

Synthesis and characterization of metallic oxides with potential use in cosmetic products

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Introduction

For many years mineral compounds, especially metallic oxides, have been commonly used in the cosmetic industry. Among others TiO_2 , ZrO_2 , ZnO , CeO_2 , Fe_2O_3 may act as sun-protection factors or pigments in cosmetic products.

It is well known that sun radiation is necessary for all living organisms. However, an excessive exposure to the sunlight can cause a lot of negative effects like sunburns, photoaging (wrinkles), photosensitivity or even skin cancers. For this reason, the employment of various sunscreens in cosmetic preparations has been increasing. Sunscreens can be defined as materials that protect the skin from UV radiation and nowadays they have been available in the forms of topical lotion, creams, ointments, gels, or sprays. Sun protection filters can be divided into two main groups characterized by different mode of action [1]. Chemical UV filters are mostly aromatic compounds with carboxyl group, like *p*-aminobenzoic acid (PABA) derivatives, salicylates, and cinnamates for UVB protection and benzophenones for UVA protection. The second group consists of mineral (physical) filters among which the most common are inorganic oxides such as TiO_2 , ZnO , ZrO_2 and lately CeO_2 [2]. The principle of physical filters is based on reflection or scattering of UV radiation. The crucial parameter in this case is an adequate particle size (20 ÷ 50 nm), which provides UV protection and transparency to the visible light at the same time. It is assumed that mineral filters do not penetrate through the skin and cannot be decomposed with the sunlight. There is a strong tendency to increase the use of inorganic filters, especially in sun care products for children and people with sensitive skin, mostly due to their low potential for producing irritant reactions and cosmetic efficacy [1].

Apart from sunscreen properties, metallic oxides are often used as pigments, especially in the decorative cosmetics formulations. Natural pigments, based on iron oxides, have been widely used since the ancient times, what can be attributed mainly to their non-toxicity, chemical stability, and variety of colors. The most common and ubiquitous iron oxide is Fe_2O_3 . It may form various crystalline structures, like rhombohedral (α - Fe_2O_3) in hematite or cubic (γ - Fe_2O_3) in maghemite. Fe_3O_4 (considered as a $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ system with different iron's oxidation states), in turn, is widely known as magnetite due to its magnetic properties. Depending on the molecular formula, iron oxides may have different colors. For example, iron(III) oxides are mainly red and brown, Fe_3O_4 is black, whilst FeOOH (anhydrous iron(III) oxide-hydroxide) may have yellow or orange shades. Many of the commonly used pigments, namely ochres, siennas or umbras are based on iron oxides. Their application is connected mainly with ceramics glazing [3], painting or cosmetics and Fe_2O_3 is one of the most commonly used iron oxides. Iron pigments are believed to be nontoxic and chemically stable, especially when produced synthetically due to elimination of any impurities found in natural iron oxides [4].

The article covers different methods of synthesis and characterization of metallic oxides with potential application in cosmetic products. The aim of our work was to synthesize and characterize some metallic oxides with potential UV protection properties or that can be applied as pigments in the cosmetic powder preparations.

Experimental

Synthesis of oxides with potential UV protection properties

TiO_2 , ZrO_2 , ZnO and CeO_2 were synthesized by a simple, template assisted sol-gel method [5]. Titanium(IV) butoxide, zirconium(IV) *n*-propoxide, zincum(II) chloride (Aldrich) and cerium(III) chloride heptahydrate (Fluka) were used as metal precursors. Triblock copolymer Lutensol® AT I I (BASF) was applied as a structure determining agent. During synthesis of CeO_2 and ZnO some amount of 2M NaOH was added to keep pH level around 10 and 8, respectively. Additionally, before the gelation step they were generously washed with ethanol for the chloride ions removal. To obtain the final products all xerogels were calcined in the air, at 450°C and 700°C.

Synthesis of iron oxides

Iron(III) oxides were prepared using different precursors and synthesis methods. Three inorganic salts of iron(II) and iron(III) were used as Fe_2O_3 precursor, namely: FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Depending on the source of Fe, the synthesis was conducted with or without an oxidation step. When FeSO_4 was used as a precursor, precipitation process had to be followed by the oxidation in order to obtain iron(III) oxide. The first method was based on the process of precipitation and oxidation. Iron(II) sulphate(VI) was used as a source of Fe_2O_3 , an atmospheric oxygen as an oxidizing agent and NaOH as a factor controlling pH value (~11) and supporting oxidation. The oxidation step took place at an elevated temperature and at various reaction times (6, 12, 18, 24, 36 h). The second method was based only on the process of precipitation, since mainly iron(III) salts were used as precursors. In both methods calcination in the air (550°C, 3 h) was performed as the last step of synthesis.

$\text{Fe}_2\text{O}_3/\text{SiO}_2$ systems were obtained by the co-precipitation process. Fe_2O_3 with SiO_2 were precipitated simultaneously during the direct synthesis. Iron(III) salts and tetraethyl orthosilicate (TEOS) were used as precursors of Fe_2O_3 and SiO_2 , respectively. Calcination, the final step of synthesis, was performed in the air, at 550°C for 3 h.

Characterization of synthesized oxides

The synthesized TiO_2 , ZrO_2 , ZnO and CeO_2 were studied by a small- and wide-angle X-ray diffraction as well as a low-temperature N_2 sorption. Their potential application as a UV shield was tested in Diffuse Reflectance UV-Vis (DR UV-Vis) experiments. Iron oxides were subjected to analogous characterization. Physicochemical properties of iron oxides, especially their colors, were evaluated by comparison with those of the standard sample of α - Fe_2O_3 ($\geq 99\%$, POCh). Synthesized iron oxides were also used as pigments in the cosmetic powder preparations.

Results and Discussion

Metallic oxides with potential UV protection properties

Synthesis of titanium, zirconium, zinc and cerium oxides led to white (TiO_2 , ZrO_2 , ZnO) and yellow (CeO_2) powders with fine particles. Low-temperature N_2 adsorption/desorption measurements give the information about textural parameters, namely the specific surface area, total pore volume and average pore diameter of the synthesized materials. Moreover, the shape of the sorption isotherm

enables classification of porous structure of the sample studied. The sorption isotherms depicted in Figure 1 determined for zinc and cerium oxides can be described as a slightly deformed IUPAC's type IV [6], indicating that the samples are mesoporous with some pores of smaller and larger sizes.

For cerium oxide calcined at 450°C a strongly outlined hysteresis loop can be observed (Fig. 1). It is characteristic of the materials with porosity in the range of mesopores ($5 \div 20$ nm) and its presence is related to the so-called capillary condensation which occurs particularly in the instance of mesopores. Figure 1 shows sorption isotherms only for two materials selected from all synthesized oxides, because the shapes of the sorption isotherms recorded for TiO_2 and ZrO_2 are nearly the same as that for ZnO.

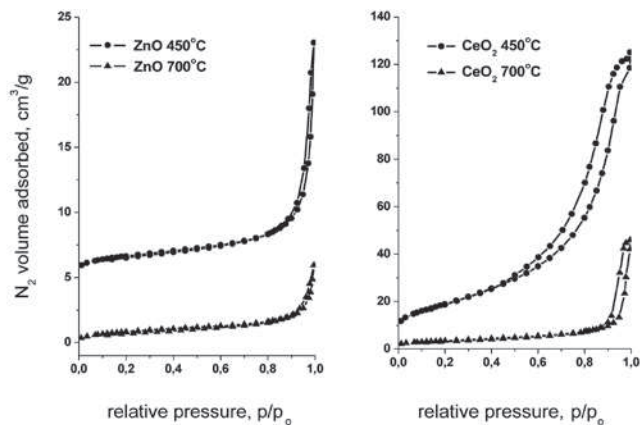


Fig. 1. Low-temperature nitrogen sorption isotherms of the synthesized ZnO and CeO_2

Higher calcination temperature (700°C) causes some changes in the shape of sorption isotherms, namely for CeO_2 the adsorption branch is getting steeper. The steepness of this branch reflects changes in the particle size as a result of the calcination process. Also the hysteresis loop becomes significantly narrower, indicating the decrease in mesoporosity. Moreover, the closure point of the hysteresis shifts to higher values of the relative pressure, suggesting an increase in the total amount of wide pores.

As already mentioned, by the means of low-temperature nitrogen sorption measurements some textural parameters may be evaluated. As evidenced by the results, the calcination temperature strongly influences textural parameters of the synthesized oxides, when higher temperature is applied the materials with smaller surface areas are obtained. The most significant decrease in the surface area is observed for CeO_2 , for which the thermal treatment at 700°C gives only $12 \text{ m}^2/\text{g}$, whereas the material calcined at 450°C has a surface area almost 6 times greater ($68 \text{ m}^2/\text{g}$). Among the oxides synthesized, ZnO had the smallest surface area of $6 \text{ m}^2/\text{g}$. Moreover, it also decreased ($3 \text{ m}^2/\text{g}$) when the higher calcination temperature was applied. When comparing the materials calcined at 450°C and 700°C, changes in the average pore sizes are also well visible. The oxides calcined at the higher temperature have pores of greater average diameter, which implies an increased contribution of pores larger than mesopores.

It is worth mentioning that the small-angle X-ray diffraction ($2\theta = 0.6\text{--}10^\circ$) method is a handy tool for material's mesoporosity determination. Applying this technique to the obtained oxides, no sharp reflexes in the mentioned 2θ range were observed. However, it does not totally neglect the mesoporosity of the synthesized oxides, especially in the context of low-temperature N_2 sorption results. High degree of particles refinement and the lack of monodispersity can be possible reasons for the presence of weak reflexes.

Wide-angle XRD patterns, shown in Figure 2, indicate that the materials obtained are pure oxides. The reflexes characteristic of specific crystallographic phases of the studied oxides are visible.

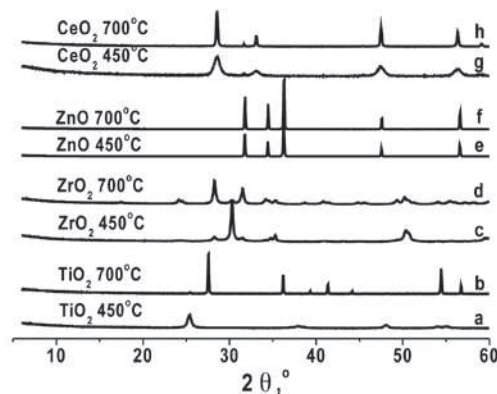


Fig. 2. XRD patterns of synthesized oxides

Depending on the calcination temperature, TiO_2 may crystallize into anatase or rutile form, which is apparent from the patterns (a) and (b), respectively. For ZrO_2 a strong relation was noted between the calcination temperature and the crystallographic phase of the product. The lower calcination temperature led to the tetragonal product (c), while the higher one to the monoclinic form (d). For ZnO and CeO_2 the applied calcination temperatures generated only one of the possible structures: wurtzite (e, f) or fluorite (g, h). However, the patterns (g) and (h) differ slightly in the width and intensity of reflexes, which indicates that CeO_2 obtained at 700°C, has particles of greater size, which can be treated as manifestation of the high-temperature sintering effect.

Potential sunscreen properties of synthesized oxides were evaluated on the basis of DR UV-Vis measurements. The results obtained for the calcined oxides are presented in Figure 3. All oxides absorb UV radiation in the range of $200 \div 400$ nm with a maximum at 220 and 300 nm. However, the absorption intensity of ZrO_2 , for wavelengths higher than 250 nm is significantly lower than that of the other oxides. It is also worth mentioning that in most cases the UV spectra of the oxides calcined at 450°C are quite similar to those of the oxides calcined at 700°C and only for TiO_2 the higher calcination temperature leads to a subtly broader absorption range.

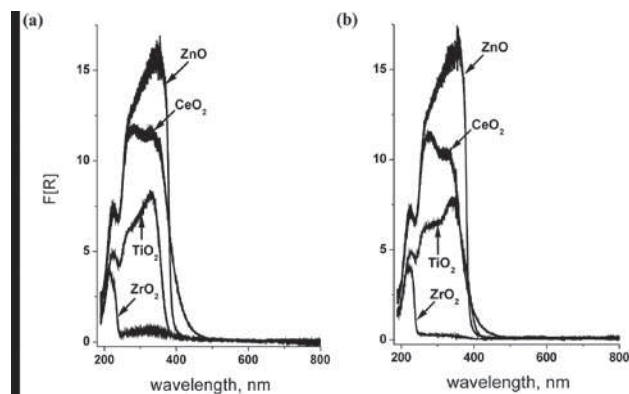


Fig. 3. DR UV-Vis spectra of synthesized oxides calcined at 450°C (a) and 700°C (b)

Iron oxides with potential use as pigments in cosmetics

Different methods of Fe_2O_3 synthesis gave the iron oxides differing in physicochemical properties, in particular in colors. In general, their synthesis was based on the precipitation reaction, but sometimes an oxidation step was required, depending on the oxidation state of iron in the salt (see the experimental part).

All the iron oxides obtained had different colors. The products of direct precipitation, when only Fe(III) salts are used and the oxidation step is neglected, were brown. However, the precipitation followed by the oxidation step led to black products, regardless the duration of the oxidation step. Thus, on the basis of visual comparison with the commercial $\alpha\text{-Fe}_2\text{O}_3$ (POCh), it can be inferred that dried

precipitates are not pure iron(III) oxides because their pigmentation differs significantly from that of the reference sample (dark red). After the calcination step, considerable changes in the samples pigmentation can be observed. Most of the materials become dark red or brown of different shades, which indicates that high-temperature treatment supports formation of good purity α - Fe_2O_3 products. Moreover, the oxidizing atmosphere during the calcination step strongly supports transformation of magnetite into the hematite form.

These preliminary observations were further confirmed by XRD analysis (Fig. 4) which revealed that calcined materials were pure and hematite-type iron(III) oxides (α - Fe_2O_3). Though, it can be assumed, with a high probability, that the variety in colors of the materials calcined can be related to differences in the particle size of the synthesized oxides. The results of XRD analysis, of the samples synthesized at 60°C , $\text{pH}=11$ and subjected to 6 h oxidation followed by the calcination, are very similar to those of the reference sample; see Figure 4c and 4a. However, the diffractogram of the sample before the calcination step (Fig. 4b) differs slightly from that of the reference material, which is clearly visible when comparing 2θ values of the main reflexes.

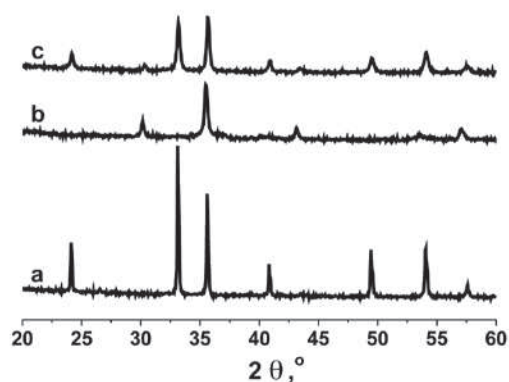


Fig. 4. XRD patterns of the synthesized materials (60°C , $\text{pH}=11$, 6h) before (b) and after (c) calcination step and of reference sample (α - Fe_2O_3) (a)

Still, it can be assumed that high temperature and atmospheric oxygen during the calcination step lead to the pure α - Fe_2O_3 . This conclusion was confirmed on the basis of DR UV-Vis analysis (not discussed in this paper).

The systems consisting of iron(III) oxide and silica have considerable significance in the cosmetic industry. They are used in the cosmetic powder preparation thanks to the favourable combination of the component properties: Fe_2O_3 acts as a pigment, whereas silica is a sebum and moisture absorbing agent, giving a smooth and matte appearance.

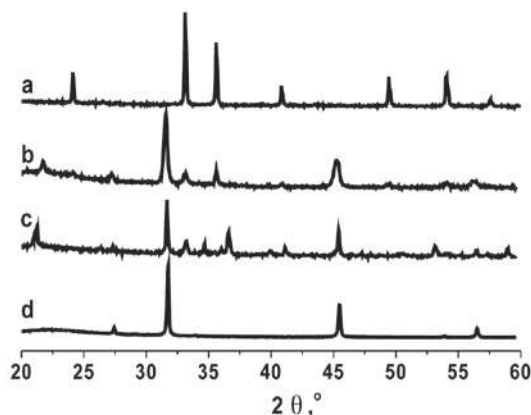


Fig. 5. Diffractograms of $\text{Fe}_2\text{O}_3/\text{SiO}_2$ systems synthesized by the co-precipitation method: samples before (c) and after (b) calcination, compared with those of the reference samples Fe_2O_3 (a) and SiO_2 (d)

According to the diffractograms shown in Figure 5, the co-precipitation method leads to the systems in which the crystallinity of both components is preserved. Comparing XRD patterns of materials before (Fig. 5c) and after (Fig. 5b) the calcination step with the diffractogram of the silica reference sample (Fig. 5d) it can be easily noticed that main reflexes at $2\theta=32^\circ$ and 45.5° are preserved. Analogous observation can be made when comparing XRD patterns of the reference α - Fe_2O_3 sample (Fig. 5a) and synthesized $\text{Fe}_2\text{O}_3/\text{SiO}_2$ systems (Fig. 5b and 5c).

Conclusions

The sol-gel method with a triblock copolymer as a structure determining agent was successfully used in synthesis of mesoporous oxides. According to the XRD patterns, the materials obtained were pure oxides with the crystallographic structure depending on the temperature of calcination. The oxides texture was mainly mesoporous. The materials synthesized can be considered as potentially good sunscreen factors as they absorb UV radiation in the range of $200\div 400$ nm, which is the target part of electromagnetic spectrum in cosmetic sunscreen formulations.

Iron(III) oxides with different colors were obtained by various methods of synthesis. XRD measurements showed that prior to the calcination step compounds obtained were not pure Fe_2O_3 . However, the calcinations process in elevated temperatures led to iron(III) oxides with a high level of purity. Also $\text{Fe}_2\text{O}_3/\text{SiO}_2$ systems were successfully synthesized by the co-precipitation technique. The samples of Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{SiO}_2$ systems can be successfully used as pigments in cosmetic powders, giving smooth and subtly colored products.

Literature

1. Serpone N., Dondi D., Albini A.: *Inorg. Chim. Acta* 2007, **360**, 794.
2. Yabe S., Sato T.: *J. Solid: State Chem.* 2003, **171**, 7.
3. Llusar M., et. al.: *J. European Ceramic Soc.* 2009, **29**, 3319.
4. Walter D.: *Thermochim. Acta* 2006, **445**, 195.
5. Nowak I., Jaroniec M.: *Top. Catal.* 2008, **49**, 193.
6. Sing K.S.W., et al.: *Pure Appl. Chem.* 1985, **57**, 603.

English translation by the Author

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