Evaluation of the photocatalytic ability of a sol-gel-derived MgO-ZrO$_2$ oxide material

**Abstract:** This paper deals with the synthesis and characterization of a novel group of potential photocatalysts, based on sol-gel-derived MgO-ZrO$_2$ oxide material. The material was synthesized in a typical sol-gel system using organic precursors of magnesia and zirconia, ammonia as a promoter of hydrolysis and methanol as a solvent. All materials were thoroughly analyzed, including morphology and particle sizes, chemical composition, identification of characteristic functional groups, porous structure parameters and crystalline structure. The proposed methodology of synthesis resulted in obtaining pure MgO-ZrO$_2$ oxide material with micrometric-sized particles and a relatively high surface area. The samples underwent an additional calcination process which led to the crystalline phase of zirconia being formed. The key element of the study was the evaluation of the effectiveness of decomposition of C.I. Basic Blue 9 dye. It was shown that the calcined materials exhibit both satisfactory adsorption and photocatalytic activity with respect to the decomposition of a selected model organic impurity. Total dye removal varied in the range of 50-70%, and was strongly dependent on process parameters such as quantity of photocatalyst, time of irradiation, and the addition of promoters.

**Keywords:** sol-gel method, oxide materials, adsorption, photocatalysis, organic dyes

1 Introduction

The main factor causing increased pollution of water systems today is considered to be the rapid rate of technological progress. In both fresh and waste water there is a need to deal with pollutants of organic origin such as phenols, hydrocarbons, aromatic amines, organic dyes, surfactants and pesticides, as well as inorganic bases and acids and others, including heavy metals. In view of the continuously increasing concentrations of hazardous substances in water systems, methods are constantly being sought for cheap, highly effective, non-invasive purification of water. Methods regarded as effective include those based on processes of adsorption and catalysis [1-4]. One of the particular variants of catalysis is photocatalysis. Interest in this process is constantly increasing, partly because of the growing number of available photocatalysts, methods for synthesizing them and possibilities of using them on a wide scale [5-7]. The effectiveness of the process is determined by a number of parameters, including the pH of the reaction environment, the presence of inhibitor ions, the dose of photoactive material, the type of radiation used, the intensity and time of irradiation, and temperature [8-10]. A key factor, however, appears to be the type of photocatalyst used. The choice of active compound is determined primarily by the method used for its synthesis, which makes it possible to design materials with defined crystallite size, specific surface area and energy gap, which plays an important role in the phenomenon of photocatalysis [11-13].

Among the semiconductors used, the most commonly mentioned is TiO$_2$, the properties of which make it the most popular photocatalyst [14-16]. This material can be obtained by various methods, including the sol-gel technique [17-18]. Other commonly used photocatalysts...
Besides titanium dioxide include the oxides ZnO, CeO₂, SnO₂, ZrO₂, WO₃, ZrO₂, and Fe₂O₃, the sulfides CdS, ZnS and PbS, and the selenides and tellurides CdSe and CdTe [19-25]; particularly noteworthy are zinc oxide and zirconium dioxide [26-28]. Studies reported in the literature have proved that the photocatalytic activity of these two oxides largely depends on the conditions of their synthesis and their crystalline structure [27-28].

An alternative to the commonly used single-oxide photocatalysts is a hybrid system consisting of at least two different oxides, for example TiO₂SiO₂, ZnO-SiO₂, and TiO₂-ZrO₂ [29-36]. In combinations of this kind, the properties of one of the oxides are enhanced by those of the other, leading to a hybrid material with a unique physicochemical and functional parameters. The physicochemical properties and photocatalytic activity of an oxide system also depend on the molar ratio of the individual oxides in the hybrid. Like single oxides, hybrids can be synthesized by numerous methods [34-36]. An increase in the activity of the initial material can also be obtained by creating modifications of semiconductors, achieved via the addition of alkaline or transition metals to pure semiconductors [37-40]. Work in this direction is also being done with the aim of obtaining semiconductors besides titanium dioxide. Oxides such as TiO₂-ZrO₂, ZnO-SiO₂, and ZrO₂-WO₃-PbS, and the selenides and tellurides CdSe and CdTe [19-25] can be obtained as photocatalysts. The properties of these materials are compared with those of those based on pure semiconductors [37-40]. Work in this direction is also being done with the aim of obtaining semiconductors besides titanium dioxide.

2 Experimental

2.1 Materials and methods

2.1.1 Preparation of MgO-ZrO₂ oxide material

The synthesis of hybrid oxide material was carried out in a reactor 500 mL in capacity, equipped with a high-speed rotary stirrer. The first step involved dissolution of the magnesia precursor – magnesium ethoxide – in methanol (200 mL). This stage lasted 30 min and was performed under vigorous stirring. Then the promoter of hydrolysis – a 25% solution of ammonia (4 mL) – and the zirconia precursor – zirconium(IV) isopropoxide – were introduced into the mixture using a peristaltic pump (speed of dosing 2 mL/min). The quantities of magnesia and zirconia precursors were selected so as to obtain materials with Mg:Zr molar ratios of 1:1 (sample WS.1), 1:2 (sample WS.2), and 1:4 (sample WS.4). The whole mixture was additionally stirred for 1 h at room temperature. The obtained alcogel was placed in a crystallizer for ageing, and was then transferred to a rotary evaporator which enabled the removal and recovery of the solvent. The final stage of the synthesis involved washing the samples with hot, distilled water and drying (105 °C, 24 h). The materials prepared in this way underwent calcination to evaluate the possibility of formation of a crystalline phase in their structure. The calcination lasted for 2 h at 800 °C. Both uncalcined samples (WS.1, WS.2, and WS.4) and calcined samples (WS.1-C, WS.2-C, and WS.4-C) were thoroughly analyzed. A schematic diagram of the synthesis of MgO-ZrO₂ oxide material appears in Fig. 1.
Sol-gel synthesis of MgO-ZrO$_2$ photocatalyst

To confirm the effectiveness of synthesis of MgO-ZrO$_2$ oxide material and the presence of characteristic bonds in its structure, FTIR spectra were recorded (Vertex 70 spectrophotometer, Bruker). The samples were analyzed with ATR equipment over a wavenumber range of 4000–400 cm$^{-1}$ (at a resolution of 0.5 cm$^{-1}$; number of scans: 64). The sample was placed on a diamond surface, it was pressed by the measuring element and the spectrum was recorded.

2.1.3 Adsorption and photocatalytic studies

The key element of the studies was the functional testing of the synthesized MgO-ZrO$_2$ oxide materials. According to many literature reports concerning the photocatalytic activity of zirconia [27-28], only materials with a crystalline phase of ZrO$_2$ exhibit such activity. For this reason, this stage of the research was carried out using the calcined samples. Evaluation of photocatalytic activity was preceded by adsorption tests to establish the equilibrium point. As a model organic impurity, C.I. Basic Blue 9 dye was used, with the properties listed in Table 1. A dye solution with an initial concentration of 5 mg/L was used.

The adsorption process was carried out over 30 min, using 100 mL of dye solution and 0.04 g or 0.08 g of oxide material. The next step was to determine the ability of the MgO-ZrO$_2$ hybrid to decompose the model organic impurity via photocatalysis. A UV laboratory reactor of type UV-RS-2 (Heraeus) was used for this purpose. In the reactor vessel, 100 mL of dye solution in a concentration of 5 mg/L and the appropriate quantity of photocatalyst (MgO-ZrO$_2$), were placed. In two cases, hydrogen peroxide in a concentration of 30% was added, to determine whether it affects the photocatalytic activity of the synthesized material. The mixture was stirred for 30 min using an IKAMAG R05 magnetic stirrer (Ika Werke GmbH). After that time irradiation took place; it was performed within 30 min and 60 min. A 150 W medium-pressure mercury lamp, generating radiation with wavelength >200 nm, was used. After the appropriate time, the lamp was switched off, the reactor system was cooled and the mixture was filtered. The filtrates, after both adsorption and photocatalysis, were subjected to UV-Vis spectroscopy (V-750 spectrophotometer, JASCO Analytical Instruments) to establish the content of unadsorbed and non-decomposed dye respectively. Absorption spectra were recorded at 664 nm. Based on the calibration curve (see Fig. 2) with the equation y=0.2078·x (where y is the measured absorbance and x is the estimated dye solution concentration) it was possible to calculate the efficiency of adsorption and of the photocatalytic decomposition of C.I.
3 Results and discussion

3.1 Physicochemical properties of MgO-ZrO$_2$ oxide materials

To confirm these findings, the dispersive parameters of the analyzed samples are given in Table 2. The particle size distributions of the synthesized materials are generally rather large, which is a result of the proposed method of synthesis. This is not without significance for their photocatalytic activity. The best dispersive parameters were observed for sample WS.4, obtained with an Mg:Zr molar ratio of 1:4. The sample has 10% of particles with diameters ≤ 2.8 µm, 50% with diameters ≤ 3.9 µm, and 90% with diameters ≤ 10.4 µm. The mean particle diameter $D_{4.3}$ for this sample is 5.7 µm, and is the lowest value among the analyzed samples. There is a clear tendency for the particle sizes of the synthesized materials to be generally large due to the high content of the uncalcined samples. In this respect, the particles of the oxide materials were partly dependent on the Mg:Zr molar ratio, with more fine particles being observed in the sample obtained with a fourfold excess of zirconium(IV) isopropoxide.

In order to evaluate the morphology of the synthesized oxide materials, their SEM images (Fig. 4) and dispersive parameters (Table 2) are presented. Samples of MgO-ZrO$_2$ materials that did not undergo calcination contain relatively fine primary particles, which are attached to each other and tend to form agglomerate structures. The calcination process caused some changes in the particles' shape and size. Particles appeared with irregular shape and relatively large size, with less tendency to form large agglomerates. This fact is probably related to the significant removal of water (humidity) from the samples due to heat treatment. The presence of physically bound water in the uncalcined samples allowed their particles to agglomerate, and for this reason the particles of the oxide materials were partly dependent on the Mg:Zr molar ratio. It should be noted that the particle sizes of the calcined samples exhibit a lower affinity to form larger aggregates.

Figure 2: Calibration curve for C.I. Basic Blue 9.

Figure 3: Adsorption and photocatalytic processes using synthesized MgO-ZrO$_2$ oxide materials.
Figure 4: SEM images of MgO-ZrO$_2$ oxide materials.
dispersive properties of the oxide material to improve as the content of zirconia increases. The same is observed in the case of the calcined samples where the best dispersive properties are exhibited by the sample labeled WS.4-C. Generally, the calcination process led to a 2 µm increase in the mean particle diameter of the MgO-ZrO₂ material.

The results of energy dispersive X-ray microanalysis (Table 3) show that the synthesized oxide materials (grouped as given) exhibit an increasing contribution of zirconium with respect to magnesium, which was the main assumption of the synthesis method. It was to be expected that the highest contribution of zirconium would be observed in sample WS.4. It may be noted that all samples are characterized by a significantly higher percentage contribution of ZrO₂, which suggests the more efficient hydrolysis of its precursor in the proposed sol-gel system. Increasing amounts of zirconium or magnesium in the oxide structure also caused an increase in the percentage contribution of the respective oxides of those elements. Samples obtained with Mg:Zr molar ratios of 1:1 and 1:2 exhibit quite similar contributions of magnesia and zirconia, which means that only by using a four times larger quantity of zirconia precursor were we able to change significantly the contribution of ZrO₂ in the structure of the oxide material and thus affect its final properties. The influence of the calcination process on the contribution of the analyzed elements was also confirmed. This heat treatment technique led to a significant decrease in the percentage contribution of oxygen, and related increases in the content of magnesia and zirconia. These results strongly confirm the effectiveness of the proposed methodology of synthesis of pure MgO-ZrO₂ oxide material.

The next stage of physicochemical evaluation involved XRD analysis. The XRD patterns obtained for the MgO-ZrO₂ oxide systems are presented in Fig. 5. These results confirm that samples of oxide materials obtained via the sol-gel method and without further calcination have a completely amorphous structure (Fig. 5a, c, e). However, 2 h of heat treatment at 800 °C was sufficient to form the crystalline phases characteristic of the respective oxides building the MgO-ZrO₂ material. The monoclinic and tetragonal structure of ZrO₂, as well as the crystalline phase of MgO, were observed. The significant influence of the Mg:Zr molar ratio on the formation of a proper crystalline structure was also confirmed. Fig. 5b presents the XRD pattern for sample WS.1-C, obtained at an Mg:Zr molar ratio of 1:1. Peaks observed at 2θ values of 30, 35, 51, 61, 64 and 75 were attributed to the crystalline phase of ZrO₂, and at 43, 62 and 79 were attributed to the crystalline phase of magnesia. Sample WS.2-C, whose XRD pattern is shown in Fig. 5d, presents quite similar 2θ values, but those related to magnesia have lower intensity. This results from the Mg:Zr molar ratio of 1:2 and the smaller quantity of magnesium in the oxide material structure. By way of confirmation, the XRD pattern of sample WS.4-C is composed only of reflections attributed to 2θ values characteristic of the crystalline phase of zirconia. The disappearance of peaks related to the crystalline phase of magnesia with an increasing quantity of zirconia in the oxide material structure probably results from the relatively low contribution of magnesium in the MgO-ZrO₂ structure and the fact that ZrO₂ inhibits the crystallization of MgO. Most likely, the small amount of magnesium oxide in the resulting material formed a dispersed, amorphous phase on the ZrO₂ surface.

Identification of characteristic functional groups in the oxide material structure was possible using FTIR analysis. Fig. 6 presents the FTIR spectra of uncalcined and calcined MgO-ZrO₂ oxide materials. The spectra of samples WS.1, WS.2 and WS.4 contain several characteristic bands (Fig. 6a). Those at 3500-3000 cm⁻¹, and 1630 cm⁻¹ are related to the stretching vibrations of -OH groups, and bending vibrations of C–OH bonds [41]. Moreover, there are three low-intensity bands at 2900 cm⁻¹, 2800 cm⁻¹, and around 1550 cm⁻¹ characteristic for stretching vibrations.

<table>
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<th>Sample name</th>
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<th>d(0.1)</th>
<th>d(0.5)</th>
<th>d(0.9)</th>
<th>D[4.3]</th>
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</tr>
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<table>
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<th>Zr</th>
<th>O</th>
<th>MgO</th>
<th>ZrO₂</th>
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<td>18.26</td>
<td>10.94</td>
<td>89.07</td>
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</table>
of C–H bonds in –CH₂ and –CH₃ groups, which suggest that some residue of the organic precursors used for synthesis of the oxide material is left in its structure. The next, weak, signal at wavenumber 1100 cm⁻¹ is attributed to stretching vibrations of Zr=O bonds [42], and that at 800 cm⁻¹ to stretching vibrations of O–Mg–O and Mg–O–Zr groups [43]. The most intense band, observed at 500 cm⁻¹, confirms the presence of both Zr=O and Mg–O bonds in the oxide material structure, which explains its intensity [44].

The spectra of the calcined samples (Fig. 6b) confirm that the heat treatment method led to a large decrease in the intensity of most bands, due to elimination of physically
adsorbed water molecules as well as the condensation of Mg–OH (or O–Mg–O) and Zr–OH (or Mg–O–Zr) groups into Mg–O or Zr=O. For this reason the most intense band observed on the spectra of the calcined samples is related to Zr=O and Mg–O bonds. These results are in agreement with previously published data [42-46].

Analysis of the porous structure parameters (Table 4) showed them to be dependent on the Mg:Zr molar ratio as well as on the calcination process. Figure 7 presents the adsorption/desorption isotherms of MgO-ZrO$_2$ oxide materials obtained without additional heat treatment. The shape of the isotherms indicates that these oxide materials can be classed as mesoporous adsorbents with relatively large pore sizes, resulting from spaces between small particles. There is no hysteresis loop which might confirm the presence of pores inside the particles. The largest surface area (137 m$^2$/g) is observed for sample WS.1, obtained with an Mg:Zr molar ratio of 1:1. This sample also has a pore volume of 0.093 cm$^3$/g and a pore diameter of 2.7 nm. The lowest value of $S_{BET}$ (83 m$^2$/g) was recorded for sample WS.4, synthesized with a fourfold excess of zirconia precursor. It was to be expected that an increase in the quantity of zirconia in the oxide material would lead to a decrease in its surface area, in view of the fact that magnesia is the component intended to expand the surface area. These results are confirmed by the quantities of adsorbed nitrogen (Fig. 7). Table 4 also shows the porous structure parameters for MgO-ZrO$_2$ samples additionally calcined at 800 °C for 2 h. The calcination process led to a significant decrease in the values of selected parameters. The tendency was the same i.e. a greater quantity of zirconia in the oxide material led to worse porous structure parameters. The largest surface area (9.5 m$^2$/g) in this group of samples was recorded for sample WS.1-C. It should be noted that in this heat treatment technique small particles are “baked”, and thus the pore volume and diameter significantly decrease, as is confirmed by the $V_p$ and $S_p$ values respectively.

### 3.2 Photocatalytic and adsorption studies

In order to establish the photocatalytic activity of the synthesized oxide materials, an attempt was made to decompose a model organic impurity in the form of C.I. Basic Blue 9 dye solution in a concentration of 5 mg/L. Samples obtained with different molar ratios of Mg:Zr that had undergone additional calcination were selected.
for this purpose (based on the previously cited literature reports which state that only the crystalline form of zirconia can act as an effective photocatalyst). The results are presented in Table 5 and in Figure 8. The photocatalytic studies were preceded by adsorption tests to evaluate the adsorption equilibrium and efficiency. During the tests the mass of photocatalyst and irradiation time were varied. Surprisingly, the synthesized MgO-ZrO\(_2\) oxide material did not itself exhibit satisfactory photocatalytic activity, even when its mass in the reaction medium was increased and the irradiation time was changed. The percentage total removal of dye from the model solution was mostly due to its adsorption. The best results for photocatalytic activity were obtained when hydrogen peroxide was used additionally as a promoter – in the case of the samples of oxide material labeled WS.1-C*, WS.2-C* and WS.4-C*. After a few days, the dye solution containing photocatalyst and H\(_2\)O\(_2\) underwent total decolorization. The results obtained using the synthesized photocatalyst without the addition of hydrogen peroxide showed that increasing the mass of the oxide material in the reaction system caused only a slight increase in its dye decomposition activity. Most importantly, significant changes were observed for samples with an increasing contribution of zirconia in their structure, which was one of the assumptions of the synthesis technique. In this case the best results for total dye removal from solution (64.2%) were recorded for sample WS.4-C_3 in a quantity of 0.08 g. It should also be noted that irradiation time was not found to have any significant effect.

The results strongly confirm the good adsorption ability of the synthesized oxide material with respect to the analyzed organic dye (C.I. Basic Blue 9). Once again, a very surprising finding was that higher adsorption efficiency was obtained in the case of samples containing larger quantities of zirconia (a larger contribution of zirconia means lower porous structure parameters). Hence the proposed methodology of synthesis provides a possibility of obtaining a novel type of MgO-ZrO\(_2\) oxide materials which can act as both adsorbents and photocatalysts, designed for the removal of colorful impurities from water systems.

4 Discussion

The novel aspect of the research presented here is the synthesis of a novel type of photocatalyst, MgO-ZrO\(_2\) oxide material, via a sol-gel route. The aim was to combine the large surface area of MgO with the semiconductive behavior of zirconia. Based on many literature reports it was clear that ZrO\(_2\) ought to exhibit photocatalytic activity [27,28,34,37]. It appears that Botta et al. [27] were correct in stating that the photocatalytic properties of zirconia are mainly determined by the synthesis route. By the selection of appropriate parameters of synthesis, it is possible to control the final physicochemical properties of the materials, and in particular the value of the energy gap, which plays a very important role in photocatalysis. The authors of the paper [28] propose the controlled hydrolysis of a zirconia precursor (ZrOCl\(_2\)·8H\(_2\)O) in the presence of 25% ammonia. After synthesis the products were calcined at 600 °C for 4 h. The methodology is thus quite similar to that proposed by us. Functional tests were performed to investigate the decomposition of Na\(_2\)EDTA, NaNO\(_3\) and K\(_2\)Cr\(_2\)O\(_7\), but the photocatalytic activity of the synthesized material was not so good as for commercial TiO\(_2\) (P-25). More important are the results presented by Basahel [24], who proved the significant
The effect of crystalline phase type as well as particle size on the photocatalytic activity of zirconia. Selecting different synthesis methods, the authors obtained materials with 24 nm sized monoclinic (m-ZrO$_2$), 18 nm sized hexagonal (c-ZrO$_2$), or 8 nm sized tetragonal (t-ZrO$_2$) structures of zirconia. During photocatalysis they used 0.1 g of catalyst, 100 mL of model organic dye solution and six 18W UV lamps. The best photocatalytic activity was observed for samples of m-ZrO$_2$, which was explained by the larger quantity of surface hydroxyls and higher porosity. In our research the dominant crystalline form of zirconia was tetragonal (t-ZrO$_2$) and the particle sizes were generally micrometric. This is valuable information, suggesting that there is a need to change the synthesis conditions to obtain materials with nanometric-sized particles, or to change the conditions of final heat treatment to obtain a photocatalyst composed mainly of m-ZrO$_2$. However, the methodology described here was proposed to obtain the hybrid material MgO-ZrO$_2$, and this is why some of the final parameters of the product are different from those of pure ZrO$_2$. Another potential way to increase the photocatalytic activity of our oxide materials is doping them with other active elements. Such research was reported by Ilkechi and Kaleji [37], who proposed doping of titania with zirconia and silicon via a sol-gel route. They used different molar ratios of reactants, and the samples after synthesis were dried and calcined in order to obtain a crystalline phase mostly of TiO$_2$. The photocatalytic activity of the material was determined using 0.08 g of catalyst, 50 mL of a model organic dye solution and a 150 W UV lamp. The best results were recorded for a hybrid sample obtained with 20% by weight of silicon and 15% by weight of zirconia. Addition of Zr to the titania structure caused the development of a crystalline structure, and Si led to better porosity of the hybrid material. The results were surprising because the hybrid material decomposed the dye with 70% efficiency, a better result than for pure TiO$_2$ (23%). Similar research, but concerning a TiO$_2$-ZrO$_2$ hybrid, was carried out by Yuan et al. [34]. They synthesized that material via a polymer templating method, and after synthesis samples were calcined at 400 °C for 4 h. The photocatalytic activity of the material was determined based on the degradation of a model organic dye solution (C.I. Basic Violet 1) using 0.1 g of catalyst and a 150 W UV lamp. Total degradation of the dye was observed after 40 min of irradiation for the samples with the highest contribution of titania. The addition of zirconia was definitely reasonable because pure TiO$_2$ did not exhibit such activity. As can be seen, there are many parameters that affect the photocatalytic activity of oxide materials based on titania, zirconia or others. The most important seems to be the selection of components of the hybrid photocatalyst, their molar ratio, an appropriate methodology for synthesis and the final heat treatment method. Only a well-defined synthesis will lead to products with desired physicochemical and functional properties suited to a wide range of applications.

Table 5: Results of photocatalytic and adsorption studies.

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<th>Sample name</th>
<th>Adsorption time (min)</th>
<th>Irradiation time (min)</th>
<th>Photocatalyst mass (g)</th>
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<th>Efficiency of photocatalysis (%)</th>
<th>Total dye removal (%)</th>
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</tbody>
</table>

* samples with the addition of photocatalytic promotor (hydrogen peroxide)
5 Conclusions

The proposed methodology for the synthesis of MgO-ZrO₂ oxide materials proved to be very efficient, especially in terms of the purity and physicochemical parameters of the final products. By changing the molar ratio of Mg:Zr, and by applying additional heat treatment (a calcination process), it was possible to design materials with unique properties such as large surface area and porosity, or with the formation of a crystalline phase. The results clearly indicate how increasing the quantity of zirconia in the MgO-ZrO₂ oxide system affects its properties. Moreover, it was found that samples after calcination have worse porous structure parameters and particle sizes, but their advantage is that they contain a crystalline structure of zirconia, which is highly important in the photocatalysis process. Studies of the photocatalytic activity of the synthesized materials in the decomposition of a model organic impurity (C.I. Basic Blue 9) did not produce satisfactory results, even when their mass in the reaction medium was increased and the irradiation time was varied. The percentage of total dye removal from its model solution was mostly due to its adsorption. The best results for photocatalytic activity were recorded when hydrogen peroxide was additionally used as a promoter. This may result from the relatively large particle sizes or too low (or too high) an energy gap, which is mostly determined by the conditions of synthesis of the oxide materials. This fact is very important, because it suggests the possibility of changing the methodology of synthesis of the MgO-ZrO₂ oxide system or supplementing it, for example with a stage of doping with photocatalytic metals.

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