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Structural Properties and Photocatalytic Activity of Ceria Nanoparticles on Vermiculite Matrix

Marta Valášková[1, 2, *], Jana Kupková[2], Kamila Kočí[3, 4], Nela Ambrožová[3],
Volker Klemm[5], and David Rafaja[5]

[1] *Nanotechnology Centre, VŠB - Technical University of Ostrava, 17. Listopadu 15/2172,*
708 33 Ostrava-Poruba, Czech Republic
[2] *IT4Innovations Centre of Excellence, VŠB - Technical University of Ostrava, 17. Listopadu 15/2172,*
708 33 Ostrava-Poruba, Czech Republic
[3] *Institute of Environmental Technology, VŠB - Technical University of Ostrava, 17. Listopadu 15/2172,*
708 33 Ostrava-Poruba, Czech Republic
[4] *Faculty of Metallurgy and Materials Engineering, VŠB - Technical University of Ostrava, 17. Listopadu 15/2172,*
708 33 Ostrava-Poruba, Czech Republic
[5] *Technical University Bergakademie Freiberg, Institute of Materials Science, Clemens-Winkler-Bau,*
Leipziger Str. 29, Zi. 19, Freiberg, Germany

Clay mineral matrices and metal oxides are of current interest because of their high thermal stability, large surface area, and good catalytic and adsorption properties. Cerium oxide (ceria, CeO_2) nanoparticles was obtained by interaction of vermiculite with $(NH_4)_2Ce(NO_3)_6$. The mean crystallite size of CeO_2 nanoparticles in the vermiculite was (8.5 ± 0.5) nm. The HRTEM micrographs confirmed the crystallite size and revealed additionally the shape of crystallites. The intercalation of the cerium reaction products into vermiculite was proven by using X-ray diffraction and ICP-AES. The incorporation of ceria into vermiculite increased the surface area from 14 to 62 $m^2 \cdot g^{-1}$ and the volume of micropores from 0.1213 to 0.3928 $cm^3 \cdot g^{-1}$, and reduced the average pore diameter from 264 nm to 58.5 nm. Under UV irradiation, decomposition of N_2O influenced by the sole CeO_2 and 36 wt% CeO_2 attached to the vermiculite was 57.7% and 53.3%, respectively, in comparison with the decomposition of 51.6% by commercial catalyst Evonik P25.

Keywords: Silicate Layer Matrix, Ceria Nanoparticles, Structural Analysis, N_2O Photocatalytic Decomposition.

1. INTRODUCTION

Layer silicates (phyllosilicates) belong to the important native clay materials, which are utilized in different areas of industry. Their benefits are low costs, high abundance, easy manipulation and harmlessness to the environment. The negative charge on the layers makes these minerals suitable to serve as layered matrices for precipitation of metallic and metal oxide nanoparticles. The combination of clay mineral matrices with metal oxide nanoparticles is currently of interest because of the high thermal stability, large surface area and good catalytic and adsorption properties. As a typical rare earth oxide, ceria (CeO_2) is able to exchange oxygen reversibly via redox processes involving the Ce^{4+}/Ce^{3+} couples and acts as an attendant of catalytically active oxygen vacancy sites.[1] Catalysts based on CeO_2 are widely used as efficient systems for oxidation of CO in the atmosphere. In clays, cerium oxide nanoparticles produce high permanent porosity, high surface area and a relatively large volume of micropores.[2] Vermiculite as a matrix (Ver) carrying CeO_2 nanoparticles (Ver/CeO_2) was used as a precursor for the production of the photocatalytic CeO_2 in ceramics.[3] Since the work[3] deals only with the structural and photocatalytic properties of cordierite/CeO_2 ceramics, it is necessary to study these properties of vermiculite/CeO_2 as a ceria precursor in the mixtures for firing ceramics.

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[*] Author to whom correspondence should be addressed.

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In this contribution, the microstructures and photocatalytic activities of cerium oxides are compared that were prepared from the $(NH_4)_2Ce(NO_3)_6$ precursor in aqueous solution (sample CeO_2) and in suspension with vermiculite (sample Ver/CeO_2). The microstructure was analyzed by using X-ray powder diffraction (XRD) as well as by using the high-resolution transmission electron microscopy (HRTEM). The photocatalytic activity of the samples was studied through the decomposition of N_2O by sole nanoparticles CeO_2, CeO_2 embedded in vermiculite, and compared with the commercial Evonik P25 catalyst.

2. EXPERIMENTAL DETAILS

2.1. Starting Materials

Vermiculite from the Paraiba region of Brazil containing a superfine particle size fraction (<2 mm), which was purchased from Grena, Ltd. Czech Republic, was milled and sieved to have the particle size <40 μm. The chemical structural formula of a half unit cell was $(Si_{3.12}Al_{0.88})(Al_{0.05}Fe^{3+}_{0.37}Fe^{2+}_{0.03}Mg_{2.50}Ti_{0.05})O_{10}(OH)_2Ca_{0.10}Na_{0.05}K_{0.17}$.[4] Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) from Sigma Aldrich and ammonium hydroxide solution (NH_4OH) from Mach-chemicals, Czech Republic, were used as ceria precursor.

2.2. Sample Preparation

Vermiculite (Ver) at aqueous dispersion 5 wt% was stirred for 15 min. The precursor of ceria was the solution of 80 ml of aqueous cerium nitrate $Ce(NO_3)_3 \cdot 6H_2O$ (0.4 M) and 13 ml of NH_4OH (1.4 M) (pH = 11) stirred for 15 min at the room temperature (sample CeO_2). The sample Ver/CeO_2 was prepared from Ver in aqueous dispersion (100 ml), which was added dropwise to the aqueous precursor of ceria, and further stirred for 3 h at 50 °C. The samples CeO_2 and Ver/CeO_2 were obtained by centrifugation and washing several times with distilled water and then dried overnight in an oven at 80 °C.

2.3. Characterization Methods

The elemental analysis of vermiculite was performed by using the energy dispersive X-ray fluorescence (XRF) spectrometer SpectroXepos (Spectro Analytical Instruments, Germany) and the atomic emission spectrometer with inductively coupled plasma (ICP-AES) Spectro Vision (Spectro Analytical Instruments, Germany). The elements in the water solution were quantified using the ICP-AES JY 24 from Spectro Analytical Instrument (Germany).

The changes in the basal lattice plane spacing of vermiculite after the reaction with $Ce(NO_3)_3 \cdot 6H_2O$ and NH_4OH were determined by using XRD analysis. The analysis of the XRD line broadening revealed the size of CeO_2 crystallites. The XRD analysis was performed with CuKα radiation on the X-ray diffractometer Ultima IV (RIGAKU, Japan). The XRD patterns of the samples pressed on the glass slide were recorded in the symmetrical Bragg-Brentano diffraction geometry in the 8–80° 2θ range with a scanning rate of 2°/min at 40 kV and 40 mA using a scintillation counter as detector.

The surface area (SA) was measured with the Sorptomatic 1990 instrument (Thermo Electron Corporation, USA) by using nitrogen as adsorbing gas. The value of S_{BET} was calculated by employing the Advance Data Processing software according to the BET isotherm. The size distributions of the micro- and mesopores were calculated by means of the Horvath-Kawazoe model.[5]

The morphology of the ceria nanoparticles and their docking on the vermiculite matrix were visualized in the high-resolution transmission electron microscope JEM 2200 FS from Jeol (Japan), which was equipped by a corrector of the spherical aberration (Cs). The Cs corrected HRTEM allows in particular the internal interfaces and borders of small crystallites to be reproduced without distortions.[6]

The decomposition of N_2O on the surface of different photocatalysts was investigated at ambient temperature in a homemade apparatus. The respective photocatalyst was spread on the adhesive tape, which was located at the bottom of an annular batch reactor, and illuminated by an 8 W Hg lamp with the maximum intensity at 254 nm. The reactor having the volume of 663 ml was filled with 968 ppm of the N_2O/He mixture (pressure of 110 kPa). A gas chromatograph with a thermal conductivity detector GC/TCD was used for analysis of the N_2O conversion during the UV irradiation (Eq. (1)):

$$N_2O \xrightarrow{\text{hv,catalyst}} N_2 + 1/2O_2 \tag{1}$$

The relative amount of converted N_2O was determined according to Eq. (2), assuming that the total pressure in the reactor can be considered as constant due to a low N_2O concentration.

$$X_{N_2O} = \frac{c^0_{N_2O} - c_{N_2O}}{c^0_{N_2O}} \tag{2}$$

In Eq. (2), $c^0_{N_2O}$ and c_{N_2O} are the N_2O concentrations prior to the photocatalytic reaction ($t = 0$) and in the course of the reaction, respectively.

3. RESULTS AND DISCUSSION

3.1. Formation of the Ver/CeO_2 Composite

The reaction conditions facilitated the hydrolysis of $(NH_4)_2Ce(NO_3)_6$ and the formation of the $[Ce_6(OH)_{12}]^{12+}$ polyoxocations and the cerium$^{(IV)}$ hydroxide $Ce(OH)_4$.[2] The reaction of the polyoxocations with Ver was assumed to follow the scheme (3):

$$\{[Ce_6(OH)_{12}]^{12+}\} + \text{Ver} \rightarrow\rightarrow [Ce_x(OH)_y] \cdot \text{Ver} + zI^+ \rightarrow\rightarrow \text{Ver}/CeO_2 \tag{3}$$

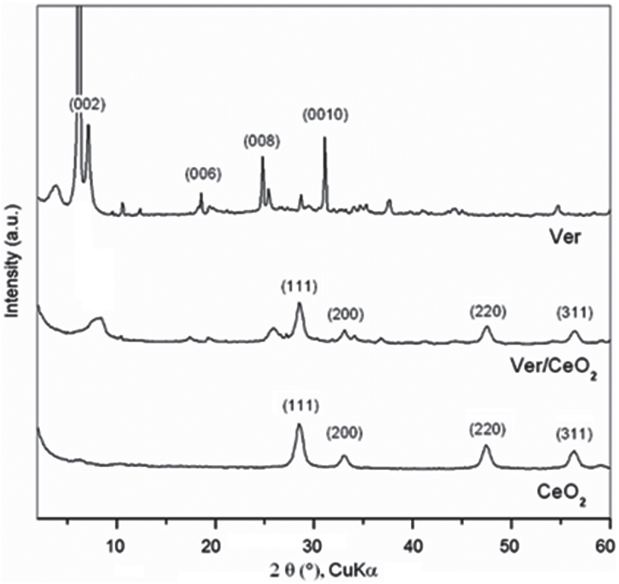

Figure 1. XRD patterns of Ver, Ver/CeO$_2$ and CeO$_2$. In the XRD pattern of Ver, only basal reflections are indexed. The XRD patterns of Ver/CeO$_2$ and CeO$_2$ show (hkl) indices of CeO$_2$.

where I^+ are the ions released from vermiculite. This assumption was verified by the ICP-AES analysis of the elements released into the water solution after washing the solid fraction of Ver/CeO$_2$, which revealed 49 $\text{mg} \cdot \text{L}^{-1}$ of Na, 23 $\text{mg} \cdot \text{L}^{-1}$ of K, 218 $\text{mg} \cdot \text{L}^{-1}$ of Mg and 105 $\text{mg} \cdot \text{L}^{-1}$ of Ca. The amounts of Fe and Al in the solution were below 0.05 $\text{mg} \cdot \text{L}^{-1}$ and 0.5 $\text{mg} \cdot \text{L}^{-1}$, respectively. A small amount 1.3 $\text{mg} \cdot \text{L}^{-1}$ of Ce in the solution (in comparison with the starting concentration of 56040 $\text{mg} \cdot \text{L}^{-1}$) suggests that cerium was firmly attached to the vermiculite matrix. The elemental analysis of Ver/CeO$_2$ revealed the ceria content of 32 wt%.

The XRD performed on the native vermiculite (sample Ver) has shown that the clay mineral contains interstratified mix-layered structure.[4] Therefore, basal reflections (Fig. 1) are doubled with the corresponding interplanar spacings equal to $d(002) = 1.4$ nm and $d(002) = 1.2$ nm. Only the first value agrees with the spacing of the basal lattice planes in pure Mg-vermiculite, which is ~1.4 nm, while the second ~1.2 nm corresponds to an incomplete occupation of hydrated interlayer cations in layer domains. In the Ver/CeO$_2$, the intensity of the basal reflection of vermiculite was much lower than in Ver due to exfoliation of layered vermiculite structure. After the cation exchange and intercalation of ceria in the interlayer, the value of the basal interlayer space was reduced to the $d(002) \sim 1$ nm.

3.2. Microstructure of the Ver/CeO$_2$ Composite

The mean size of the CeO$_2$ crystallites was determined from the XRD line broadening by using the Williamson-Hall method[7] to be (9.0 ± 0.1) nm and (8.5 ± 0.5) nm in CeO$_2$ (prepared in aqueous solution) and Ver/CeO$_2$ (prepared in suspension with vermiculite), respectively. HRTEM micrographs (Fig. 2) confirmed these crystallite sizes and revealed additionally the shape of crystallites. Whereas the CeO$_2$ crystallites that were prepared in aqueous solution possessed regular form with pronounced crystal facets, the boundaries of the CeO$_2$ crystallites grown in the suspension with vermiculite were blurred. This difference in the habitus of the crystallites indicates the interaction between CeO$_2$ and vermiculite in the Ver/CeO$_2$ composite, which is a precondition of the docking of CeO$_2$ nanocrystallites on the vermiculite surface.

3.3. Surface Area and Porosity

For Ver, Ver/CeO$_2$ and CeO$_2$, the S_{BET} values of 14.6, 61.7 and 96.3 $\text{m}^2 \cdot \text{g}^{-1}$ were determined, respectively. Sample CeO$_2$ showed a wide size distribution of the nanopores ranging from 1 to 50 nm (Fig. 3). In Ver, the pores size distribution was bimodal. Small pores had the size between 10 and 200 nm; large pores were larger than 300 nm. The Ver/CeO$_2$ composite showed a unimodal distribution of the pore sizes that had the maximum between 50 and 200 nm. According to HRTEM (Fig. 4), such pores occur in the

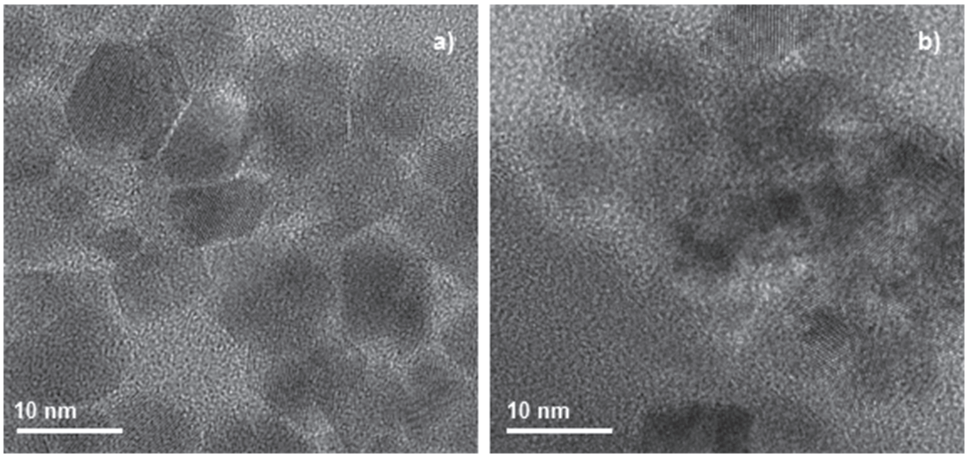

Figure 2. Cs corrected HRTEM micrographs of: (a) CeO$_2$ crystallites prepared in aqueous solution and (b) CeO$_2$ crystallites prepared in suspension with vermiculite (Ver/CeO$_2$ sample).

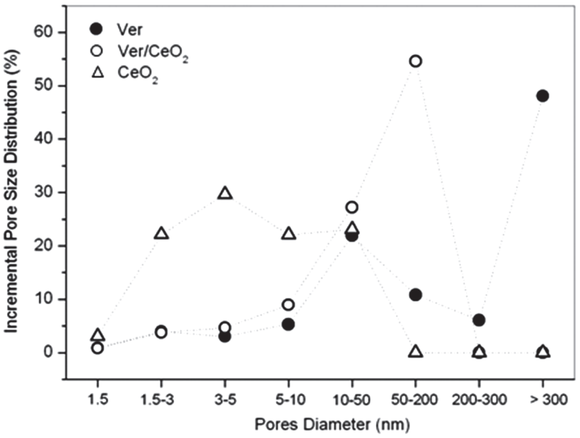

Figure 3. Pore size distribution of Ver, Ver/CeO_2 and precipitated CeO_2.

clusters of the CeO_2 crystallites and between the vermiculite surface and the CeO_2 clusters. Sole CeO_2 showed the micropore volume of $0.1519\ cm^3 \cdot g^{-1}$ and the average pore diameter of 4.63 nm. In sample Ver, the micropore volume was $0.1213\ cm^3 \cdot g^{-1}$ and the average pore diameter 264 nm. The addition of ceria to vermiculite increased the volume of micropores in Ver/CeO_2 to $0.3928\ cm^3 \cdot g^{-1}$ and reduced the average pore diameter to 58.5 nm.

3.4. Photocatalytic Decomposition of N_2O

Finally, the photocatalytic decomposition of N_2O by sole CeO_2 and by CeO_2 embedded in vermiculite was studied and compared with the commercial Evonik P25 catalyst (Fig. 5). At the same conditions, the photolysis of N_2O (without photocatalysts) was determined to reach 44.7% after 18 h. With CeO_2, the decomposition of N_2O was much more efficient. It reached 57.7% and 53.3% for CeO_2 and Ver/CeO_2, respectively. The commercial catalyst Evonik P25 containing TiO_2 decomposed 51.6% of N_2O.

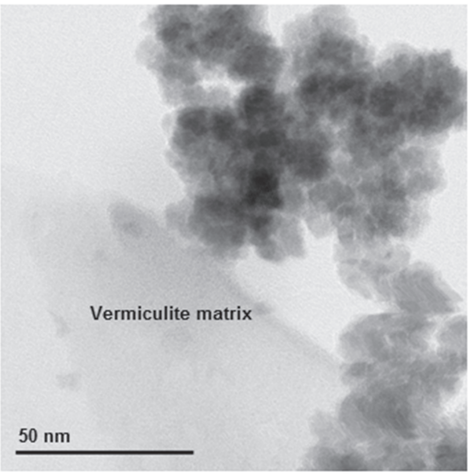

Figure 4. Structure of the clusters of CeO_2 nanocrystallites attached to vermiculite matrix (Ver/CeO_2 sample), as seen by HRTEM.

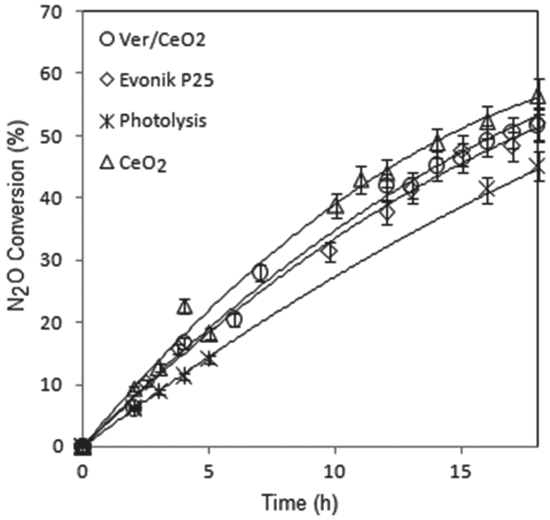

Figure 5. Time dependence of the N_2O conversion (% with the error bars) for different photocatalysts and photolysis.

4. CONCLUSIONS

The nanocrystallites of CeO_2 with the size of (9.0 ± 0.1) nm and with regular shape were prepared by reaction of cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and ammonium hydroxide solution (NH_4OH). Vermiculite with 36 wt% of firmly attached ceria nanoparticles was obtained through the reaction of vermiculite with $[Ce_6(OH)_{12}]^{12+}$ polyoxocation and cerium(IV) hydroxide, $Ce(OH)_4$. The mean crystallite size of the CeO_2 nanoparticles attached to the vermiculite matrix was (8.5 ± 0.5) nm. Because of the reaction with vermiculite, the CeO_2 nanocrystallites had irregular shape. Cerium oxide nanoparticles increased the surface area of vermiculite and contributed to a relatively high volume of micropores. Under UV irradiation, the vermiculite/CeO_2 containing 32 vol% CeO_2 exhibited only slightly lower photocatalytic activity for decomposition of N_2O than sole CeO_2, but the photocatalytic activity was still comparable with the commercial TiO_2 catalyst Evonik P25. Moreover, the benefit of such vermiculite with well-anchored ceria nanoparticles is guarantee of its environmentally safe use.

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