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Abstract. Materials with MgO nanocrystallites were prepared by sol-gel synthesis. Alcogels were dried either supercritically at 538 K or in supercritical CO\(_2\). Conventional drying was also applied. Structure studies were performed by X-ray diffraction, scanning and transmission electron microcopies. Nitrogen adsorption/desorption measurements were also performed. Calcination of dry gels at 723 K under vacuum yielded MgO nanocrystallites. In the studied materials the presence of the amorphous phase was observed. It is also stated that MgO nanocrystallites are immersed in an amorphous matrix. Morphology of supercritically dried samples is similar; rough surface of powder particles is observed. Powder particles of conventionally dried sample are more compact. Size of MgO crystallites is generally similar for all samples and equal to about 7 nm despite the drying conditions of alcogels. The specific surface area and the volume of mesopores are the greatest for the sample supercritically dried at 538 K.

Introduction

MgO is a highly ionic crystalline solid with interesting properties such as electrical insulation, high temperature stability and chemical inertness. It is of simple stoichiometry and crystal structure and it can be prepared in widely variable particle sizes and shapes [1]. MgO has many applications in catalysis, adsorption and in the synthesis of refractory ceramics [2-5]. Catalytic properties of MgO powders depend mainly on the crystallite size and specific surface area; structure defects and acid-basic site concentration also play an important role [6]. MgO as a support of catalysts is of interest because it has the ability to avoid sintering and evaporation of metal atoms.
The chemical and physical properties required for catalytic application can now be defined at the beginning of the sol-gel synthesis procedure. Moreover this procedure is widely used in the preparation of the components for optical fibers, glasses, supports, ceramic materials, electronic semiconductors, etc.

The technique developed by H.M. Rietveld [7,8] enriched by many others scientists appeared to be very valuable for structural analyses of nearly all classes of crystalline materials.

The aim of the present work is the presentation of the results of structure analysis of nano-crystalline MgO powder material and the comparison with those previously obtained for similar materials [9] prepared by sol-gel synthesis.

Material and research methodology

A magnesium methoxide solution (Aldrich, 8.96 wt.% in methanol), methanol (POCh), and toluene (POCh) were used as precursors in the sol-gel synthesis. The details of the synthesis methods for preparing nanoscale magnesium oxide by supercritical drying are described by Utamapany in [5]. The wet gels were conventionally aged for 3 days. After aging, alcogels were dried either supercritically at 538 K (sample labelled as Aero) or in supercritical CO₂ (sample labelled as Aero-CO₂). Additionally, the conventional drying procedure was applied to prepare the xerogel sample (sample labelled as Xero). The xerogel sample was prepared as follows. After aging alcogel was loosened for a few days to allow slow evaporation of the solvents. Next, the alcogel was vacuum-dried at room temperature for 12 hours. Finally, the sample was heated at 60°C until constant weight was obtained i.e. about 48 hours. Nanoparticles of magnesium oxide were obtained by heat treatment of magnesium hydroxide alcogels/xerogel samples at 723 K under dynamic vacuum using the following conditions: ramp from room temperature to 723 K at 0.5 K/min and hold at 723 K for 5 hours. The whole process of heat treatment took about 15 hours.

X-ray diffraction patterns were collected on an X-Pert Philips diffractometer equipped with a secondary curved graphite monochromator. Morphology of materials was analyzed using SEM (JEOL JSM-6480) and TEM (JEOL 3010) techniques. Nitrogen adsorption-desorption isotherms measured at 77 K with a Micromeritics ASAP 2000 instrument were used to obtain the value of the specific surface area, \( S_{BET} \) and the total volume of mesopores, \( V_p \).

Results and discussion

SEM images presented in figure 1 show the morphology of the powder particles. Surface roughness of Aero-CO₂ and Aero samples is distinct and quite similar whereas the powder particles of Xero sample are more compact. These differences in powder morphology are the result of the different alcogel drying conditions. TEM images with the electron diffraction pattern shown in figure 2 indicate that the powder particles of Aero sample are built of MgO nanocrystallites which are immersed in an amorphous matrix. Similar observations were obtained for previously studied Aero-CO₂ and Xero samples [9]. The above conclusions are confirmed by the HRTEM image in figure 3. The electron microscopy results are in good correlation with the ones of the X-Ray Diffraction (XRD) studies. The Rietveld refinement plot for the Aero sample (experimental and calculated X-ray diffraction patterns and residual profile at the bottom) is presented in figure 4. Similar plots were obtained for the other sam-
amples. Broadened diffraction lines of periclase, the only crystalline form of magnesium oxide, are observed.

Figure 1. SEM images of Aero-CO$_2$ (a), Aero (b) and Xero (c) samples.

Figure 2. TEM images of Aero sample: bright-field (a), dark-field (b) and electron diffraction pattern (c).
The $R_{wp}$ and $S$ values obtained during Rietveld refinement are of the order of 8.5% and 1.8, respectively. They seem to be satisfactory owing to the nanosize of MgO crystallites and due to the presence of the amorphous phase. Lattice parameters of MgO phase for the studied samples, determined by the Rietveld refinement procedure, appeared to be slightly bigger than the ones found in the ICDD file.

Figure 3. HRTEM image of Aero-CO$_2$ sample with electron diffraction pattern.

The crystallite sizes and lattice distortions were analyzed using the Williamson-Hall method [10]. The Toraya PRO-FIT procedure [11] was applied for the determination of the full-width at the half maximum parameter (FWHM) of individual diffraction lines. For this procedure the selected line profile was a Pearson VII function. This function was also used for the Rietveld refinement. Similar plots were obtained for the other studied samples. Analysis of the Williamson-Hall plots (not presented here) indicated that the main contribution to diffraction line broadening comes from the small crystallite sizes.

Figure 4. Rietveld refinement plot for Aero sample.
The crystallite size distribution shown in figure 5 was determined with the FW(1/5)/(4/5)M procedure proposed by R. Pielaszek [12]. The width measurement of the same diffraction line at 1/5 and 4/5 of the peak maximum (FW1/5M and FW4/5M, respectively) allows determining the average crystallite size \( <R> \) and the dispersion of sizes \( \sigma \). These parameters enable the determination of the gamma crystallite size distribution. The dispersion parameter \( \sigma \), is a measure of the crystallite size polydispersity and is defined by equation

\[
\sigma = \sqrt{\langle R^2 \rangle - \langle R \rangle^2}
\]  

(1)

The values of \( <R> \) and \( \sigma \) parameters obtained by the Pielaszek procedure and the average crystallite sizes estimated by the Williamson-Hall method are presented in table 1. A good agreement between the results of both approaches is observed.

![Figure 5. Size distribution of MgO crystallites.](image)

Table 1. Lattice \( (a_o) \), crystallite size \( (D, <R>, \sigma) \) and lattice distortion \( (<\Delta a/a>) \) parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( a_o ), lattice parameter</th>
<th>Williamson-Hall</th>
<th>FW(1/5)/(4/5)M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rietveld [nm]</td>
<td>ICDD [nm]</td>
<td>( D ) [nm]</td>
</tr>
<tr>
<td>Xero</td>
<td>0.4226(1)</td>
<td>0.4213</td>
<td>7.5(9)</td>
</tr>
<tr>
<td>Aero-CO2</td>
<td>0.4227(1)</td>
<td>0.4213</td>
<td>6.0(9)</td>
</tr>
<tr>
<td>Aero</td>
<td>0.4229(1)</td>
<td>0.4213</td>
<td>7.2(9)</td>
</tr>
</tbody>
</table>

The porosity characterization of the studied MgO materials was performed by nitrogen adsorption/desorption measurements. The specific surface area \( S_{BET} \) was determined by using the BET equation and the total mesopore volume \( V_p \) was calculated according to the BJH method from the desorption branch (Table 2). The specific surface area \( S_{BET} \) of Aero-CO2, Aero and Xero samples before the heat treatment were 440 m\(^2\)/g, 325 m\(^2\)/g and 690 m\(^2\)/g, respectively.
### Table 2. Porosity parameters.

<table>
<thead>
<tr>
<th></th>
<th>Aero-CO₂</th>
<th>Aero</th>
<th>Xero</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{BET}$ [m²/g]</td>
<td>$V_\text{p}$ [cm³/g]</td>
<td>$S_{BET}$ [m²/g]</td>
<td>$V_\text{p}$ [cm³/g]</td>
</tr>
<tr>
<td>238</td>
<td>0.49</td>
<td>293</td>
<td>0.86</td>
</tr>
</tbody>
</table>

The specific surface area and the total volume of mesopores is the greatest for the Aero sample dried supercritically at 538 K. The lowest specific surface area was obtained for Xero sample dried conventionally. Differences in specific surface areas are the result of different drying conditions of alcogels. The calcination process is the same for the studied samples and gives a similar size of MgO crystallites.

### Conclusions

Apart from MgO nanocrystallites the studied powder materials contain also an amorphous phase. MgO nanocrystallites are immersed in an amorphous matrix.

Both X-ray diffraction analysis and TEM observations show that the size of MgO crystallites is quite similar for all studied materials and equal to about 7 nm despite different drying conditions of the alcogels. Generally the similar size of MgO crystallites in these materials is the result of the calcination processes which are the same for all samples.

The specific surface area and the total volume of mesopores is the greatest for the Aero sample dried supercritically at 538 K. Different morphology of powder particles of the studied MgO materials, differences in the specific surface areas and in mesopore volumes are the result of different drying conditions of alcogels.

### References