku węgla metodą karbonizacji. Otrzymany węglan magnezu poddano termicznemu rozkładowi, prowadzonemu stopniowo w odpowiednich warunkach temperaturowych do uzyskania produktu finalnego – tlenku magnezu. W reakcji strącania uwzględniono następujące warunki eksperymentalne: pH medium reakcyjnego, temperaturę, sposób i szybkość dozowania reagentów. Określono właściwości dyspersyjne oraz profile zwilżalności w układach wodnych tlenku magnezu. W celu sprawdzenia charakteru adsorpcyjnego wytworzonych produktów wyznaczono wielkość powierzchni właściwej BET, wielkość i objętość porów. Ponadto produkt poddano identyfikacji metoda rentgenograficzną. Dowiedziono istotnego wpływu warunków prowadzenia procesu na parametry fizykochemiczne otrzymanego MgO oraz wyłoniono produkty o najbardziej reprezentatywnych właściwościach.

*słowa kluczowe: MgO, precipitacja, carbonatyzacja, skład ziarnowy, morfologia powierzchniowa, zwilżalność, właściwości adsorpcyjne*