Preparation and characterization of the nanostructured cerium dioxide sorbents

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AIM: Preparation and characterization of CeO_2 nano-sorbents used for the removal of pesticides and nervous agents.

Sample preparation

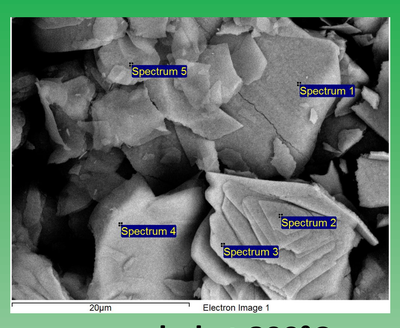
- An input material for preparation of samples was cerium(III) nitrate, $Ce(NO_3)_3.6H_2O$, dissolved in deionized water.
- An insoluble cerous carbonate precipitated using NH_4HCO_3 (**precursor 1**) and using homogeneous hydrolysis of urea (**precursor 2**).
- Cerium(III) carbonate was filtered, washed with deionized water number of times and dried at 110 °C in a box drying apparatus for several hours to remove excess water and to form CeO_2.
- The temperature treatments of the precursors were done in an open porcelain crucibles at temperatures ranging between 500 °C/2 h and 800 °C/2h, step 100 °C in muffle furnace.

Experimental techniques

- **SEM (Scanning Electron Microscopy)** – TESCAN LYRA 3XMU FEG/SEM microscope with an Xmax 80 Oxford Instruments detector for EDX
- **XRPD (X-Ray Powder Diffraction)** – X'PERT PRO diffractometer by PANALYTICAL, CoKα irradiation (λ = 0.1789 nm), Bragg-Brentano geometry, 2θ range 20° ÷ 135°
- **MS (Mössbauer Spectroscopy)** – at room temperature in transmission geometry using a ^{57}Co(Rh) source, velocity calibration performed by α-Fe, data evaluated using the program CONFIT
- **SQUID (Superconducting Quantum Interference Device)** – Quantum Design MPMS, magnetization curves measured at room (300 K) and low (2 K) temperatures with maximal applied magnetic field ± 70 kOe (7 T), field-cooled (FC)/zero-field-cooled (ZFC) curves

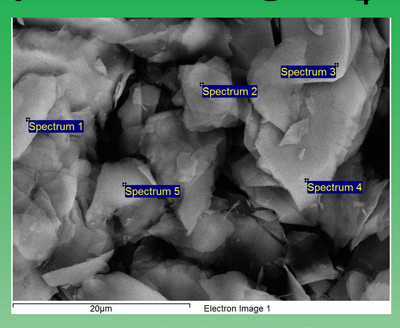
Microstructure

Precipitation using NH_4HCO_3



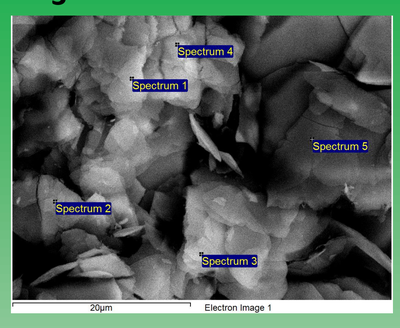
annealed at 800°C

1	2	3	4	5
52.98	81.21	81.41	78.34	67.52
47.02	18.79	18.59	21.66	32.48



annealed at 500°C

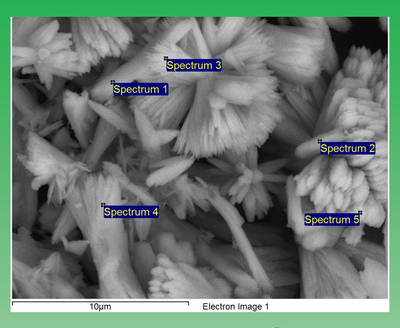
1	2	3	4	5
75.55	79.54	79.57	80.52	82.11
24.45	20.46	20.43	19.48	17.89



precursor 1

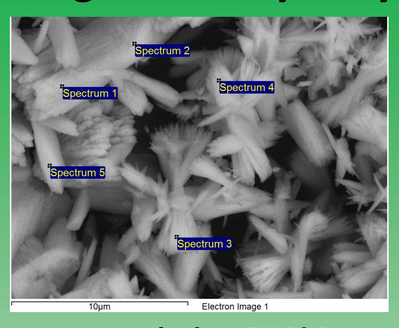
1	2	3	4	5
85.99	78.80	86.95	86.52	85.07
14.01	21.20	13.05	13.48	14.93

Homogeneous hydrolysis



precursor 2

Spect.	1	2	3	4	5
O (at. %)	82.81	85.46	87.19	88.80	89.06
Ce (at. %)	17.19	14.54	12.81	11.20	10.94

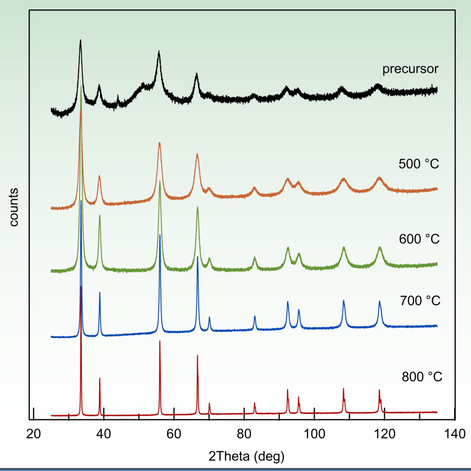


annealed at 500°C

1	2	3	4	5
80.49	79.84	81.32	82.00	77.28
19.51	20.16	18.68	18.00	22.72

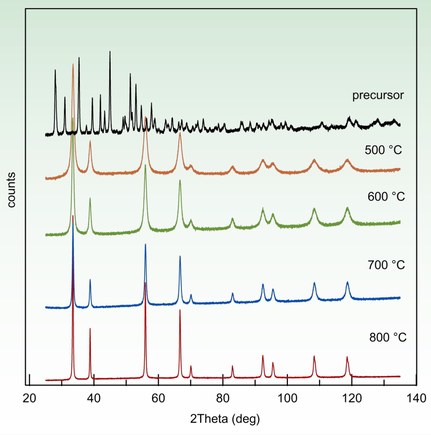
annealed at 800°C

1	2	3	4	5
80.08	77.49	82.08	27.70	77.63
19.92	22.51	17.92	72.30	22.37



a – lattice parameter, *d* – crystallite size

	a (nm)	*d* (nm)
precursor	0.543346(5)	9.60(4)
500 °C	0.541472(36)	8.87(5)
600 °C	0.541405(13)	13.00(0)
700 °C	0.541372(15)	29.30(0)
800 °C	0.541359(11)	70.35(0)

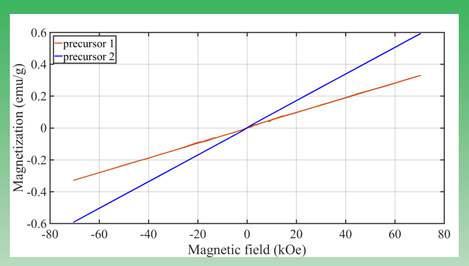


a – lattice parameter, *d* – crystallite size

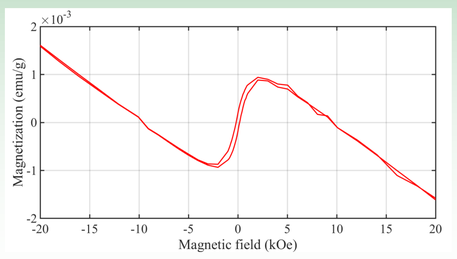
	a (nm)	*d* (nm)
precursor	-	-
500 °C	0.541746(22)	9.91(10)
600 °C	0.541299(21)	13.92(10)
700 °C	0.541303(19)	24.49(10)
800 °C	0.541218(6)	44.68(10)

Magnetic properties

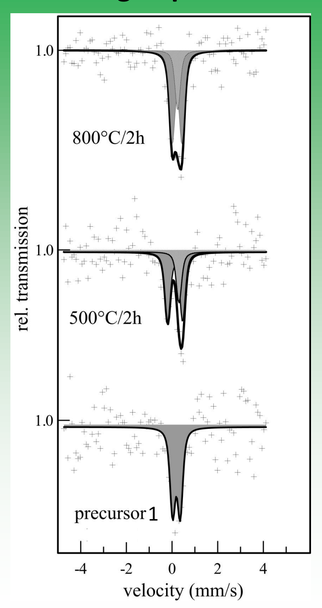
Precursors 1 and 2



600°C/2h annealing of precursor 1



Mössbauer spectroscopy: annealing of precursor 1



- Both precursors show linear dependence of magnetization on the applied external magnetic field.
- Hysteresis loops of annealed samples exhibit ferromagnetic response at low magnetic fields followed by a para- and diamagnetic behaviour at higher fields.
- Saturation magnetization of annealed powders is very low (thousandths of emu/g) without clear dependence on the annealing temperature.
- As confirmed by Mössbauer spectroscopy the ferromagnetic response comes from the low amount of iron oxide nanoparticles (units of ppm).
- Hyperbolic shapes of the FC/ZFC curves in the temperature range 2 K – 300 K at constant magnetic field 1 T indicate paramagnetic behaviour of CeO_2 with the Curie constant about $3 \cdot 10^{-7}$ (emu·K)/(g·Oe).

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