SYNTHESIS AND PHOTOCATALYTIC APPLICATIONS OF TITANIUM DIOXIDE
PŘÍPRAVA A APLIKACE FOTOKATALYTICKÝ AKTIVNÍHO OXIDU TITANICITÉHO

SUMMARY OF DOCTORAL THESIS
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ABSTRACT
Hydrolysis conditions for different Ti-alkoxides were examined considering the impact of water to alkoxide ratio and temperature. The prepared hydrolysates and sintered TiO₂ nanoparticles were examined with XRD, DTA – TGA, SEM – EDS, BET and PCCS analysis in order to identify the impact of hydrolysis on properties of prepared anatase particles. Magnetite nanoparticles were synthetized by easy one step precipitation method from Mohr’s salt solution and their crystallinity, size and surface properties were examined investigating the influence of temperature and coating by polycarboxylate ether superplasticizer. For immobilization of TiO₂ on surfaces of magnetite combined method using the selected nanoparticles of TiO₂ and Ti-alkoxides hydrolysis is performed in order to obtain photocatalytically active core–shell powder catalystsator with enhanced adsorptive properties. Also the investigation on the applications of TiO₂ on surfaces of Mn-Zn ferrite is done with studying the surface treatment by CVD deposition of C and Au layer. Photocatalytic activity of selected prepared photocatalystsators is evaluated upon decomposition of methylene blue and isopropanolic and ethanolic vapors for Mn-Zn ferrite in experimental chemical reactor with magnetically holded powdered photocatalystor beds.

KEYWORDS
Titanium oxide, anatase, photocatalytic activity, core-shell powder photocatalystator, magnetite, Mn-Zn ferrite, Ti-alkoxides, hydrolysis, sol-gel, nanoparticles.
ABSTRAKT
V práci je zkoumán vliv podmínek na průběh hydrolýzy alkoxidů titanu a vlastností připravovaných nanočástic oxidu titančitého s důrazem na teplotu a množství vody přítomné v systému. Připravované hydrolyzáty alkoxidů titanu a nanočástice oxidu titančitého připravené z hydrolyzátů jsou studovány metodami XRD, DTA – TGA, SEM – EDS, BET a PCCS. Nanočástice magnetitu byly syntetizovány pomocí precipitační reakce z roztoku Mohrovy soli a jejich krystalová struktura, velikost a povrchové vlastnosti byly sledovány s vyhodnocením vlivu teploty a při modifikaci povrchu polykarboxyletherovým superplastifikátorem. Pro upevnění TiO₂ na povrch magnetitu byla použita kombinovaná metoda aplikace vybraných nanočástic TiO₂ s hydrolyzou TiO₂ pomocí alkoxidů titanu za účelem přípravy fotokatalyticky aktivního core-shell práškového katalyzátoru s vylepšenými vlastnostmi adsorpce na povrchu. Studovány byly možnosti aplikace TiO₂ na povrch Mn-Zn feritu, kdy byl studován vliv depozice tenkých vrstev C a Au na morfologii povrchu. Fotokatalytická aktivita vybraných připravených materiálů byla studována pomocí dekompozice methylenové modři v roztoku a par isopropanolu a ethanolu rozkládaných pomocí Mn-Zn feritu v experimentálním chemickém reaktoru s magnetickým polem stabilizovaným ložem nosiče katalyzátoru.

KLÍČOVÁ SLOVA
TiO₂, anatas, fotokatalytická aktivita, core-shell práškové fotokatalyzátorů, magnetit, Mn-Zn ferrity, alkoxidy titanu, nanočástice
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1 AIM OF THE THESIS

Aim of present study is to investigate the methods of preparation of TiO$_2$ in the photocatalytic active form of anatase and its application in magnetically active powder core-shell photocatalysators and a preparation of powder photocatalysators with evaluation of their photocatalytic activity. The following objectives of work were identified:

- Literature review on preparation of TiO$_2$ by hydrolysis and its modifications and preparation of inert powdered substrate for photocatalytically active TiO$_2$.
- Synthesis of TiO$_2$ in photocatalytical modification of anatase, studying the hydrolysis conditions of used titanium alkoxide mixtures.
- Preparation of inert powder substrates for the TiO$_2$ deposition processes, characterisation of the prepared materials.
- Deposition of TiO$_2$ on the surface of the prepared and selected magnetic inert holders.
- Photocatalytic activity studies on the prepared TiO$_2$ core-shell materials.

2 THEORETICAL PART

2.1 CHARACTERISTICS OF TiO$_2$

TiO$_2$ is thermally stable compound, which is inert against acids, bases and insoluble in most solvents. Its most known application since commercial exploitation in beginning of 20$^{th}$ century is its use as a pigment in industry. The reason for this application is high refractive indice, which result in high reflectivity from the surfaces. Another reason for such applications is also opacifying power and brightness of small TiO$_2$ particles. TiO$_2$ naturally occurs in three crystallographic forms: anatase, rutile and brookite.

![Fig. 1. Crystallographic forms of TiO$_2$, A – Anatase, B – Rutile and C – Brookite. Brookite has orthorombic crystal structure, anatase and rutile form tetragonal structure. Anatase and brookite are in elevated temperatures exceeding 600°C unstable and undergo transition into the rutile form, which is most stable structure of TiO$_2$, melting in temperatures above 1 750 °C. Some facts about crystallographic forms of TiO$_2$ are mentioned in following table:](image-url)
Tab. 1 Density, reflective index, space group and band-gap (Eg) values of TiO₂

<table>
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<tr>
<th>Modification</th>
<th>$n_D$</th>
<th>Eg (eV)</th>
<th>Space group</th>
<th>$\rho$ [g·cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brookite</td>
<td>2.583</td>
<td>3.14</td>
<td>Pbca</td>
<td>4.15</td>
</tr>
<tr>
<td>Anatase</td>
<td>2.488</td>
<td>3.3</td>
<td>I4₁/amd</td>
<td>3.90</td>
</tr>
<tr>
<td>Rutile</td>
<td>2.609</td>
<td>3.1</td>
<td>P4₂/mnm</td>
<td>4.25</td>
</tr>
</tbody>
</table>

Since the discovery of photolysis activity of TiO₂ on sunlight, enormous effort have been devoted to the research of TiO₂ materials, leading to many promising applications in areas ranging from photovoltaics, sensors to photocatalysis. From the forms of TiO₂, anatase is performing the best photocatalytic activity due to its higher band gap value.

2.1.1 Mechanism of photocatalytic performance

Photocatalysis happens in certain conditions, after irradiation of TiO₂ surface by UV light with higher energy than energy of light with $\lambda = 388$ nm for anatase, respectively $\lambda = 413$ nm for rutile. After irradiation the electrons and holes are created and before their own recombination they are participating in surface reactions. There are many kinds of reactions, which can be accomplished through photocatalysis. These can involve oxidations and oxidative cleavages, reductions, geometric and valence isomerizations, substitutions, condensations, polymerizations, etc. Basic scheme of photocatalytic decomposition is shown in figure 2. [1, 2]

The valence bond holes are powerful oxidants with potential of +1.0 to +3.5 V against normal hydrogen electrode depending on the semiconductor and pH. As good reductants the conduction band electrons are used showing measurable potential of +0.5 to -1.5V against normal hydrogen electrode. Simplified mechanism of reactions of electrons and holes on active sites is proposed in following figure:

Fig. 2 Mechanism of photocatalytic decomposition

Capability of electrons and holes reducing and oxidizing an adsorbate in active site can be explained by following cascade of reactions: [3]
According to the mentioned equations, formation of singly oxidized electron donor and a singly reduced electron acceptor is achieved during photocatalytic decomposition, repetition of reactions leads to the complete mineralization of organic adsorbates on the surface of TiO$_2$.

**Hydroxyl radical**

The most important reactive specie formed during photocatalytic reaction is considered to be OH radical. Although there are two major possible ways of its formation, it is generally concluded that the hole capture is proceeding directly through adsorbed OH and not via water first, therefore reaction 6 is more likely to be prevalent than reaction 5. In general, it is believed, that radical-cation of water formed at reaction 5 may be neutralized before decomposing into OH$^-$ radical. It is also mostly assumed, that the irradiated surface is OH covered and therefore the hole is directly transferred to OH. Therefore involvement of the surface-bonded hydroxy radical in heterogeneous photocatalytic conversions conducted in contact with an aqueous solution must be considered in each scheme. [4] Even in acidic conditions, proposing the surface-bonded OH radical creation has significance, during considering of reaction scheme. The presence of OH radical on the surface of TiO$_2$ upon irradiation is so obvious, proved and known fact, that it is used as chemically equivalent to surface-trapped hole and these terms are used interchangeably by investigators. It can be concluded, that principal charge trapping event is formation of surface OH group, which is initiating primary oxidation chemistry of adsorbates bonded at the surface, before diffusing into the bulk solution. Various studies of photocatalytic decomposition confirmed hydroxylated intermediates formation in aqueous TiO$_2$ suspensions during decomposition. Such products could be formed by homolytic attack of hydroxyl radical on $\pi$ system of organics or by hydration of singly oxidized intermediates. [1, 2, 4, 5,]

**Superoxide radical**

Another important specie which appeared at earlier mentioned cascade of reactions, is superoxide radical O$_2$$^-$. Its formation is conducted according to the equation 8, where in general the A stand for the adsorbed O$_2$. It was observed, that photocatalytic activity is completely suppressed in the absence of an electron scavenger, such as molecular oxygen. As the conduction band of TiO$_2$ is almost completely isoenergetic with the reduction potential of oxygen in inert solvents, adsorbed oxygen serves as an efficient trap for
photogenerated electrons. Superoxide is highly active and apart of attacking other adsorbed molecules, can be also source for another hydroxyl radical formation, which is described by following reactions. [2]

\[
\begin{align*}
\bullet & \text{TiO}_2 (e_{\text{cb}}^-) + O_{2\text{ads}} + H^+ \rightarrow \text{TiO}_2 + \cdot \text{HO}_2 \leftrightarrow O_2^- + H^+ \\
\bullet & 2 \text{HO}_2^+ + H^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\bullet & \text{H}_2\text{O}_2 + O_2^- \rightarrow \cdot \text{HO} + \text{O}_2 + \cdot \text{HO}^- \\
\bullet & \text{H}_2\text{O}_2 + h\nu \rightarrow 2\cdot \text{HO}^- \\
\bullet & \text{H}_2\text{O}_2 + \text{TiO}_2 (e_{\text{cb}}^-) \rightarrow \cdot \text{HO} + \cdot \text{HO}^-
\end{align*}
\]

(7) (8) (9) (10) (11)

Oxygen concentration dependence has been explained as involving O\textsubscript{2} adsorption and depletion, both in the dark and during illumination, at photocatalyst surface. It is attacking both neutral substrates and adsorbed radicals and ions. This attack occurs before desorption from the surface since the presence of dissolved superoxide traps in solution does not inhibit photocatalytic oxidative reactivity. [6] Also, according to reactions of oxygen superoxide radical, a protonation-reduction-protonation sequence is capable to generate hydrogen peroxide H\textsubscript{2}O\textsubscript{2}. This species is one of initiate oxidative functional groups for interconversions.

### 2.2 PREPARATION AND DEPOSITION OF TiO\textsubscript{2} BY SOL-GEL PROCESSES

Nowadays, there is possible to distinguish two deposition pathways of TiO\textsubscript{2} for usage in photocatalytic decomposition. TiO\textsubscript{2} is either used in powder form, taking advantage of powder usage (higher surface area than when applied on the surface of holder) or as immobilized media on the porous inert holder. First pathway of application is slightly economically disadvantageous due to the requirement on the withdrawal from the cleaned photocatalytic system. [7] Although usage of TiO\textsubscript{2} on immobilized media with the porous inert holder shows lower photocatalytic rate, due to the economical impacts, its usage is broader than in powder form. Another advantage is a possibility to apply very thin layer of TiO\textsubscript{2}, which leads to the short diffusion length for pollutants and formed electron holes and electrons. It is advantageous to improve the specific surface by pore introduction into the surface of such materials. [7, 8]

#### 2.2.1 Sol-gel method

One of the most common and very effective way, how to obtain TiO\textsubscript{2} photocatalyst, is sol-gel method. It can be used for preparation of powders with narrow distribution and thin coatings with homogenous crystallite structure. In a typical sol-gel process, a colloidal suspension or sol, is formed by controlled hydrolysis and polycondensation reaction of inorganic metal salts or organometallic precursors. During the process, liquid sol is transformed into a solid gel phase during polymerization and loss of solvent. Advantages of sol-gel method are homogenous, transparent and porous crystallite structures preparation accompanied with easibility, purity and low-cost of prepared materials.
Hence some disadvantages are limiting the use of substrate in surface coating, as such produced coating needs to be thermal treated at several hundreds of °C to prepare crystalline structure. Therefore the substrate must be able to withstand high temperature treatment. High temperature also means, that the inertness of substrate toward reaction with surface treatment at high temperatures needs to be examined in order to prevent the drop in surface properties. [9]

**Mechanism of sol-gel**

Starting compounds in sol-gel are metal alkoxides, or metal acetylacetates. These precursors are hydrolysed and produced sol undergoes polycondensation and polymerization.

In general, the overall process can be divided into several steps:

- Preparation of sol by controlled hydrolysis of alkoxides.
- Formation of gel through polycondensations of sol and crosslinkings of oxides and alcohols leading to the increase of viscosity.
- Syneresis of gel which is characterized by ongoing polycondensation reaction and aging of the gel.
- Drying of gel when molecules of water and solvents are removed by heating.
- Calcination of the dried gel for removing the rests of organic compounds and hydroxyl groups from xerogel.

During calcination, heating at temperature 200 – 300 °C, removes remained traces of organic compounds, whereas heating at temperature 300 – 400 °C removes hydroxyl traces in structure and initiate the formation of crystallite structures of surface coatings. This microstructure can be also affected by usage of various additives during sol-gel process, for example polyethyleneglycols are responsible for porosity, or varying molar rates of sol components and used solvent mixture. [9, 10]

### 2.2.2 Sol – gel thin film TiO₂ deposition processes

There was developed many different pathways of deposition of thin TiO₂ surfaces on various substrates. Brief information about thickness of coating and characteristics of methods are given below. [10]

- Spin coating – method based on circulating of substrate with coating dispersion. Speed of rotation, concentration of sol, type of solvent and surface tension have impact on the thickness of layer. Possible range of thickness is varying between 1 – 200 µm.
- Dip coating – substrate is put into the coating dispersion and withdrawn with controlled rate. Thickness of surface layer is driven by rate of withdrawing, viscosity of sol and angle of withdrawing. Highly optical quality is obtained with thickness of coating between 20 nm – 50 µm.
- Cappillary coating – in this method, under the surface of substrate, coating cylindric roller partially dipped into the coating dispersion is rotating creating menisc and laminar coating conditions are created. Homogenous, highly optical quality thin film with thickness around 15 µm is created.
• Cell coating – the coating dispersion is poured into the cell created by two planes of substrates. Thickness of coating depends on the thickness of cell created between planes of substrate.
• Flow coating – the coating dispersion is poured on the substrate. Thickness depends on the angle between substrate and poured dispersion, viscosity and rate of evaporation of solvent. Advantage is easy smoothing of surface defects of substrate.
• Print coating – this method is done by printing of liquidous coating dispersion on various substrates surfaces. It is a quick process with possibility of regulation of surface thickness during printing and with good reproducibility and reduced waste production. Printing is possible to introduce on the ceramic, metallic, organic semiconductor and biopolymeric substrates. [7 -9]

2.3 HYDROLYSIS OF TRANSITION METALS
In sol-gel processes, the formation and growth of nanoparticles of TiO$_2$ are accomplished by hydrolysis and condensations of alkoxides precursors. Main disadvantage of this process is the fact, that Ti$^4$ ions are highly electropositive and easily undergo nucleophilic attack by water, which leads to the fast and uncontrollable hydrolysis resulting into various specious of precipitates. [11, 12] Due to the fast kinetics of hydrolysis and condensation reactions of TiO$_2$ alkoxides, relatively little information is available concerning progressive structural evolution in transition metal oxide systems.

2.3.1 Mechanism of hydrolysis
In general, hydrolysis is process when interactions of atoms lead to the exchange of charge between filled $3a_1$ bonding orbital of water molecule and empty $d$ orbitals of the transition metals (M). When dissolved in pure water, metal cations M$^{z+}$ are solvated by water molecules, establishing following equilibria, defined as hydrolysis: [13]

\[ [\text{M(OH}_2\text{)]}^{z+} \leftrightarrow [\text{M-OH}]^{(z-1)+} + \text{H}^+ \leftrightarrow [\text{M=O}]^{(z-1)+} + 2\text{H}^+ \tag{12} \]

There are three types of ligands presented in noncomplexing aqueous media:

• M(OH$_2$) – Aquo
• M-OH – Hydroxo
• M=O – Oxo

Then the rough formula for inorganic precursor can be written as $[\text{MO}_x\text{H}_{2N-R}]^{(z-R)+}$. $N$ is the coordination number of water molecules around M, Z is the charge and R is molar ratio of hydrolysis. If R = 0, the precursor is aquo-ion, when

\[ R = 2N \] precursor is an oxy-ion and similarly, another oxo-hydroxo complex $[\text{MO}_t\text{(OH)}_{N-x}]^{(N+x-z)-} (R > N)$, hydroxo-aquo complex $[\text{M(OH)}_x\text{(OH}_2\text{)}_{N-x}]^{(z-x)+} (R < N)$ and finally hydroxo complex $[\text{M(OH)}_N]^{(N-2)-} (R = N)$ can be formed.

Charge density on the metal, number of metal ions bridged by hydroxo or oxo ligand and number of hydrogen atoms contained in the ligand are facilitating the hydrolysis whereas increasing number of hydroxo ligands coordinating M is
inhibiting it. Precise nature of formed complex during hydrolysis is dependent on charge, coordination number and electronegativity of metal and pH of aqueous solution. Figure 7 shows diagram for the presence of aquo, hydroxo and oxo ligands upon charge of metal cations and pH.

As can be concluded from the diagram in figure 3, the hydrolysis of low-valent cations with $Z < 4$ yields aquo, hydroxo or aquo-hydroxo complexes with decreasing pH, while oxo or oxo-hydroxo complexes are formed at high valent cations with $z$ higher than 5. Tetravalent metals are on the border therefore they have ability to form all kind of complexes depending on the pH. [13]

Fig. 3 The effect of pH of solution and charge of M [13]

Partial-charge model was derived from the diagram in figure 7 expressing the quantification of pH relation with the valence of M. When interaction of atoms proceeds, each participating atom has positive or negative partial charge. Transfer of electrons will stop as soon as the electronegativity of all partners in system is equal to the average value of electronegativity. [13]

### 2.3.2 Hydrolysis and condensation of transition metal alkoxides.

For coordinatively saturated metals in the absence of catalyst, the result of hydrolysis and condensation occur by nucleophilic substitution involving nucleophilic addition where at the and the proton is transferred from the attacking molecule of water to alkoxide or hydroxo-ligand within the transition state and removal of protonated species as either alcohol (alcoxolation) or water (oxolation). When $N - z > 0$, also olation can occur as condensation reaction. Products of hydrolysis and condensation of Ti-alkoxides are below.

- Hydrolysis $\rightarrow$ M-OH + ROH
- Ac oxolation $\rightarrow$ M-O-M +ROH
- Oxolation $\rightarrow$ M-O-M + H$_2$O
- Olation $\rightarrow$ M-OH-M + ROH ; M-OH-M + H$_2$O
Overall reactions happening during the condensation of Ti alkoxides can be written as follows: [13, 14]

\[
\equiv \text{Ti-OR} + \text{H}_2\text{O} \rightarrow \equiv \text{Ti-OH} + \text{R(OH)} \quad (13)
\]

\[
\equiv \text{Ti-OH} + \text{RO-Ti≡} \rightarrow \text{Ti-O-Ti≡} + \text{R(OH)} \quad (14)
\]

Thermodynamics of hydrolysis, alcoxolation and oxolation are governed by the strength of entering nucleophile, electrophilicity of M and partial charge and stability of leaving group. These reactions are favoured when \(\delta(\text{O}) \ll 0, \delta(\text{M}) \gg 0,\) and \(\delta(\text{H}_2\text{O}) \text{ or } \delta(\text{ROH}) >0.\)

Thermodynamics of olation depend on the strength of the entering nucleophile and electrophilicity of the metal. The kinetics of olation are fast because \(N–Z > 0\) and no proton transfer occurs in the transition state.

3 EXPERIMENTAL PART

3.1 USED METHODS

3.1.1 X-ray diffraction analysis

X-ray diffraction (XRD) is an analytical technique used for phase identification of crystalline material. Crystals are regular arrays of atoms and X-rays can be considered as waves of electromagnetic radiation. Atomic electrons scatter X-ray waves by a phenomenon known as elastic scattering, producing secondary spherical waves emanating from electrons. Regular array of atoms produces a regular array of spherical waves. These waves are cancelling each through destructive interference, they add constructively in a few specific directions which are determined by Bragg’s law in equation following reaction:

\[
2d \sin \theta = n\lambda 
\]

\(d\) is spacing between diffracting planes of atoms, \(\theta\) is the incident angle, \(n\) is any integer and \(\lambda\) is wavelength of the beam. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted.

3.1.1 Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy (UV-VIS) is a method based on the absorption of certain portion of light from ultraviolet or visible range (from 200 to 800 nm) by transmissive samples. These samples are containing molecules with \(\pi\)-electrons or non-bonding electrons (n-electrons). These types of electrons are able to absorb the energy in the form of ultraviolet or visible light to be excited to higher anti-bonding molecular orbitals. The more easily excited the electrons, the longer the wavelength of light which is absorbed. [15]

3.1.1 Turbidimetry

This method is measuring the loss of intensity of transmitted light due to the scattering effect of particles suspended in solvent. Light is passed through a filter.
creating a light of known wavelength which is then passed through a cuvette containing a solution. A photoelectric cell collects the light which passes through the cuvette.
The decrease of light intensity is corresponding to the elastic scattering of radiation beam by suspension of colloidal particles. In Turbidimetry, the detector is placed in line with source of light beam. Very similar method is nephelometry, where the detector is placed in 90° angle towards the source of light and the scattered light intensity is measured. It is possible to measure turbidity with UV-Vis spectrophotometer.

3.1.2 Scanning electron microscopy
The scanning electron microscopy (SEM) is a method which uses a focused beam of high energy electrons to generate a variety of signals on the surface of solid specimens. These signals carry information about the sample’s surface and topography together with composition. Also the samples can be observed in various conditions: vacuum, wet conditions and wide range of cryogenic or elevated temperature.
Most common SEM mode is a detection of secondary electrons emitted by atoms excited with electron beam. Number of electrons detected is varying with specimen topography. Image of sample topography is created by collection of secondary electrons that are emitted using special detector. In general, higher the conductivity of sample is, then better resolution can be obtained. Samples with low conductivity are either measured with lower voltage, or can be coated with carbon or metals to become more conductive. [16]

3.1.1 Photon correlation spectroscopy
Photon correlation spectroscopy (PCS) or dynamic light scattering (DLS) is a light scattering technique for studying the properties of suspensions and colloidal solutions. It is absolute, non-invasive and nondestructive method.
When light hits sufficiently small particles (from nanometer up to few μm scale) it scatters in all directions according to the principle of Rayleigh scattering. The light source is laser with wavelength below 250 nm. When its monochromatic and coherent light beam hits particles in solution, the scattering intensity fluctuates over the time. Fluctuation is consistent with the theory of Brownian motion as the particles measured are so small, that they are undergoing these diffusive movements. [17]

3.1.2 TGA – DTA Analysis
Thermal gravimetric analysis (TGA) with Differential thermal analysis (DTA) belong to Thermal Analysis group of techniques.
In TGA analysis, changes in physical and chemical properties of materials are measured as a function of weight change with increasing temperature or time at constant temperature. For this technique a precision balance and programmable furnace is needed.
3.1.3 Infrared spectroscopy

Infrared spectroscopy (IR spectroscopy or Vibrational Spectroscopy) is kind of absorption spectroscopy. Absorption of light with wavelengths in IR range ($\lambda = 0.7 – 350 \mu m$) is observed by this method. Samples can be presented in solid, liquid or gaseus form. The result of the measurement is the infrared spectrum recording the variation of absorption or transmittance within sampled IR wavelength range. [18]

Recorded IR spectrum is essentially a graph of infrared light absorbance/transmittance on axis $y$ and frequency or wavelength on axis $x$. Frequency units used are reciprocal centimeters (cm$^{-1}$). Units of IR wavelength are commonly given in micrometers ($\mu m$).

3.1.1 BET analysis

Based on Brunauer–Emmett–Teller (BET) theory [19] which aims to explain the physical adsorption of gas molecules on a solid surface, this analysis is used for the estimation of surface area and pore size distribution of solid materials using gas adsorption. The BET theory refers to multi layer adsorption, and usually works with non-corrosive gases (nitrogen, argon, carbon dioxide) as adsorbates.

3.1.2 Magnetization measurement

Most common system for measurement of magnetic properties is Vibrating Sample Magnetometer (VSM) used for measure of magnetic properties of materials as a function of magnetic field, temperature and time. Powders, solids or liquids can be measured by this system. [20]

Principle of measurement is the interaction of material placed in uniform magnetic field (H), which leads to the formation of magnetic moment in studied magnetically sensitive sample. Typically, sample is place into the sensing coil, and undergoes sinusoidal motion as mechanical vibration. Magnetic flux changes induce a voltage in sensing coil proportional to the magnetic moment of the sample. Variable temperatures are applied to the sample as well. [20]

3.1.1 Conductivity and pH measurement

Conductivity and pH measurements techniques belongs to the electroanalytical methods. These techniques study an analyte by measuring the potential and current in electrochemical cell containing analyte. [21]

3.1.1 XPS measurement

X-Ray photoelectron spectroscopy (XPS) known also as Electron Spectroscopy for Chemical Analysis (ESCA) is a method used for quantitative and qualitative measurement of surfaces. Principle is measuring the photoemission of the solid samples after the the interaction of X-Rays with energy range 300 – 1000 eV with the surface depth of 0 – 12 nm. Kinetic energy of photoemitted electrons is plotted against the number of detected electrons. To obtain minimum error, UHV vacuum is
needed in this method as the detectors of photoemitted electrons are typically placed in one meter distance from the analyzed sample. [22]

4 RESULTS AND DISCUSSION

4.1 HYDROLYSIS OF TITANIUM ALKOXIDES

For measurement of kinetics of Ti-alkoxide hydrolysis in neutral conditions, three kinds of Ti alkoxides were used: titanium tetraethoxide (TIETH), titanium tetreraisopropoxide (TIPP) and Titanium tetrabutoxide (TIBUT), with increasing molar ratio of Ti-alkoxide/water ($R$) in order to observe the change in kinetics rates. $R$ was set to 0.5; 1; 2; 4; 8; 16. Same amount of Ti-alkoxides was used in each hydrolysis measurements.

For hydrolysis the approximately 2.000 g of alkoxide was used dispersed in 2.000 g of solvent (ethanol, isopropanol, 1-butanol). Calculated amount of water was mixed with the 5.000 g of solvent and upon vigorous stirring accomplished by test tube mixer was added through syringe to the previously prepared alkoxide solution placed in turbidimeter cuvette. After adding all solvent solution with water into the solution of Ti-alkoxide with solvent, formed solutions were mixed for further ten seconds and then were placed directly to the turbidimeter and measurement of turbidity started. Hydrolysis was done in turbidimetric cuvette with septa and solvents and other chemicals were carefully added with syringe to prevent any possible impact of air humidity on the alkoxides samples.

4.1 RESULTS OF HYDROLYSIS OF TITANIUM ALKOXIDES

Analyzing the turbidimetry for estimation of kinetic rate of hydrolysis, the measured data for different $R$ during hydrolysis are shown in table 2. The X stands for no recorded turbidity after twelve hours of measurement, $T_{\text{max}}$ represents the crossing of the measurement range of turbidimeter, reaching value over 1000 NTU.

Tab. 2. Prepared samples of hydrolysates of Ti-alkoxides with varying $R$

<table>
<thead>
<tr>
<th>Alkoxide</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIETH</td>
<td>$T_{\text{max}}&lt;60s$</td>
<td>$T_{\text{max}}&lt;15s$</td>
<td>$T_{\text{max}}&lt;5s$</td>
<td>$T_{\text{max}}&lt;2s$</td>
<td>$T_{\text{max}}&lt;2s$</td>
<td>$T_{\text{max}}&lt;2s$</td>
</tr>
<tr>
<td>TIPP</td>
<td>$X^*$</td>
<td>$T_{\text{max}}&lt;800s$</td>
<td>$T_{\text{max}}&lt;60s$</td>
<td>$T_{\text{max}}&lt;5s$</td>
<td>$T_{\text{max}}&lt;2s$</td>
<td>$T_{\text{max}}&lt;2s$</td>
</tr>
<tr>
<td>TIBUT</td>
<td>$X$</td>
<td>$X$</td>
<td>$T_{\text{max}}&lt;1500s$</td>
<td>$T_{\text{max}}&lt;60s$</td>
<td>$T_{\text{max}}&lt;5s$</td>
<td>$T_{\text{max}}&lt;5s$</td>
</tr>
</tbody>
</table>

* Althought, no measured turbidity was observed after 12 hours, the growth of transparent crystals was observed, which were analyzed in further measurements in this chapter.

4.1.1 Kinetic study

Turbidity of solution of alkoxide was measured upon rapid addition of water in solvent with the turbidimeter. For isopropoxide and butoxide, two molar ratios were selected for the estimation of impact of temperature on the hydrolysis. Titanium
isopropoxide was measured with $R = 1$ with used solvent isopropanol, butoxide was measured at $R = 2$ with used solvent n-butanol.

To get the value of induction time ($t_{\text{induction}}$) the linear slope in range of high development of turbidity was analysed by applying linear function on the end of steep increasement of turbidity, typically for the last five values of turbidity recorded before the exceeding of the measuring range of turbidity to reveal value of time on axis $x$. The induction times with projected linear regresions equations from last five values of turbidity are presented in table 8.

As can be seen on figures 4 and 5 with increasing temperature, the induction time was reduced and furthermore however for TIBUT sample the reduction of induction time is not as big as for the TIPP sample. With higher temperature, higher rate of hydrolysis is observed for both samples as concluded in table 3.

Fig. 4. Hydrolysis at different temperatures turbidity increasement for TIBUT $R = 1$
Fig. 5. Hydrolysis at different temperatures turbidity increasement for TIPP $R = 2$

Tab. 3 Induction time evaluation from kinetic measurements with linear regression equations

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>TIPP $R = 1 t_i$ (s)</th>
<th>25</th>
<th>35</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear regression equation</td>
<td>$y = 13.06x - 3352.9$</td>
<td>$y = 12.36x - 6081.3$</td>
<td>$y = 7.392x - 4619$</td>
<td></td>
</tr>
<tr>
<td>TIBUT $R = 2 t_i$ (s)</td>
<td>1 057</td>
<td>969</td>
<td>846</td>
<td></td>
</tr>
<tr>
<td>Linear regression equation</td>
<td>$y = 2.1893x - 2315$</td>
<td>$y = 13.85x - 13428$</td>
<td>$Y = 11.728x - 9921$</td>
<td></td>
</tr>
</tbody>
</table>

4.1.2 DTA – TGA analysis

As can be seen on figures 6 - 8, the main loss of weight is detectable upon heating until 300°C, after that, only small loss of weight in range of 1 – 2 % is seen. Heatflow from sample is corresponding to the loss of weight mainly in range above 200 °C where upon changing the rate of weight decrease, the heatflow reduces. For the evaluation of mass loss in this range, the derivation of weight upon temperature was used. This procedure was done for all analysed samples. Steep crystallization peak can be furthermore observed, when heatflow from sample arrises quickly for a while with negligible change in weight of sample.
Fig. 6 DTA – TGA analysis of TIETH with different R
Derivation of temperature is presented for Ti-alkoxide hydrolysate samples with lowest R to maintain the figures comprehensible.

Fig. 7 DTA – TGA analysis of TIPP with different R
Fig. 8 DTA – TGA analysis of TIBUT with different $R$.
Table 4 concludes the obtained data. For TIPP samples with $R = 0.5$ and 1.0 the two possible crystallization peaks were identified, in TIBUT samples X represents no recorded value as no particle formation happened in 12 hours range.
Tab. 4 Crystallization temperatures and weight loss in temperature range 220 – 320 °C for different $R$ of hydrolysed Ti-alkoxides

<table>
<thead>
<tr>
<th>Molar Ratio ($R$)</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight loss (%)</td>
<td>15.7</td>
<td>10.3</td>
<td>9.8</td>
<td>9.2</td>
<td>5.9</td>
<td>1.0</td>
</tr>
<tr>
<td>$T_{\text{cryst}}$ (°C)</td>
<td>350.7</td>
<td>355.0</td>
<td>357.9</td>
<td>365.0</td>
<td>396.8</td>
<td>417.8</td>
</tr>
<tr>
<td>TIPP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight loss (%)</td>
<td>34.9</td>
<td>19.5</td>
<td>14.3</td>
<td>25.01</td>
<td>23.2</td>
<td>13.0</td>
</tr>
<tr>
<td>$T_{\text{cryst}}$ (°C)</td>
<td>337.0</td>
<td>329.7</td>
<td>374.5</td>
<td>368.8</td>
<td>368.3</td>
<td>422.3</td>
</tr>
<tr>
<td>TIBUT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight loss (%)</td>
<td>X</td>
<td>X</td>
<td>26.5</td>
<td>23.4</td>
<td>18.4</td>
<td>20.7</td>
</tr>
<tr>
<td>$T_{\text{cryst}}$ (°C)</td>
<td>X</td>
<td>X</td>
<td>363.1</td>
<td>365.57</td>
<td>382.6</td>
<td>388.3</td>
</tr>
</tbody>
</table>

4.1.1 XRD analysis
XRD in temperate cell with increasing temperature steps in temperature range 350 – 370°C was performed. All sintered hydrolysates performed the crystallization onto the anatase phase. Results of Scherer’s equation calculated crystallite size of
anatase phase for molar ratio of Ti-alkoxides with increasing temperature are demonstrated in table 5.

Tab. 5 Size of anatase crystallites with temperature treatment

<table>
<thead>
<tr>
<th>Ti-alkoxide</th>
<th>0.5</th>
<th>2</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIETH $S_{\text{BET}}$ (m$^2$·g$^{-1}$)</td>
<td>8.64</td>
<td>X</td>
<td>51.4</td>
</tr>
<tr>
<td>TIPP $S_{\text{BET}}$ (m$^2$·g$^{-1}$)</td>
<td>4.166</td>
<td>X</td>
<td>118.8</td>
</tr>
<tr>
<td>TIBUT $S_{\text{BET}}$ (m$^2$·g$^{-1}$)</td>
<td>X</td>
<td>8.64</td>
<td>83.58</td>
</tr>
</tbody>
</table>

As can be observed, the specific surface changes with applied molar ratio. The observed differences were also reported when sintering the hydrolysed samples as when the Ti-alkoxides hydrolysates with lowest $R$ were sintered, the formation of grey to black powders was observed with bulky structure, whereas all Ti-alkoxides samples with $R = 16$ exhibited white colour after sintering.

4.2 SYNTHESIS OF MAGNETIC NANOPARTICLES

Herein we discuss simple one-step precipitation method for pure magnetite production from solution of Mohr’s salt $(\text{NH}_4)_2\text{Fe}($SO$_4$)$_2$·6H$_2$O. As bases NaOH and Na$_2$CO$_3$ were used for the precipitation with no further adjustment of ratios of Fe$^{2+}$ and Fe$^{3+}$ salts. As it was concluded in few studies, the possible formation of magnetite can be accomplished using only ferrous salts as the starting compound for precipitation. Moreover control over the particles morphology can be observed varying the temperature of reaction. [22 – 25]

The polycarboxylic superplasticizer Glenium ACE 40 is applied during synthesis in order to treat surface of nanoparticles with carbon layer in further coating process by
TiO$_2$ nanoparticles and for the reduction of agglomeration of particles during the precipitation. Polycarboxylate superplasticizers (PCE) are applied in the concrete mixtures preparation for the advantage of reducing the needed water – cement ratio for enhanced manipulation with cement mixtures. Although the intensive research explaining their function is recently carried out, their working principles lack of a full understanding. It can be assumed that in general their ability is to interact with the surfaces of hydrating particles and reducing the viscosity of such solutions.

### 4.2.1 Synthetic procedure

Precipitation of nanoparticles was done according to method, developed in earlier work of Author of thesis. [26] Stock solution of Mohric salt was prepared with concentration of 0.030 mol·dm$^{-3}$. The yellow to orange colored solution was stabilized adding droplets of sulfuric acid to reach pH $\leq 3$ resulting in transparent solution. Bases solutions were prepared with concentration of 0.1 mol·dm$^{-3}$.

Furthermore the apparatus consisting of three necked flask with thermometer, heater and bubble cooler has been used as shown in figure 30 for measurements of pH and conductivity upon increasing amount of base added and the temperature impact on the rate of precipitation and appearance of magnetic particles was evaluated while varying the temperature of precipitation reaction. For measurement at 0°C the Dewar container with ice water was used.

![Apparatus for the magnetic nanoparticles preparation](image)

**Fig. 9.** Apparatus for the magnetic nanoparticles preparation

### 4.2.2 Precipitation kinetics

Table 7 concludes the reaction rates comparison with changing temperature for precipitation with sodium hydroxide. Surprisingly the formation of magnetic particles was observed much earlier than first detectable phase formation by XRD.

<table>
<thead>
<tr>
<th>Temperature ($°C$)</th>
<th>0</th>
<th>22</th>
<th>60</th>
<th>95 – 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance of green rusts</td>
<td>t $&lt;$ 5 s</td>
<td>t $&lt;$ 5 s</td>
<td>t $&lt;$ 5 s</td>
<td>t $&lt;$ 5 s</td>
</tr>
<tr>
<td>Presence of magnetic properties</td>
<td>-</td>
<td>50 min</td>
<td>15 min</td>
<td>3 min</td>
</tr>
<tr>
<td>Precipitation time</td>
<td>-</td>
<td>180 min</td>
<td>35 min</td>
<td>t $&lt;$ 10 min</td>
</tr>
</tbody>
</table>
For precipitation at 0°C even after 24 hours there was no visible observation of black magnetic precipitates, nor any response to the external magnetic force. Dark green precipitates were formed without any change of color during reaction.

4.2.3 Measurement of pH and conductivity

In table 8 the pH of collected magnetic samples, these are also emphasized on the figures 10 and 11 showing the development of pH and conductivity during precipitation reaction. Sample of 15 ml was withdrawn every 7 minutes after addition of 5 – 10 ml of base solution into the boiling solution of Mohr’s salt. It was cooled down to 22 °C and pH and conductivity was measured. In order to prevent withdrawal impact of samples during synthesis, the relative volume of base (V_r) was used as a value for axis x where V_r = V / V_t. The V stands for actual volume of base after addition in the reaction mixture and V_t is total volume of base added during precipitation.

Fig. 10. Changes of pH of Mohr’s salt solution with added volume of base
Tab. 8 Collected samples of nanoparticles

<table>
<thead>
<tr>
<th>Synthesis and parameters</th>
<th>Synthesis 1 NaOH</th>
<th>Synthesis 2 NaOH + 2 ml ACE40</th>
<th>Synthesis 3 Na_2CO_3 + 2ml ACE40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>pH</td>
<td>6.1</td>
<td>10.0</td>
<td>6.6</td>
</tr>
</tbody>
</table>
During the precipitation the very first observed change of colorless solution was the appearance of turbidity with significantly orange color formation, which changed with time into the bright green and then turning into the dark green and dark blue resulting in brown to black color at higher pH > 9. Agglomeration of precipitates at high pH was observed as the black precipitates were sedimenting and clear solution over them was formed when finishing the synthesis. This behaviour was affected by ACE 40 application as at the pH range above 9 the highly turbid black solution was formed with no observed sedimentation for further 5 hours after finishing synthesis.

### 4.2.4 DTA – TGA analysis of magnetite nanoparticles

In order to verify the presence of superplasticizer on surface of magnetic particles, the DTA – TGA analysis was performed in oxygen atmosphere for samples of NaOH base and NaOH base with ACE 40 presence. Analyzed samples were 2 and 4 according to table 8. Results are presented in figures 12 and 13. Both samples were exhibiting the same rate of initial loss of weight until 250°C. Then analyzing the differences between prepared magnetite samples, it is observed that the sample 4 including the treatment with the superplasticizer compared to sample 2 with no surface treatment shows in temperature range of 250 – 500°C a loss of 2.7 % weight whereas only 1.21 % of mass loss for sample 2 is observed. The main difference is observed in temperature range above 500°C, where the magnetite sample with no surface treatment is exhibiting loss of 5.9 % of weight,

![Conductivity changes with increasing pH](image.png)
whereas the surface treated magnetite is showing only 0.5% loss of weight. Differences of heatflows of measured samples are observed too.

Fig. 12. DTA – TGA analysis of prepared magnetite particles sample 2

Fig. 13 DTA – TGA analysis of prepared magnetite particles with ACE 40 sample 4
4.2.1 XRD analysis of magnetite nanoparticles

XRD analysis using the XRD D8 DISCOVER was done on samples showed in table 8. Figures 14 and 15 show the diffraction patterns with identification of crystalline phases for very first magnetic samples withdrawal and for samples with lowest conductivity recorded.

Fig. 14 XRD of first magnetically active particles during nanoparticles precipitation
In figure above, the M stands for magnetite diffraction line, G stands for the goethite diffraction peak and U stands for the unknown diffraction pattern, which was formed and S was identified as a possible traces of sodium sulfate appearing as probably impurity which remained when washing particles with distilled water.
Fig. 15 XRD of magnetic samples during lowest conductivity measured
Analyzing the XRD patterns in figure 15, only magnetite phase appeared. According to obtained XRD spectra, the best crystallinity is obtained for the particles synthetized with the use of sodium hydroxide base. With applying the ACE 40 superplasticizer the broader peaks of formed particles were recorded. Appeared phases in the lower pH range (\( \text{ph} \approx 6 \)) were identified as goethite and magnetite.

### 4.2.2 SEM - EDS analysis of magnetite nanoparticles

Analyzing the particle morphology and size and composition of found samples was done by SEM – EDS analysis using SEM QUANTA 200 F with measuring of EDS spectra of sample 3 containing the unknown phase. Its analysis is shown in figure 16.

Fig. 16 EDS analysis of the sample 3 with unknown diffraction pattern
Figure 17 shows the prepared and collected nanoparticles according to the table 14. For all samples except sample 3 the same resolution was used.

Fig. 17 SEM analysis of prepared magnetic particles
Morphology of samples is changing with the pH during precipitation and is dependent on usage of ACE 40 superplasticizer. With its use the particle size
compared to the first synthesis with NaOH usage is significantly lower. Remarkable
difference can be observed in particles morphology for sample 3. Agglomeration of
particles was observed.

**4.3 TiO\textsubscript{2} APPLICATION ON MAGNETIC PARTICLES AND
PHOTOCATALYTIC STUDIES**

Samples of prepared magnetite in pH range above 9 as mentioned in table 8 were
coted with anatase large scale produced TiO\textsubscript{2} particles and selected synthetized
amorphous TiO\textsubscript{2} (EXP TiO\textsubscript{2}) particles prepared according to the work of Cihlar and
coworkers [28] by hydrolysis of TIPP with \( R = 100 \) with basic properties as shown
in following table:

Tab. 9 Properties of used TiO\textsubscript{2} particles

<table>
<thead>
<tr>
<th>TiO\textsubscript{2} particles</th>
<th>Size (nm)</th>
<th>Specific surface area (m\textsuperscript{2}·g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK 20 TiO\textsubscript{2}</td>
<td>15 – 35</td>
<td>70 - 110</td>
</tr>
<tr>
<td>KRONOS TiO\textsubscript{2}</td>
<td>15</td>
<td>&gt; 225</td>
</tr>
<tr>
<td>EXP TiO\textsubscript{2}</td>
<td>4.4</td>
<td>354</td>
</tr>
</tbody>
</table>

For coating of magnetite, samples 2 and 4 from table 8 were selected to perform the
TiO\textsubscript{2} coatings without and with surface treatment by hydrolysis of TIPP with \( R = 2 \).

**4.3.1 Turbidity measurement of TiO\textsubscript{2} coated nanoparticles**

Table 10 shows the turbidity of core-shell particles prepared from nanosized
magnetic particles. Particles were dispersed for 30 min by sonification and then
attracted by magnetic force with neodymium magnet in order to sample remanence
turbidity, which could be attributed to the TiO\textsubscript{2} released from the surface of
nanoparticles. Marked samples (A, B, C, D) are studied by further analysis.

Tab. 10 Turbidity measurement of prepared particles

<table>
<thead>
<tr>
<th>Particle coating</th>
<th>(NTU)</th>
<th>With TIPP treatment (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK 20 TiO\textsubscript{2} + NaOH</td>
<td>65.3</td>
<td>5.95</td>
</tr>
<tr>
<td>PK 20 TiO\textsubscript{2} + NaOH + ACE 40</td>
<td>11.2</td>
<td>6.71</td>
</tr>
<tr>
<td>KRONOS TiO\textsubscript{2} + NaOH</td>
<td>74.1</td>
<td>5.21</td>
</tr>
<tr>
<td>KRONOS TiO\textsubscript{2} + NaOH + ACE 40</td>
<td>15.1</td>
<td>2.4</td>
</tr>
<tr>
<td>EXP TiO\textsubscript{2} + NaOH</td>
<td>61.4 (A)</td>
<td>7.5 (C)</td>
</tr>
<tr>
<td>EXP TiO\textsubscript{2} + NaOH + ACE 40</td>
<td>13.3 (B)</td>
<td>2.9 (D)</td>
</tr>
</tbody>
</table>

The presence of superplasticizer on the surface of the nanoparticles of magnetite has
big influence on the remanence turbidity measured after 30 min of ultrasonification
of prepared particles. In general, the TIPP coating procedure helps to the decrease of
the remanence turbidity.

**4.3.2 XRD analysis of TiO\textsubscript{2} coated nanoparticles**

XRD with Rietveld’s analysis was done. Results of appeared phases and their
quantification for samples A – D EXP TiO\textsubscript{2} are given in following table:
Tab. 11 Rietveld’s analysis of phases formed.

<table>
<thead>
<tr>
<th>Phase (weight)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>26</td>
<td>30</td>
<td>74.6</td>
<td>84.3</td>
</tr>
<tr>
<td>Magnetite</td>
<td>72</td>
<td>70</td>
<td>19.9</td>
<td>15.7</td>
</tr>
<tr>
<td>Hematite</td>
<td>2</td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rutile</td>
<td></td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

With application of hydrolysed TIPP the content of TiO$_2$ increased significantly. When applying the ACE 40 superplasticizer the surface of particles remained consisted and formed from anatase and magnetite phases whereas the hematite and rutile appeared at surface treated with TIPP and small amount of hematite appeared when only nanomagnetite particles were coated.

4.4 DEPOSITION OF TiO$_2$ ON THE SURFACE OF Mn-Zn FERRITE

Deposition of TiO$_2$ was performed as described in work of Solny and co-workers. [28] In each procedure, the amount of TIPP was set to be equivalent to 1.0 g of pure TiO$_2$ content and was mixed with 10 ml of isopropanol together with 5.0 g of Mn-Zn ferrite particles. The mixture was left mixing with glass stirrer for 60 minutes at room temperature, then the temperature was increased to 80°C to dry the solvent and after that formed particles were put into the crucible with temperature set to increment of 2 °C per minute up to 350 °C and threshold of 4.5 hours. Also the intent to prepare the mesoporous surface was done, using the PK 20 PRETIOX anatase nanoparticles from large scale industry producer PRECHEZA, with average size diameter $D_{50} = 15 – 35$ nm and surface area $S_{BET} = 70 – 110$ m$^2$·g$^{-1}$. For procedure to produce the mesoporous surface with high specific surface area the 0.5 g of PK 20 particles were used and introduced into the TIPP solution with isopropanol followed by 10 min ultrasonification before the ferrite introdution.

4.4.1 SEM – EDS analysis of TiO$_2$ coated Mn-Zn ferrite

SEM analysis of surface of uncoated and coated ferrite shows following figure:

Fig. 18 Coating of ferrite, resolution 5000x (1- pure ferrite, 2- ferrite coated by TIPP hydrolysis, 3- ferrite coated with combined TIPP and PK 20 TiO$_2$ deposition)
For better formation of desired surfaces of TiO$_2$ the C and Au coating was introduced on the surface of ferrite prior to coat it by TiO$_2$ with TIPP coating process to see, if the binding of TiO$_2$ on the surface improves. In following figure, the surface of Au and C sputtered ferrite (Au and C) are shown together with TiO$_2$ deposited on the C and Au coated surfaces of ferrite.

![Fig. 19 TiO$_2$ coating of Au and C sputtered Mn-Zn ferrite surfaces](image)

Coated particles by sputtering of C and Au showed formation of lumps of TiO$_2$, which was confirmed by EDS analysis. It was also observed, that after 10 sputtering sequences the formation of homogenous thin layer over the surface of Mn-Zn ferrite appeared.

1.1.1 Photocatalytic decomposition of methylene blue

Testing the photocatalytic decomposition of methylene blue, it was found, that a big adsorption properties can be denoted to the use of superplasticizer for the synthesis of nanoparticles. Therefore, the photocatalytic activity was estimated for samples of nanoparticles as characterized in chapter 4.3.1 by synthesis 1 using the NaOH as base for precipitation, which were coated with TiO$_2$ anatase nanoparticles either directly, or in dispersed solution of hydrolysed TIPP. In table 12 for better explanation, the methodology of samples which appear in this chapter is given with used methods of preparation.
Table 12 Methodology of photocatalytically tested core-shell samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation</th>
<th>TiO₂ application</th>
<th>Heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration</td>
<td>Average values of C / C₀ obtained from all samples for photocatalytic tests during measurement in dark</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH + Kronos TiO₂ + TIPP</td>
<td>Synthesis 1</td>
<td>Kronos TiO₂ dispergated in hydrolysed TIPP</td>
<td>370 °C in N₂ atmosphere</td>
</tr>
<tr>
<td>NaOH + Kronos TiO₂</td>
<td>Synthesis 1</td>
<td>Kronos TiO₂ dispergated in isopropanol</td>
<td>150 °C in oxygen atmosphere</td>
</tr>
<tr>
<td>NaOH + EXP TiO₂ + TIPP</td>
<td>Synthesis 1</td>
<td>EXP TiO₂ dispergated in hydrolysed TIPP</td>
<td>370 °C in N₂ atmosphere</td>
</tr>
<tr>
<td>NaOH + PK 20 TiO₂ + TIPP</td>
<td>Synthesis 1</td>
<td>PK 20 TiO₂ dispergated in hydrolysed TIPP</td>
<td>370 °C in N₂ atmosphere</td>
</tr>
</tbody>
</table>

Figure 20 shows the decomposition rate as the decrease of concentration (C) of methylene blue with irradiation time compared to the initial concentration (C₀) as measured for the absorption of light at λ = 664 nm. Table 13 assumes the decomposition rate of used samples in mol·h⁻¹·g⁻¹.

Table 13 Decomposition rate of photocatalytic samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Decomposition of MB 180 min (%)</th>
<th>Decomposition rate (mol·h⁻¹·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH + Kronos TiO₂ + TIPP</td>
<td>21</td>
<td>3.5·10⁻⁵</td>
</tr>
<tr>
<td>NaOH + Kronos TiO₂</td>
<td>33</td>
<td>5.5·10⁻⁵</td>
</tr>
<tr>
<td>NaOH + EXP TiO₂ + TIPP</td>
<td>40</td>
<td>6.7·10⁻⁵</td>
</tr>
<tr>
<td>NaOH + PK 20 TiO₂ + TIPP</td>
<td>34</td>
<td>5.7·10⁻⁵</td>
</tr>
</tbody>
</table>

Fig. 20 The decomposition of methylene blue with core-shell magnetite samples
Photocatalytic performance was not estimated for ACE 40 treated magnetite nanoparticles coated with TiO₂ as those exhibited high adsorption properties and
adsorbed in 40 minutes nearly all presented methylene blue, resulting in transparent solution.

4.4.1 Photocatalytic decomposition of ethanolic and isopropanolic vapors

For measurement in the experimental reactor, 3 samples of ferrites were selected as mentioned in the chapter 4.4 samples 1, 2, 3. These were held in reactor by magnetic force and the photocatalytic decomposition of the ethanolic and isopropanolic vapors were evaluated by collecting the FTIR spectra of the circulating vapors. In figure 21 typical observed spectra changes are evaluated in 2D FTIR figure with showing intensity of recorded spectra by color change. The red cross marks the position of the CO$_2$ IR absorbance peak.

![FTIR spectra](image)

Fig. 21 Ferrite decomposition of ethanolic vapors in UV FTIR spectra showed same intensity for absorbance peak at 2974 cm$^{-1}$. The decrease of absorbance to 50% of original size after UV lamp was turned on was recorded as relative half time of decomposition ($t_{1/2}$) which is shown in the following table:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pure ferrite</th>
<th>Ferrite coated by TIPP</th>
<th>Ferrite coated with PK 20 +TIPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{1/2}$ ethanol (min)</td>
<td>$t_{1/2} &gt; 60.0$</td>
<td>10.5</td>
<td>10.0</td>
</tr>
<tr>
<td>$t_{1/2}$ isopropanol (min)</td>
<td>$t_{1/2} &gt; 60.0$</td>
<td>37.5</td>
<td>22.9</td>
</tr>
</tbody>
</table>

As can be seen the combined PK 20 TiO$_2$ + TIPP hydrolysis coated ferrite exhibits the relatively highest photocatalytic decomposition as the recorded $t_{1/2}$ values are smallest. In case of ferrite without any surface treatment, the $t_{1/2}$ values couldn’t be obtained as the halftime of decomposition was not reached in 60 min when measurement proceeded.
5 CONCLUSION

Evaluation of the impact of conditions of the hydrolysis of Ti-alkoxides on properties of formed hydrolysates was done. The study confirmed that water concentration, especially water to alkoxide ratio $R$ and temperature conditions of hydrolysis reactions, affect the kinetics of Ti-alkoxide hydrolysates formation and their properties. By turbidimetric studies of hydrolysis kinetics, the induction time was evaluated for TIETH, TIPP and TIBUT alkoxides dissolved in ethanol, isopropanol and n-butanol. Furthermore, the formation of crystallite phases in hydrolysed Ti-isopropoxide isopropanolic mixtures with low content of water reported as hydrolysis molar ratio ($R = 0.5$) was confirmed. Their formation was supported with the temperature treatment at 50 °C or aging of hydrolysed mixture. DTA – TGA analysis confirmed the impact of water content during hydrolysis on the crystallization temperatures. Higher crystallization temperature of anatase phase with increasing of $R$ during hydrolysis was observed. The study found, that amount of chemisorbed solvent in prepared hydrolysates is $R$ dependent. For low values of $R$, the higher amount of solvent is chemisorbed in formed hydrolysates structure. With increasement of solvent chemisorbed, the reduction of solvent presence was obtained.

Calculating the crystallites size of anatase phase formed with use of Scherrer’s equation from the XRD measurements revealed that with higher content of chemisorbed solvents the size of crystallites decreased. This finding can be attributed to large imperfections and defects in the structure of such formed crystallites rather, than to the claim that very small particles were received. The observation of XRD measurement in atmospheric conditions in temperate cell with increasing temperature, showed according to Scherer’s formula size growth of imperfect crystallites with higher amount of chemisorbed solvent happened with increasing temperature treatment whereas crystallites formed from hydrolysates with lower content of chemisorbed solvent preserved their original size or exhibited smaller growth of the size. Moreover, higher specific surface area was obtained for the prepared crystallized anatase nanoparticles by heat treatment of hydrolysates with higher $R$ during synthesis and lower amount of chemisorbed solvent.

Synthesis of magnetite nanoparticles by simple precipitation of magnetite nanoparticles from Mohr’s salt solution by strong and moderate bases (NaOH, Na$_2$CO$_3$) was done. Conditions of the precipitation considering the temperature and the modification by surface-active compounds were examined. It was found that precipitation reaction is temperature depended, showing no evolution of magnetite nanoparticles at low temperature of 0 °C and performing the highest precipitation rate using boiling solutions. Quite interestingly, the formation of earlier observed 2D shaped particles was observed at temperature range around 60°C. It is possible that needles of presented goethite phase, which presence was confirmed by XRD and SEM analysis, are formed during precipitation reactions converted into the magnetite and are able to drive the magnetite evolution direction.
Conductivity and pH measurements were done in order to estimate range of pH and conductivity in which the precipitation occurs. It was found that application of surface modifying compound consisted of polycarboxylic ether based superplasticizer ACE 40 had impact on the reaction intermediates formation, but showed negligible impact on the pH and conductivity range during precipitation of magnetite. With usage of ACE 40 formation of unknown magnetically active crystalline phase was discovered, showing no match to any known diffraction pattern respecting its elemental composition determined by EDS analysis. This phase consisted of the very first magnetically active compounds formed during precipitation with NaOH and during further precipitation was later in reaction transformed into the magnetite nanoparticles. Using the ACE 40 during precipitation leaded to lower size of agglomerates of magnetite nanoparticles. 

Prepared magnetite nanoparticles were starting material for the deposition of TiO₂ in photocatalytic form of anatase on their surface. Two deposition techniques were examined using either hydrolysis of TIPP with \( R = 2 \), or combined method with selected TiO₂ anatase nanoparticles dispersed by ultrasonification in hydrolysed TIPP. Core-shell powder photocatalysts with high specific surface area (137 – 150 \( \text{m}^2 \cdot \text{g}^{-1} \)) and broader band gap value (2.3 – 3.2 eV) were prepared. Photocatalytic measurement of methylene blue decomposition showed that particles are having both the photocatalytic properties as well as very high adsorptive properties. Taking into account such properties, prepared core-shell nanoparticles are very promising candidates for future decomposition studies work.

Mn-Zn ferrite with macroscopic dimensions with deposited TiO₂ in anatase form was prepared by either coating of its surface by hydrolysed Ti-alkoxide or by dispersing the anatase nanoparticles in hydrolysed Ti-alkoxide. Problems with not adhering lumps of TiO₂ coating were observed, reduced when using the hydrolysed Ti-alkoxide deposition with anatase nanoparticles. Evaluation of impact of sputtering of the Au and C layers onto the ferrite surface prior to coating it by hydrolysed TIPP was done. It was observed, that sputtered coating helped to the adherence of the anatase layer deposited by hydrolysis of TIPP on the modified surface of ferrite showing only crackings of layer due to the heat-treatment. Photocatalytic decomposition of solvents vapors was done on the photochemical reactor invented by Ptacek and co-workers [29].

To conclude, magnetic nanoparticles and microscale compounds with enhanced adsorptive and photocatalytic properties are extensively studied with various methods. Increasing knowledge in this area leads to preparation of novel materials with extraordinary properties. In proposed thesis, the development of novel materials have been done together with the identification of some previously unknown processes.
6 LITERATURE

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- Clarinette player
- Driver licence B