Degradation of crystal violet over heterogeneous TiO$_2$-based catalysts: The effect of process parameters

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Abstract

In this study, modified sol-gel method was employed to synthesize the pure and Zr-doped titania catalysts. Brunauer-Emmett-Teller (BET) method was applied to determine porosity, X-ray diffraction (XRD) analysis was used to study crystal structure, scanning electron microscopy (SEM) was used to investigate morphology and Fourier transform infrared spectroscopy (FTIR) was used to examine surface properties/total acidity of the obtained catalysts samples. Photocatalytic activity was tested in the reaction of crystal violet (CV) dye decolourization/degradation under UV light irradiation. The effects of several photocatalysis operational parameters were considered, such as catalyst dosage, initial dye concentrations, duration of UV irradiation treatment, as well as catalysts calcination temperatures and dopant amounts. The obtained results indicated faster dye decolourization/degradation with the increase of the catalyst dosage and the decrease of initial CV concentrations. The Zr-doping affects photocatalytic properties, i.e. CV decolourization/degradation of the prepared catalytic materials. Thus, addition of 5 wt.% of ZrO$_2$ to titania increases photocatalytic effect for ~15% and addition of 10 wt.% of ZrO$_2$ improves the photocatalytic efficiency of titania for nearly 30%.

Keywords: titania, Zr-doping, nanopowders, heterogeneous catalysts, photocatalytic activity
tion and formation of crystal defects, which can lead to significant improvement in its photocatalytic properties. Zirconium has been successfully used as a dopant for titania, which can be ascribed to the fact that Ti and Zr belong to the same group of elements and their tetravalent cations have comparable ionic radii [12]. In addition, relevant oxides of both elements (TiO₂ and ZrO₂) are n-type semiconductors with similar physico-chemical properties, which probably lead to their interaction during catalyst preparation [13].

To the best of our knowledge, there are no studies reporting synthesis of Zr-doped titania via modified sol-gel method using zirconium(IV) oxochloride octahydrate as a precursor, while only a few papers investigated the influence of doping on catalyst activity of titania and photocatalytic reactions of degradation/decolorization of the selected organic dye [11,12,14–16]. The present study reports economy of degradation activity of titania and photocatalytic reactions of dye.

2.1. Catalyst preparation

Titania-based catalysts were synthesized via modified sol-gel method using titanium isopropoxide (Aldrich Co.) as a precursor. In the first step two solutions were prepared. The first solution was made by dissolving the calculated/measured amount/volume of titanium isopropoxide in 2-propanol according to stoichiometry under inert conditions. Then, the second solution was made by mixing water and 2-propanol in volume ratio 1 : 3 which was added to the first solution drop by drop under vigorous stirring in nitrogen atmosphere for one hour. The molar ratio Ti : H₂O was adjusted to 1 : 6 and pH of the resulting suspension to 10 by 1 M NaOH. The obtained precipitate was filtered, washed with distilled water and finally with the mixture of isopropanol and water. After that, the powder sample was dried at 105–110 °C for 3 h, and then calcined for additional 3 h at different temperatures of 450, 600 and 800 °C. The catalytic sample was heated to the desired temperature at a heating rate of 10 °C/min. All chemical reagents were applied as received from commercial source (analytical purity) without further purification.

The Zr-doped samples were prepared by using ZrOCl₂ · 8 H₂O (Sigma Aldrich, Co.) diluted in distilled water. Three doped titania samples were obtained by adding 2.5, 5.0 and 10.0 wt.% of ZrO₂. After drying for 3 h at 105 °C, the doped catalysts samples were calcined at two different temperatures (600 and 800 °C) for 3 h, using the heating rate 10 °C/min. The used chemicals were of analytical grade and no additional purification was performed. The obtained catalysts were denoted as: X-Zr-TiO₂-T, where X stands for the amount in wt.% of added ZrO₂ and T for calcination temperature.

2.2. Catalyst characterization

In order to determine the specific surface area and porosity of catalyst, BET and Barett-Joyner-Halenda (BJH) methods were used, respectively. XRD method was used for characterization of catalyst structure, and the surface morphology was estimated by SEM. FTIR method was used for evaluation of surface properties of catalysts, i.e. determination of Lewis (LAS) and Bronsted acid sites (BAS) as catalytically active sites.

BET surface area measurements were performed on a Micromeritics ASAP 2010 based on adsorption/desorption of liquid nitrogen at appropriate temperature and pressure (LTN2 AD) by He as carrier gas. The average pore diameters and pore volumes were determined by BJH method. Prior to measurements, all catalyst powder samples were degassed.

XRD analysis was carried out on a Philips APD-1700 diffractometer using Cu-anticathode and monochromator in operating mode of 40 kV and 55 mA. Data were collected in the 2θ scan range between 10 and 80°. The average crystallite sizes were calculated by using Scherrer equation [17]:

$$d = \frac{k \cdot \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where λ is X-ray wavelength, k is constant 0.9, β is the peak width at half maximum, and θ is the Bragg angle. The weight fraction of anatase (Wₐ) in the powder was calculated by the following equation developed by Spurr et al. [18,19]:

$$W_a = \frac{1}{1 + 1.265 \times \frac{I_a}{I_R}} \times 100$$  \hspace{1cm} (2)

where I₋ and I₋₋ are (integrated) peak intensities of the most intense peaks for anatase 101 and rutile 110 peaks/phases, respectively.

The surface morphology of the catalysts was investigated by scanning electron microscope SEM JOEL JSM-6460LV. Sample preparation for SEM imaging was performed by coating with gold layer. Operating conditions in SEM imaging were: acceleration voltage 25 kV, 30 mA current at a working distance of 50 mm during 180 s.

In order to evaluate catalyst surface acidity, FTIR analysis was carried out by KBr pellet technique. FTIR spectra measurements before and after pyridine adsorption were recorded on a Win Bometem Easy spectrome-
2.3. Photocatalytic activity

In order to test photocatalytic activity of the catalysts, degradation of crystal violet (CV) dye was tested under irradiation of UV lamp (Roth Co., 16 W, 2.5 mW/cm², with maximal emission at 366 nm). The UV lamp was located at a distance of 10 cm from the reaction model solution, which was magnetically stirred during the experiments with a constant speed. CV dye solution (10 ml) was placed in quartz reaction tube covered with 0.5 mm thick quartz disk-cover, and then irradiated with UV light. Before UV illumination, catalysts had been mixed with crystal violet test-solution at constant stirring during 24 h in dark in order to establish adsorption-desorption equilibrium of dye molecules onto the catalysts surface. This was performed in order to avoid adsorption of CV dye on the catalysts surfaces during the photocatalytic reaction. The decolorization/degradation process was monitored by measuring maximal absorbance of CV solution (at \( \lambda_{\text{max}} = 590 \text{ nm} \)) using UV/Vis spectrophotometer (Schimadzu Co.). At specified time-intervals, aliquots were withdrawn from the solution, then centrifuged and filtrated before measuring.

III. Results and discussion

3.1. Textural properties

The textural properties (nitrogen adsorption-desorption isotherms, pore size distribution curves, BET specific surface area, average pore diameter and pore volume) of the pure and Zr-doped titania powders calcined at different temperatures are presented in Figs. 1 and 2 and summarized in Table 1. All samples were calcined at selected temperatures (i.e. 600 and 800 °C) in order to incorporate zirconium into titania according to recently reported data [6,11,13].

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) [m² g⁻¹]</th>
<th>( d_p ) [nm]</th>
<th>( V_p ) [cm³ g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂-450</td>
<td>34.3</td>
<td>8.3</td>
<td>0.075</td>
</tr>
<tr>
<td>TiO₂-600</td>
<td>28.1</td>
<td>11.2</td>
<td>0.070</td>
</tr>
<tr>
<td>TiO₂-800</td>
<td>22.4</td>
<td>13.7</td>
<td>0.065</td>
</tr>
<tr>
<td>2.5-Zr-TiO₂-800</td>
<td>10.1</td>
<td>28.9</td>
<td>0.057</td>
</tr>
<tr>
<td>5-Zr-TiO₂-600</td>
<td>40.6</td>
<td>6.5</td>
<td>0.088</td>
</tr>
<tr>
<td>5-Zr-TiO₂-800</td>
<td>37.4</td>
<td>7.7</td>
<td>0.072</td>
</tr>
<tr>
<td>10-Zr-TiO₂-600</td>
<td>46.8</td>
<td>5.3</td>
<td>0.099</td>
</tr>
<tr>
<td>10-Zr-TiO₂-800</td>
<td>43.3</td>
<td>6.1</td>
<td>0.083</td>
</tr>
</tbody>
</table>

In general, all investigated catalytic samples exhibited type IV sorption isotherm curves, which indicated the presence of mesoporosity accompanied with possible capillary condensation of adsorbent in gaseous and/or liquid phase. The nitrogen adsorption/desorption isotherm curves of the pure and Zr-doped titania are shown in Figs. 1a and 1b, respectively. The pure titania catalysts samples calcined at selected temperatures exhibit typical S-shape behaviour of type IV sorption isotherm with a type H1 hysteresis loop, while the Zr-doped titania samples calcined at selected temperatures were characterized with type IV sorption isotherm with a type H3 hysteresis loop according to IUPAC classification [20,21].

These observations are typical for mesoporous materials. The noticed hysteresis loops indicate the presence of mostly cylindrical pore shapes in the pure titania sample, while the Zr-doped titania samples have cracks-like and/or conical pores. The isotherms of the doped titania catalytic samples were shifted slightly downward, and their hysteresis loops were shifted to rather higher relative pressures. The incorporation of higher amount of dopant into titania caused shifts of hysteresis loops to somewhat higher relative pressures (not shown). The application of higher calcination temperatures for the Zr-doped titania shifts the hysteresis loops to moderately

![Figure 1. Nitrogen adsorption-desorption isotherm for: a) TiO₂-450, b) 2.5-Zr-TiO₂-800 samples](image-url)
higher relative pressures (not shown). These changes are in agreement with a fact that specific surface area of the doped titania catalysts increases with the increase of Zr amount (Table 1).

Figure 2 shows the pore size distribution of the titania-based catalytic samples. The bimodal pore sizes distributions in the pure titania samples show that all TiO\textsubscript{2} catalysts have two types of pores: micropores or pores at (near-edge) micro-meso pore boundary, and typical mesopores characterized with the average pore diameter of about 8 nm (Fig. 2a). The doped titania catalytic samples are characterized with atypical bi-modal or multi-modal distributions of pore sizes. Consequently, the catalytic Zr-doped titania samples have at least two different pore sizes: micropores, probably presented as interstices among titania primary crystallites, and mesopores, characterized with the average pore diameter of 45 nm probably associated with interstices among secondary crystallites and relatively poorly dispersed dopant (Fig. 2b). It is important to note that somewhat higher volume of mesopores with greater average pore size is observed in the case of the doped titania powders. The incorporation of higher Zr-amount causes the existence of bimodal and/or multimodal pore size distribution typical for the revealed materials mesoporosity. Volume fraction of mesopores characterized with greater average pore diameter fairly increased with the increase of zirconia weight percentage. The increase of calcination temperature affected a shift of maxima in pore size distribution curves to mesopores with larger average pore diameter, and their volume ratios slightly increased (not shown).

The estimated BET surface area of the pure titania catalyst sample calcined at 450 °C is 34.3 m\textsuperscript{2}/g (Table 1), which is slightly smaller than previously reported [22]. Doping of titania with 5 and 10 wt.% of ZrO\textsubscript{2} results in somewhat larger pore volumes and specific surface areas. In addition, the specific surface area and pore volume of the doped samples increase with Zr-content (Table 1). The observed behaviour can be explained by initial sintering during calcination at elevated temperature or inhomogeneous dispersion of Zr\textsuperscript{4+} ions.

3.2. Microstructural characterization - XRD

Figure 3 shows XRD patterns of the pure and Zr-doped titania powders after calcinations at different temperatures. All diffraction peaks of the pure titania calcined at 450 °C are characteristics of exclusively anatase crystal phase (Fig. 3a). The XRD pattern of the pure titania calcined at 600 °C has peaks of both anatase and rutile phases, while predominantly rutile crystal phase is present in the sample calcined at 800 °C.

However, the XRD pattern of the doped titania sample 5-Zr-TiO\textsubscript{2}-600, calcined at 600 °C, shows peaks characteristic of titania anatase phase, negligible fraction of rutile phase and probably a small amount of brookite titania phase (Fig. 3b). Whereas, the XRD pattern of the sample 5-Zr-TiO\textsubscript{2}-800, calcined at 800 °C, shows peaks typical for both anatase and rutile phases as well as probably some traces of monoclinic and/or tetragonal zirconia phase. The addition of 5 wt.% ZrO\textsubscript{2} resulted in slighter retarding of anatase-to-rutile phase transformation at elevated temperatures (Fig. 3b). The increase of calcination temperatures and addition of ZrO\textsubscript{2} also improved the crystalline structure of the photocatalyst, which is confirmed with stronger and sharper XRD peaks (Fig. 3). The authors were not able to identify only few weak peaks appearing after doping.

The XRD pattern of the doped titania catalyst sample 10-Zr-TiO\textsubscript{2}-600 calcined at 600 °C displays peaks characteristic of titania anatase phase, and probably a small amount of brookite titania and/or monoclinic/tetragonal zirconia phases (Fig. 3b). Moreover, the XRD pattern of the doped titania sample 10-Zr-TiO\textsubscript{2}-800 calcined at 800 °C shows peaks typical for both anatase and rutile phases and probably a small amount of ZrTiO\textsubscript{4} and/or monoclinic zirconia phase. The addition of 10 wt.% ZrO\textsubscript{2} resulted in noticeable retarding of anatase-to-rutile phase transformation at elevated temperatures (Fig. 3b).

Having in mind that ionic radius of Zr\textsuperscript{4+} ion (0.072 nm) is somewhat larger than one of Ti\textsuperscript{4+} ion (0.053 nm) [23], it is expected that Zr\textsuperscript{4+} ions could re-

![Figure 2. Pore size distribution of: a) TiO\textsubscript{2}-450, b) 2.5-Zr-TiO\textsubscript{2}-800 samples](image)
place Ti\(^{4+}\) in the titania lattice. This should cause a XRD shift of titania to somewhat lower diffraction angles in comparison to the pure titania. It is observed (Fig. 3.) that the diffraction peaks of anatase and rutile phases in the doped titania catalysts are gradually shifted to lower angles compared to the pure titania. This is additional confirmation that Zr\(^{4+}\) ions enter into the titania lattice substituting Ti\(^{4+}\) ions. The registered new diffraction peak of ZrTiO\(_4\) in the doped titania 10-Zr-TiO\(_2\)-800 sample indicates that the substitution of Ti\(^{4+}\) with Zr\(^{4+}\) ions in titania becomes saturated at 800 °C and when Zr\(^{4+}\) ions increase to the appropriate content.

In general, addition of 10 wt.% ZrO\(_2\) cause retarding the anatase-to-rutile phase transformation and growth of anatase crystallites at elevated temperatures.

Phase composition of titania-based materials is very important as initial research in the topic indicating that photocatalytic activity was related to the existence of the single anatase phase [24], but following studies point out to the importance of both anatase and rutile crystal phases for photocatalytic activity of the titania-based materials [25–27]. It was also reported [28] that a mixture of anatase, rutile and brookite phases exhibits higher photocatalytic activity than single anatase phase.

### 3.3. Microstructural characterization - SEM

Figure 4 shows the SEM images of the pure and Zr-doped titania samples. The SEM image of the pure titania TiO\(_2\)-800 sample calcined at 800 °C shows typical spherical morphology consisting of small primary particles. The presence of interparticles pores can be easily observed (Fig. 4a). After Zr-doping morphology of the calcined particles is completely changed (Fig. 4b). A lot of fine particles with specific morphology are observed in the Zr-doped titania. This is confirmed with the observed increase of the specific surface area of the doped titania samples (Table 1).

![Figure 4. SEM micrographs of catalyst samples: a) TiO\(_2\)-800 and b) 10-Zr-TiO\(_2\)-800](image)

### 3.4. Microstructural characterization - FTIR

FTIR spectrum of the pure titania (calcined at 450 °C) after pyridine adsorption is presented in Fig. 5a. The
peaks for Lewis acid sites (LAS) at 1624, 1587 and 1438 cm\(^{-1}\) are present, along with peaks for Brønsted acid sites at 1540 cm\(^{-1}\). The band at 1540 cm\(^{-1}\) is the characteristic for pyridinium cation and is formed as a result of pyridine interaction with Brønsted acid sites (Fig. 5a) [29].

According to FTIR spectra, the calcined Zr-doped titania is characterized with increased intensity of the LAS at 1438 cm\(^{-1}\), 1587 and 1626 cm\(^{-1}\) compared with counterpart bands of the pure titania (Fig. 5). This indicates on a slightly greater number of the Lewis acid sites on the surface of the doped titania (Fig. 5b). The bands around 1540 cm\(^{-1}\) in both catalytic samples have similar intensity, so both catalyst samples probably possess comparable number of Brønsted acid sites. The surface of the titania. The photocatalytic CV degradation is improved over the Zr-doped titania because of its improved physico-chemical properties and improved mechanism of CV decolourization/degradation process compared to the pure titania. Namely, the Zr-doped titania has bimodal/multimodal distribution of pore sizes in comparison to bimodal-pore size distribution in the case of the pure titania powder. Bimodal/multimodal pore size distribution can enable reactant(s) to more easily reach the catalytically active sites. In addition, sufficiently large pore volume facilitates an easier transport of reactant(s) to the catalytically active sites, and diffusion of the products back to the reaction mixture [30].

The incorporation of zirconium into titania caused the formation of particles with larger specific surface areas and pore volumes in comparison to their pure counterparts except for 2.5-Zr-TiO\(_2\)-800 (Table 1). The achieved photocatalytic activity of the Zr-doped titania catalysts increased with the increase of Zr-content (Fig. 6). In general, all physico-chemical properties of...
the Zr-doped titania were improved with the increase of Zr-content. These improvements highly affected their photocatalytic performances and resulted in superior photocatalytic ability of catalysts 10-Zr-TiO\(_2\)-600 and 10-Zr-TiO\(_2\)-800 in CV degradation (Figs. 6 and 7). The authors confirmed, similarly to other literature reports, that better crystallinity of the Zr-doped titania [26], and presence of titania mixed crystal phases (anatase-rutile-brookite and ZrTiO\(_4\)) [25–28] improve catalytic efficiency of the Zr-doped titania. Moreover, it is believed that the observed higher total acidity of the Zr-doped titania surface (of the samples 10-Zr-TiO\(_2\)-600 and 10-Zr-TiO\(_2\)-800) is responsible for better catalytic ability in the process of the photocatalytic degradation of CV [31–34]. In the case of the Zr-doped titania with 10 wt.\% of ZrO\(_2\), the increase of the calcination temperature from 600 to 800 °C caused a slight decrease of the photocatalytic activity under the same experimental conditions (Fig. 7).

We proposed that the incorporation of Zr\(^{4+}\) ions into titania can generate additional formation of O\(_2^−\) and \(^{•}\)OH radicals that can take part in the successive photocatalytic subreactions responsible for CV degradation. The introduction of sufficient amount of Zr\(^{4+}\) ions into titania lattice can restrict the recombination rate of photogenerated electrons and holes, thus enhancing the photocatalytic efficiency of the pure titania. In the case of Zr\(^{4+}\) ions, the rate of charge carriers (electrons and holes) detrapping is high, which has positive influences on photocatalytic efficiency of the Zr-doped titania. The induced oxygen vacancies by incorporation of Zr\(^{4+}\) ions into titania can additionally capture photogenerated electrons thus limiting the charge carriers recombination rate. The generated oxygen vacancies support the process of oxygen adsorption and increase the interaction between photoinduced electrons of oxygen vacancies and adsorbed oxygen favouring photocatalytic reactions and improving adsorption and degradation of CV dye molecules [35]. Oxygen adsorbed onto doped titania after accepting electron is reduced to O\(_2^−\), and surface hydroxyl group is converted to hydroxyl radical \(^{•}\)OH by an acceptance of hole. Both O\(_2^−\) and \(^{•}\)OH radicals further assisted CV degradation. Therefore, the introduction of the appropriate amount of Zr\(^{4+}\) ions into titania lattice significantly improved photocatalytic activity of the pure titania [35]. With the presence of Zr\(^{4+}\) ion in titania lattice, the following reactions are possible [35]:

\[
\begin{align*}
\text{TiO}_2 + hv(\text{UV}) & \rightarrow \text{TiO}_2 + e_{\text{CB}}^- + h_{\text{VB}}^+ \\
h_{\text{VB}}^+ + \text{OH}^- & \rightarrow ^{•}\text{OH} \\
h_{\text{VB}}^+ + \text{H}_2\text{O} & \rightarrow ^{•}\text{OH} + \text{H}^+ \\
e_{\text{CB}}^- + \text{O}_2 & \rightarrow \text{O}_2^{•} \\
\text{X-Zr-TiO}_2\cdot \text{T(Zr}^{4+}\text{-TiO}_2) + hv(\text{UV}) & \rightarrow \text{X-Zr-TiO}_2\cdot \text{T(Zr}^{4+}\text{-TiO}_2) + e_{\text{CB}}^- + h_{\text{VB}}^+ \\
\text{Zr}^{4+} + e_{\text{CB}}^- & \rightarrow \text{Zr}^{3+} \\
\text{Zr}^{3+} + \text{O}_2 & \rightarrow \text{Zr}^{4+} + \text{O}_2^{•} \end{align*}
\]

**Influence of catalyst dosage**

The influence of catalyst doses (amounts from 0.030 to 0.075 g) on the CV degradation process is shown in Fig. 8. It can be noticed that concentrations of the selected dye have decreased with the increase of the catalyst amounts when both pure and Zr-doped titania catalysts were used (Fig. 8). Higher amounts of both catalysts mean that there are larger numbers of catalytically active sites as well as larger numbers of adsorbed photons that may result in the enhanced photocatalytic activity.

**Influence of initial CV concentrations**

The effect of initial CV concentrations from 0.005 to 0.010 mmol/dm\(^3\) was investigated for the constant cata-
that physico-chemical properties of the pure titania were
UV irradiation energy, small catalyst dosages and un-
SOCV, under relatively mild operational conditions (low
types of catalysts were tested for degradation of the dye
photocatalysts. The photocatalytic e

titania-based nanostructured materials as promising

IV. Conclusions

Modified sol-gel method was used as relatively sim-
ple procedure for preparing the pure and Zr-doped
titania-based nanostructured materials as promising photocatalysts. The photocatalytic efficiencies of both
types of catalysts were tested for degradation of the dye
CV, under relatively mild operational conditions (low
UV irradiation energy, small catalysts dosages and un-
modified pH value). The obtained results have indicated
that physico-chemical properties of the pure titania were
significantly influenced by the doping with zirconium.
As a result, doped catalysts have demonstrated signif-
ically higher photocatalytic activity in degradation of
CV.

It can be concluded that the achieved bi-
modal/multimodal distribution of pore sizes as well as higher amount of greater mesopores in size in
the case of the Zr-doped titania herein resulted in
greater photocatalytic activity. In addition, the presence
of mixed crystal phases (anatase, rutile and/or brookite
and ZrTiO₄) and improved crystalline structure, as well as higher total surface acidity in the case of
Zr-doped titania can also be related to more effective
photocatalytic activity compared to the pure titania
catalyst.

Relations between

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