VSB TECHNICAL UNIVERSITY OF OSTRAVA | FACULTY OF ELECTRICAL ENGINEERING AND COMPUTER SCIENCE | DEPARTMENT OF PHYSICS

MAGNETITE TRANSFORMATIONS ANALYSIS IN Fe-OXIDE/CeO_2 REACTIVE SORBENTS BY FIRST-ORDER REVERSAL CURVE DIAGRAMS

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AIM: Microstructural and magnetic characterization of magnetically separable CeO_2/Fe-oxide powder sorbents applicable towards selected pesticides. Analysis of magnetite transformation in dependence on calcination temperature and CeO_2 content.

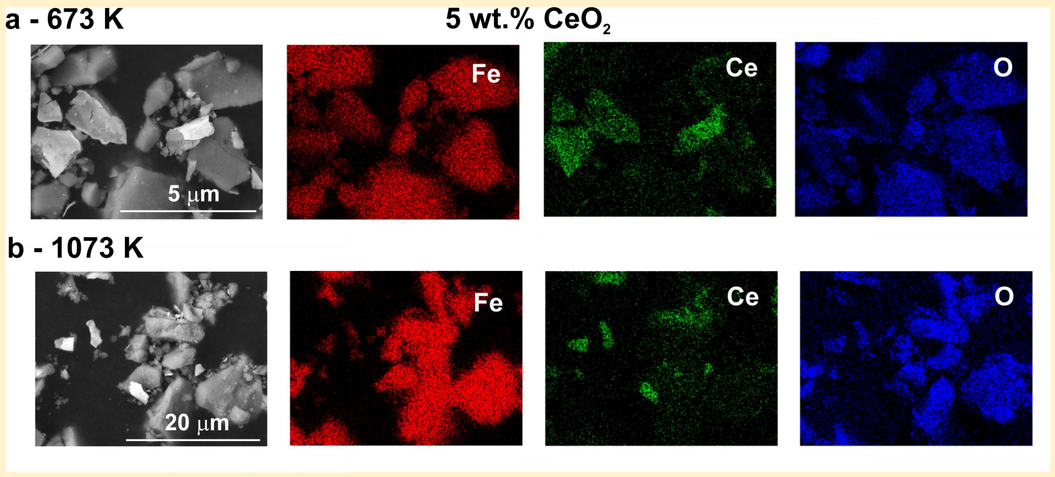
SAMPLE PREPARATION

- **Magnetically separable sorbent** – composite material consisting of iron oxide serving as a magnetically separable core or carrier and cerium dioxide (CeO_2) serving as active constituent capable to destroy dangerous chemicals
- **Magnetite core** – synthesized by the co-precipitation of the Fe^{2+} (ferrous sulphate monohydrate) and Fe^{3+} (ferric sulphate) salts from cheap and commercially available raw materials
- **CeO_2/Fe-oxide reactive sorbents**
  - ferrimagnetic core re-dispersed in the solution containing cerium (III) nitrate, and the cerium (III) carbonate prepared by precipitation with ammonium hydrogen carbonate
  - cerous carbonate/magnetite precursor annealed in a muffle furnace at various temperatures T_a ranging from 473 to 1073 K for 2h
  - two series of sorbents with **5 and 38 wt.% CeO_2** annealed at different temperatures

EXPERIMENTAL TECHNIQUES

- **XRD (X-Ray Diffraction)** – X'PERT PRO diffractometer (Panalytical) equipped with Co Kα radiation (λ = 0.17902 nm) , 2θ range 20° - 135°, evaluation – Rietveld structure refinement method by using the HighScore Plus program and the ICSD database
- **SEM (Scanning Electron Microscopy)** – TESCAN LYRA 3XMU FEG/SEM, accelerating voltage 20 kV, equipped with an X-Max80 Oxford Instruments energy-dispersive X-ray (EDX) detector
- **VSM (Vibrating-Sample Magnetometer)** – Microsense EZ9, room temperature (RT) magnetization and virgin curves - maximal magnetic field 1600 kA/m, first-order reversal curves (FORC) with step 8 kA/m
- **PPMS (Physical Property Measurement System)** – Quantum design, Inc., field-cooled (FC) and zero-field-cooled (ZFC) curves in the temperature range 2-293 K in magnetic field of 8 kA/m

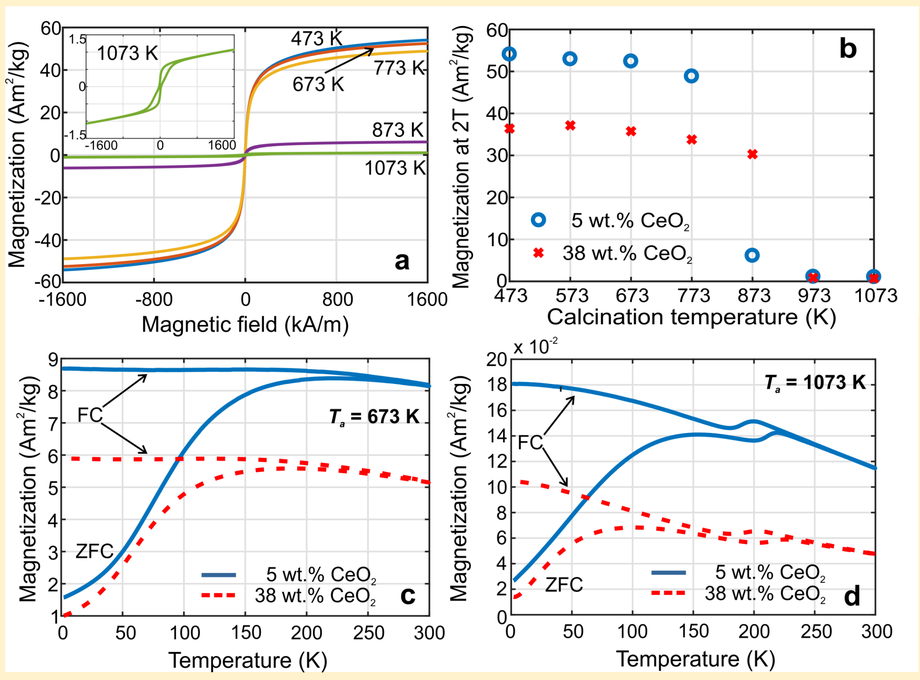
SEM-EDX



SEM images and EDX distribution maps of Fe, Ce, and O of 5 wt.% CeO_2 sorbents calcined at 673 K (a) and 1073 K (b).

- Powders contain a mix of grains of different sizes, some are enriched in Ce, others are Ce depleted.

MAGNETIC PROPERTIES



(a) Room temperature magnetization curves of sorbents with 5 wt.% CeO_2 measured at different calcination temperatures T_a. (b) Magnetization at magnetic field 2T depicted as a function of T_a. ZFC-FC curves of samples with 5 and 38 wt.% CeO_2 calcined at 673 K (c) and 1073 K (d).

XRD

The results of Rietveld analysis of sorbents calcined at T_a temperature; phase content (A), lattice parameters (a, b, c), microdomain size (d).

T_a (K)	CeO_2			Fe_3O_4			γ-Fe_2O_3				α-Fe_2O_3			
	A (%)	$a = b = c$ (nm)	d (nm)	A (%)	$a = b = c$ (nm)	d (nm)	A (%)	$a = b$ (nm)	c (nm)	d (nm)	A (%)	$a = b$ (nm)	c (nm)	d (nm)
5 wt.% CeO_2														
473	5.4	0.5394	3.2	42.9	0.8368	8.3	51.7	0.8341	0.8299	11.8	-	-	-	-
573	4.8	0.5413	3.4	28.4	0.8333	11.7	66.8	0.8391	0.8258	8.3	-	-	-	-
673	5.3	0.5411	6.4	32.5	0.8331	14.6	62.2	0.8402	0.8247	8.7	-	-	-	-
773	5.0	0.5408	8.4	25.7	0.8383	7.8	61.6	0.8329	0.8322	11.3	7.7	0.5031	1.3736	40.3
873	4.2	0.5408	10.4	-	-	-	3.3	0.8368	0.8323	11.5	92.5	0.5034	1.3751	41.9
973	4.6	0.5408	12.3	-	-	-	-	-	-	-	95.4	0.5034	1.3747	47.4
1073	4.7	0.5409	14.0	-	-	-	-	-	-	-	95.3	0.5035	1.3748	51.3
38 wt.% CeO_2														
473	37.8	0.5412	6.2	62.2	0.8340	8.7	-	-	-	-	-	-	-	-
573	37.9	0.5416	6.4	62.1	0.8357	8.8	-	-	-	-	-	-	-	-
673	38.7	0.5415	6.3	61.3	0.8351	8.6	-	-	-	-	-	-	-	-
773	38.2	0.5412	7.1	24.1	0.8358	7.3	37.7	0.8348	-	10.4	-	-	-	-
873	37.9	0.5409	7.2	37.3	0.8356	6.9	16.0	0.8382	-	15.5	8.8	0.5036	1.3752	9.4
973	38.0	0.5404	10.4	-	-	-	-	-	-	-	62.0	0.5037	1.3755	45.3
1073	38.0	0.5408	17.6	-	-	-	-	-	-	-	62.0	0.5036	1.3752	60.6

- Transformation of magnetite and maghemite to hematite depends on calcination temperature and CeO_2 content.
- For sorbents with 5 wt.% CeO_2 the contribution of hematite occurs at temperature 773 K.
- For sorbents with 38 wt.% CeO_2 the iron oxide transformation is slower and hematite is detected only at a temperature of 873 K.
- Microdomain size of CeO_2 and hematite gradually grows with increasing calcination temperature.

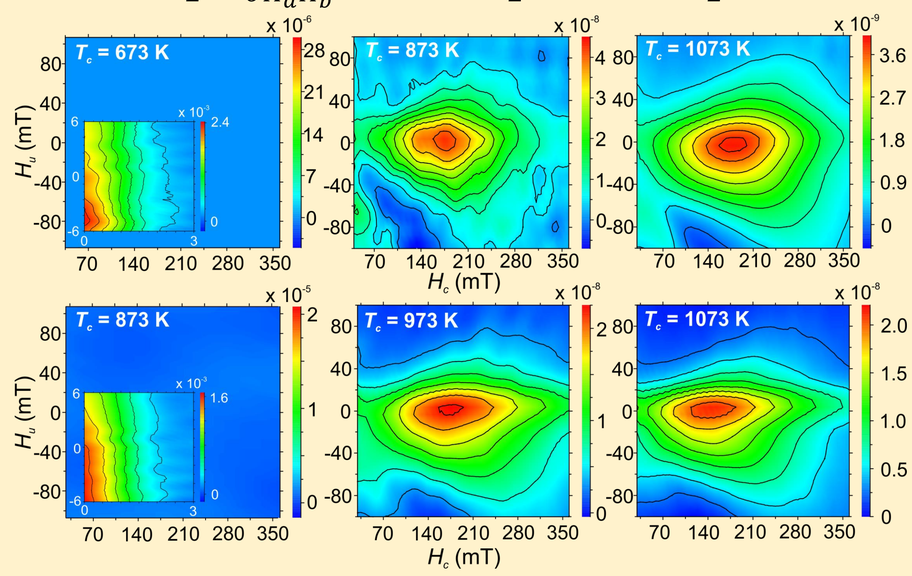
FORC DIAGRAMS

Map $\rho(H_a, H_b)$ of the magnetic response of all particles in a sample with irreversible magnetizations in terms of the coercivity (switching field) $H_c = H_{sw}$ and magnetic interaction field $H_u = H_{int}$ distribution:

$$\rho(H_a, H_b) = -\frac{1}{2}\frac{\partial^2 M(H_a, H_b)}{\partial H_a H_b}, H_c = \frac{H_b - H_a}{2}, H_u = \frac{H_b + H_a}{2}$$

5 wt.% CeO_2

38 wt.% CeO_2



- The maximum close to zero (samples calcined at 673 K and 873 K of 5 and 38 wt.% CeO_2) indicates the presence of magnetite and maghemite.
- Clear contours with one central peak correspond to the dominance of the hematite (873 – 1073 K for 5 wt.% CeO_2; 973 – 1073 K for 38 wt.% CeO_2).
- Results of FORCs refer to a slowing down of the transformation of iron oxides in samples with a higher content of CeO_2 and correspond well to the XRD results.
- Henkel plots obtained from virgin and hysteresis loops at RT are convex curves showing negative (dipolar) magnetic interactions for all samples. The strongest interactions observed at the magnetic field ΔH are close to the H_c peak of the FORC diagrams.

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