Original article

Effect of magnetite transformations on degradation efficiency of cerium dioxide-magnetite composite

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ABSTRACT

Present investigations are focused on synthesis of magnetite/cerium dioxide reactive sorbents in various weight ratios of components and their characterization of chemical and magnetic properties. The morphology and changes in magnetic transformations in dependence on composition are followed by electron microscopy, X-ray diffraction, Mössbauer spectroscopy and magnetic measurements at room and low temperatures. Degradation efficiency is evaluated from a decomposition of the organophosphorus pesticide parathion methyl using prepared reactive sorbents. The experimental results reveal that the degradation efficiency, expressed by rate constant (mol/h) in dependence on amount of cerium dioxide content (vol.%), is independent on kind of iron oxide but increases with cerium dioxide content. On the contrary, saturation and remanent magnetizations are highly sensitive to relative ratio of iron oxides; magnetite, maghemite and hematite, originating from the initial magnetite transformations in dependence on sample composition.

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1. Introduction

The rare earth cerium oxide or cerium dioxide belongs presently to frequently studied topic. It is prepared by various synthetic procedures and characterized with large number of experimental methods. Among technologies, e.g., sol-gel methods, homogeneous hydrolysis [1], hydrothermal synthe-

sis [2,3], precipitation methods using oxalate, ammonium hydroxide and ammonium carbonate [4–6] can be mentioned. Cerium dioxide and cerium dioxide-based composites are used in different technological applications [7]. These include a wide range of catalytic applications [8], solid oxide fuel cells [9,10], oxygen sensors [11], glass-polishing [12], an ultraviolet absorbent, e.g., for cosmetic use [13,14], reactive sorbents [15–17]. The last decade assumes also importance in the medical field. Thanks to cerium dioxide self regenerating antioxidant properties, it represents a promising antioxidant for healing numerous untreatable oxidative-stress-related diseases [18–21].
2. Experimental

2.1. Materials and sample preparation

The input materials for the sample preparations were purchased as reagent-grade chemicals from Sigma Aldrich (Steinheim, Germany). The cerium carbonate was prepared from the commercial Ce(NO₃)₃·6H₂O (purity 99.9%) and NH₄HCO₃ (purity 99.5%) by precipitation method published elsewhere [15]. Briefly, the carbonate precursor was prepared by preparation of an aqueous solution of Ce(NO₃)₃ (0.2 mol L⁻¹) with an excess of NH₄HCO₃ (0.5 mol L⁻¹) under stirring. After the precipitation process, the agitation continued for one more hour and the precipitate was left in the solution until the next day. The precipitate was separated by filtration, washed with deionized water and dried overnight at 110 °C. Subsequently the adequate mass of cerium carbonate and artificial magnetite (Fe₃O₄ particle size 50-100 nm) was mechanically mixed in ratios from 0/100 up to 50/50 (CeO₂/Fe₃O₄). The mixture of cerium carbonate/Fe₃O₄ were subjected to annealing process at 500 °C for 2h in air atmosphere. During annealing cerium carbonate transforms into cerium oxide (CeO₂).

2.2. Scanning and transmission electron microscopy, X-ray diffraction, particle size analyzer

The morphology of samples were followed by TESCAN LYRA 3XMU FEG/SEM scanning electron microscope at accelerating voltage of 20 kV, equipped with an X-Max80 Oxford Instruments detector for energy-dispersive X-ray (EDX) analysis. FEI Titan Themis 60–300 cubed high resolution transmission electron microscope with a high sensitivity EDX system (0.7 srad solid angle) operating at 300 kV was used for selected samples to see their morphology in more details.

X’PERT PRO diffractometer (Panalytical) equipped with Cu Kα radiation (λ=0.17902 nm) was used for diffractogram measurements in the range of 2θ = 20°–135°, steps = 0.01°, and time/step 5 s. Rietveld structure refinement method [33] using the HighScore Plus program and the ICSD database [34] were applied to analyze the relative abundance of phases (A) and their basic parameters, lattice constant (a) and mean micro-domain size (d).

Particle-size distribution was measured by laser diffraction particle size analyzer MasterSizer 3000, Malvern Instruments Ltd.

2.3. Magnetic and Mössbauer measurements

Room temperature magnetic measurements in an applied external field of ±1600 kA/m (±2T) were performed using vibrating sample magnetometer (VSM) EZ9 (Microsense, Massachusetts, USA). This equipment was used also for measurements of the initial (virgin) curve, MVIR(H), and magnetizations at increasing (MUP) and decreasing (MDOWN) positive magnetic fields. These characteristics are needed for determination of the Henkel plot: ΔM(H) = MVIR(H) – (MUP(H) + MDOWN(H))/2.

A physical property measurement system (PPMS, Model P935A, San Diego, USA) quantum design was applied for measurements of hysteresis loops with maximal magnetic field of ±4000 kA/m (±5 T) and zero-field-cooled (ZFC) and field-cooled (FC) curves in the magnetic field of 8 kA/m and in the temperature range (2–293 K).

Mössbauer spectroscopy (MS) measurements were done in transmission geometry at room temperature using a ⁵⁷Co (Rh) source. Calibration of the velocity scale was performed with a-Fe at RT and the isomer shifts are given with respect to its Mössbauer spectrum. All spectra were evaluated using the transmission integral approach in the program CONFIT [35]. The experimental points were analysed by double- and single-line components yielding values of isomer shift (δ) and quadrupole splitting (Δ). The relative representation of these subcomponents is denoted by A.

2.4. Degradation efficiency

Degradation efficiency was determined from parathion methyl (PM) decomposition into 4-nitrofenol (FN); see Ref. [15] for more details. The simple reaction PM→FN is assumed and kinetics of such reaction is followed either on a weight loss...
of PM or an increase of FN amount. Under presumption that no other reaction exists the loss of PM should be equal to the increase of FN. This was valid in present study.

3. Results and discussion

3.1. Morphology, phase and chemical composition

Chemical analysis was done by EDX in SEM on powders spread on a conductive tape. Several areas were selected at each sample and the integral values were measured. Along with large area analyses, the point EDX analyses of individual phases were measured as well. As an example, the sample of nominal composition $\text{Fe}_3\text{O}_4+10\text{ wt.\% Ce}_2(\text{CO}_3)_3$ after calcination treatment (500 °C/2h/air) is shown in Fig. 1.

To follow changes in phase composition of the mixed samples after calcination treatment, both input powders, i.e. magnetite and cerium carbonate, were also treated separately by the same calcination parameters. The morphology of initial magnetite is seen in Fig. 2a and X-ray diffractogram analysed using ICSD 20596 data sheet is depicted in Fig. 2b. The

<table>
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<td>67.2</td>
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<td>Spectrum 7</td>
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<td>Spectrum 7</td>
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<td>Spectrum 8</td>
<td>69.4</td>
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Fig. 1 – Sample of nominal composition $\text{Fe}_3\text{O}_4+10\text{ wt.\% Ce}_2(\text{CO}_3)_3$ after calcination treatment; left panel – area EDX analyses from the spread powder, right panel – local analyses from individual constituents. The obtained compositions (in at.%) are shown below.

Fig. 2 – Morphology as seen in SEM, secondary electrons (a) and XRD diffractogram (b) of magnetite in the initial structural state.
calcination treatment at 500 °C for 2 h in air did not bring any visible changes in morphology as seen in Fig. 3a. Nevertheless the XRD measurement (Fig. 3b) yielded a mixture of three Fe-oxides, namely hematite, \( \alpha \)-Fe\(_2\)O\(_3\), maghemite, \( \gamma \)-Fe\(_2\)O\(_3\), and initial magnetite Fe\(_3\)O\(_4\) analysed using data sheets 15840, 35643, and 20596, respectively.

The calcination treatment has transformed cerium carbonate into cerium dioxide formed by thin relatively large plates seen in Fig. 4a simultaneously with its diffractogram in Fig. 4b confirming pure cerium oxide analysed by 28753 ICSD data sheet. The relative ratios of oxide phases measured by XRD are summarised in dependence on the initial nominal sample composition in Table 1. The results show predominantly magnetite transformation during calcination treatment.

EDX elemental mapping in TEM was used for two selected samples (S5 and S9) to visualize qualitatively elements distribution. In both samples (Fig. 5a,b) we could observe large Ce-rich oxides and fine Fe-rich oxides with almost no chemical intermixing and with morphology similar to the initial state. The same image was found in other mixed samples: the morphology and lay-out was similar to that seen in Fig. 1 right.

The particle size distribution is depicted in Fig. 6. The sample with the lowest cerium dioxide content (S4) follows the distribution of Fe-oxide particles. At higher cerium dioxide contents the peaks of distributions follow either peaks corresponding to Fe- and Ce-oxides or the visible broadening of distributions are present reflecting particle agglomerations.

The analysis of XRD patterns has yielded the size of microdomains of cerium dioxide varying between 8 and 10 nm, while those of Fe-oxide phases was approximately ten times larger. The lattice parameters of individual phases in the samples slightly fluctuated within the range of experimental error. No systematic elongation or contraction of lattice parameters indicate substitution of Fe\(^{3+}\) (Fe\(^{2+}\)) in CeO\(_2\) or Ce\(^{4+}\) in Fe-oxide phases. The samples S5 and S7 have shown higher contents of magnetite and maghemite but a reason for it is at present unclear.

3.2 Macro- and micromagnetic properties

The magnetic measurements at room temperature were used for determination of basic magnetic parameters, saturation and remanent magnetizations and coercivity and parameters needed for Henkel plots [36]. Hysteresis loops including detail at low magnetic fields are shown in Fig. 7 for initial magnetite (S1), magnetite after calcinations’ treatment (S2) in the left panel and those of cerium dioxide (S3) in the right panel. The curve of cerium dioxide consists of ferromagnetic contribution well visible in detail and the diamagnetic contribution reflected by decreasing magnetisation at higher magnetic fields due to a negative magnetic susceptibility. A decrease in saturation magnetization of the S2 sample is due to transformation of magnetite into mainly haematite contributing with its low value of saturation magnetization. The hysteresis loops of the mixed samples are presented here by means of their magnetic characteristics shown in dependence on sample composition in Fig. 8.

A low spread of the coercivity values in the samples corresponds to the similar morphology of the samples seen in SEM micrographs. On the other hand, the non-monotonic changes in saturation and remanent magnetizations follow changes in the Fe-oxide representation. The higher relative representation of magnetite and maghemite vs. haematite in the samples S5 and S7 (Fig. 8 upper panel) markedly influence the magnetization. While haematite is weakly ferromagnetic of saturation magnetization 0.3 Am\(^2\)/kg at room temperature, the magnetite and maghemite are ferrimagnetic yielding visibly higher values of saturation magnetization ranges between 60 up to 100 Am\(^2\)/kg [37]. Their higher content in these samples contributes to increase in magnetization. The same tendency is documented in Henkel plots in Fig. 9 representing the above mentioned formula \( \Delta M(H) \) graphically. The negative dependences document prevailing magnetic dipolar (magneto statically dipole-dipole) interactions. They are produced by the magnetic moment of each grain with prevailing influence of the Fe-oxides. The highest peak intensity of the \( \Delta M(H) \), ~4.87 Am\(^2\)/kg, was obtained for the initial magnetite (S1) sample. As in previous observations, the intensity of peaks of the S5 and S7 samples abundant in magnetite and maghemite are higher compared to the other mixed compositions. The reason for these “anomalies” is unknown in this moment. It can be only speculated that it could come to an unthought-of conditions during calcinations treatment.

The Mössbauer spectroscopy was applied and the phases and hyperfine interactions analysed to complete macroscopic magnetic properties. The selected Mössbauer spectra measured at room temperature are shown in Fig. 10. The spectra
Fig. 4 – Morphology as seen in SEM, secondary electrons (a) and XRD diffractogram (b) of cerium dioxide obtained from the cerium carbonate after calcinations' treatment at 500 °C/2 h/air.

Table 1 – Phase composition of samples determined by XRD and Mössbauer phase analysis (MS, only ferromagnetic phases).

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>Sample</th>
<th>Method</th>
<th>Fe$_3$O$_4$ wt.%</th>
<th>α-Fe$_2$O$_3$</th>
<th>γ-Fe$_2$O$_3$</th>
<th>α-FeOOH</th>
<th>CeO$_2$</th>
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<tr>
<td>Fe$_3$O$_4$</td>
<td>S1</td>
<td>XRD</td>
<td>100.0</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Fe$_3$O$_4$/500 °C/2 h/air</td>
<td>S2</td>
<td>XRD</td>
<td>3.0</td>
<td>67.9</td>
<td>29.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO$_2$ (Ce$_2$(CO$_3$)$_3$)/500 °C/2 h/air</td>
<td>S3</td>
<td>XRD</td>
<td>8.1</td>
<td>66.8</td>
<td>22.6</td>
<td>1.7</td>
<td>100.0</td>
</tr>
<tr>
<td>Fe$_3$O$_4$+5 wt.%</td>
<td>S4</td>
<td>XRD</td>
<td>3.2</td>
<td>70.3</td>
<td>21.9</td>
<td></td>
<td>4.6</td>
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<tr>
<td>Ce$_2$(CO$_3$)$_3$/500 °C/2 h/air</td>
<td>S5</td>
<td>XRD</td>
<td>9.8</td>
<td>66.3</td>
<td>21.0</td>
<td>1.5</td>
<td>8.3</td>
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<td>Fe$_3$O$_4$+10 wt.%</td>
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<td>XRD</td>
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<tr>
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<td>51.5</td>
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Fig. 5 – EDX maps of constituent elements distribution in calcinated samples with nominal composition Fe$_3$O$_4$+10 wt.% Ce$_2$(CO$_3$)$_3$ (a) and Fe$_3$O$_4$+50 wt.% Ce$_2$(CO$_3$)$_3$ (b).
of S1, S2, and mixed S4 up to S9 samples were evaluated with a set of Lorentzian sextuplets represented ferromagnetic phases. Besides them also the double-line components were present in middle of all samples and they are seen also in spectra presented in Fig. 10. Similar spectra are seen and discussed in Ref. [38]. In case of the S1 and S2 samples the hyperfine parameters, δ and Δ, ~0.23 mm/s and 0.35 mm/s, of double-line component can be ascribed to Fe³⁺ ions. In the mixed samples S4 up to S9 this sub-component was present as well but another paramagnetic component yielding the similar hyperfine parameter as obtained for cerium dioxide introduced therein after was detected. The representations of these components were low usually around 1%. The spectrum of cerium dioxide (S3) sample was fitted by double-line component with the isomer shift δ = 0.12 mm/s and quadrupole splitting Δ = 0.58 mm/s (86%) and single-line component with δ = 0.25 mm/s (14%) which, similarly as in previous studies [30], evidenced of presence of Fe-atoms.

The ferromagnetic components were i) magnetite represented by values of the hyperfine induction B ~ 48.6 T and ~ 46.6 T, of the isomer shift δ ~ 0.38 mm/s and ~ 0.60 mm/s, and of the quadrupole splitting Δ ~ −0.02 mm/s and ~ 0.0 mm/s, ii) maghemite of parameters B ~ 50.3 T, δ ~ 0.27 mm/s, and Δ ~ 0.04 mm/s, and iii) haematite B ~ 51.5 T, δ ~ 0.37 mm/s, and Δ ~ −0.18 mm/s. These Fe-oxide phases support the results obtained above by XRD. Nevertheless, the other component of hyperfine parameters B ~ 41 T, δ ~ 0.47 mm/s, and Δ ~ −0.25 mm/s was detected. It could be ascribed to goethite.

The relative representations of ferromagnetic phases detected by MS are present together with XRD data in Table 2. The
slight differences in values between both methods are due to higher sensitivity of Mössbauer spectrometry on iron containing phases and their ordering.

3.3. Degradation efficiency

As was mentioned above a searching for magnetically separable sorbents is in progress for the several last years. Here, the degradation efficiency of set of the samples with varying initial compositions of magnetite/cerium carbonate and calcinated at the same conditions was tested for the degradation of parathion methyl (PM) and its conversion into 4-nitrofenol (FN). During this chemical procedure the rate of chemical reaction determines the decreasing amount of PM and increasing amount of FN. Both components can be measured simultaneously. This reaction can be expressed by simplified relation \( c_{PM} = c_{PM0} \exp(-k t) \), where \( k \) is rate constant and \( c_{PM0} \) is the initial concentration of PM compound and \( c_{PM} \) is concentration of PM compound at time \( t \). The same dependence can be written also for FN component. The changes of \( k \) in the tested samples are depicted in Fig. 11. It seems that \( c_{PM} = c_{FN} \) is valid up to approximately 25 vol.% CeO\(_2\). The slight differences observed at higher CeO\(_2\) contents can imply more complicated reaction. It appears also that presence of Fe-oxides slightly moderate the rate of decomposition.

4. Conclusions

Present investigations are devoted to magnetically separable reactive sorbents prepared as composite of different weight contents of the magnetite/cerium carbonate (100/0 up to 50/50) subjected to calcination treatments at 500 °C for 2 h in air.

Various characterization experimental methods have revealed a number of structural and physical aspects. The main conclusions can be summarised subsequently.

- Commercial magnetite (Fe\(_3\)O\(_4\)) contains also small amount of maghemite and α-FeOOH detected by highly sensitive Mössbauer spectroscopy.
Temperature treatment (500 °C/2 h/air) of magnetite leads to the transformation into maghemite and hematite and decreases the content of α-FeOOH.

All these iron-oxides are present also in other samples in different amounts.

X-ray diffraction of treated cerium carbonate (500 °C/2 h/air) confirms its transformation into cerium oxide of the fluorite-like crystalline structure and flake-form.

X-ray diffractogram analysis yields slightly different CeO2 content compared to nominal one.

Differences between XRD and Mössbauer results in representation of individual phases are due to dissimilar sensitivity of both experimental methods.

Dispersion in micro-domain and particle size data despite the same treated parameters for all samples (500 °C/2 h/air) imply that more attention should be done to conditions of sample preparation and of their subsequent treatment.

Magnetic characteristics, saturation and remanent magnetizations, are determined by type and content of iron-oxide. While magnetite (Ms = 90–100 Am²/kg) and maghemite (Ms = 60–80 Am²/kg) are ferrimagnetic with only slight difference in Ms at room temperature, haematite is weakly ferromagnetic (Ms ~ 0.3 Am²/kg) and its higher content in the samples (S2, S4, S6, S8, S9) contributes to the lower value of Ms. Hyperfine induction values (B) are comparable for all three Fe-oxides and no important differences among samples are therefore visible.

The degradation efficiency seems to be independent on type of iron-oxide but increases with content of cerium dioxide.

Insufficiency of present studies is that no information concerning cerium dioxide was obtained in spite of various experimental methods. Some studies of other authors show that cerium dioxide can contain besides dominant diamagnetic Ce⁴⁺ ions also paramagnetic Ce³⁺ ions mainly at particle surfaces due to vacancy-type-defect formation. The ratio of Ce⁴⁺ and Ce³⁺ ions could contribute to better explanation of the degradation efficiency.

Conflicts of interest

The authors declare no conflicts of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2020.02.068.

REFERENCES


