Auto-Combustion Synthesis of CeO_2 Nanopowders and Photocatalytic Properties.

Djani Faiçal
Molecular Chemistry Laboratory and Environment
University of Biskra
Biskra, Algeria
f.djani@univ-biskra.dz

Bouchel Wissem
Molecular Chemistry Laboratory and Environment
University of Biskra
Biskra, Algeria
wisseme.bouchel@gmail.com

Mazouzi Djamel
Molecular Chemistry Laboratory and Environment
University of Biskra
Biskra, Algeria
djamel.mazouzi@univ-biskra.dz

Hamouche Djennat
Molecular Chemistry Laboratory and Environment
University of Biskra
Biskra, Algeria
djennathammouche@gmail.com

***Abstract*— Nano-particles of CeO_2 with the smallest average particle size (200 nm) and uniform morphology, well-dispersion, especially with single crystal of CeO_2 were obtained from a mixed solution of Cerium nitrate $Ce(NO_3)_3.6H_2O$, glycine $C_2H_5NO_2$ and water by auto-combustion method. The synthesized CeO_2 powders were characterized as the crystalline phase identification by X-ray diffraction (XRD), the morphology by scanning electron microscopy (SEM), Nano-particles of CeO_2 also were characterized by: particle size distribution, Fourier transform infrared spectroscopy, uv-vis spectroscopy. The effect of CeO_2 samples on degradation of methyl red (MR) was investigated.**

Keywords—Nano-particles, CeO_2, combustion, degradation, photocatalytic

I. INTRODUCTION

The application of materials depends on their size and morphology, therefore, the focus has recently been on control of size and shape [1, 2]. CeO_2 has attracted more and more attention due to its unique oxygen storage capacity and high ionic conductivity. Because of these characteristics, CeO_2 has potential applications in catalysts, gas sensors, solid oxide fuel cells and so on [3-5]. In recent years, utilizing CeO_2 as photocatalysts to treat wastewater has been of increasing interest. For example, Zhou et al. [6] demonstrated that the as-prepared ceria nanomaterial could be used for the removal of pentavalent arsenic [As(V)] and hexavalent chromium [Cr(VI)] in wastewater treatment. Xiao et al. [7] reported that hierarchical CeO_2 nanocrystal microspheres synthesized could effectively remove Cr(VI) and Rhodamine B(RhB) from simulated wastewater. It is well known that there is a close relationship between structures and properties for ceria nanomaterials. In the past few years, CeO_2 nanostructures with various size and morphology, such as nanoparticles, nanorods, nanowires, nanotubes and nanopolyhedrons, have been successfully fabricated by a variety of methods [8-10]. In this work, we focused on the shape and size control of CeO_2 particles by auto-combustion method. The process exploits the advantages of cheaper precursors, a simple preparation method and a resulting ultrafine, homogenous powder, the samples of CeO_2 Nano-particles were used as photocatalysts to degrade methyl red (MR) [11].

II. EXPERIMENTAL

A. Preparation

CeO_2 oxide was synthesized by auto-combustion (Au.C). Cerium nitrate $Ce(NO_3)_3.6H_2O$, glycine $C_2H_5NO_2$ and distilled water were used as reagents and solvent, respectively. The auto-combustion employing glycine as fuel. Aqueous solutions of glycine and of the metal nitrates were prepared separately and then mixed together with agitation. The mixture is heated between 50 to 60 minutes until achieving combustion with formation of cinders. The resulting products are submitted to grinding until we had a fine powder.

The obtained solid precursors were finally crushed to make the characterization analysis [12]. The reaction is as follows:

$$18\ Ce(NO_3)_3.6H_2O + 28\ C_2H_5NO_2 \longrightarrow$$

$$18\ CeO_2 + 56\ CO_2 + 41\ N_2 + 178\ H_2O$$

B. Characterization

XRD Patterns were collected on a Bruker AXS D8-advance diffractometer employing Cu Kα radiation. In all diffractograms, a step size of 0.02º (2h) was used with a data collection time of 15s. Data were collected between 2θ values of 10° and 80° using standard θ/2 geometry. Identification of crystalline phases was carried out by comparison with JCPDS standards. The unit cell parameters were obtained by fitting the peak position of the XRD pattern using the Match and X'pert Highscore programs [13].

Infrared transmission spectra were performed on a Fourier transform spectrometer (FTIR) Shimadzu 8400S. A granular technique employing KBr (1 mg of sample added to 200 mg of KBr) was used and the spectra were recorded in the 400-4000 cm-1 range [14].

The analysis of the distribution of the grain size of the samples was employed in order to show the influence of the complexing agent, solvents and the synthetic methods employed on the particle size by laser granulometry. After calcination at 800 °C, the powder was dispersed in deionized water in a beaker with magnetic stirring and combined under ultrasound for 15 minutes. Powder size distribution was characterized with a laser particle size analyzer (Mastersizer 2000, Malvern) [15].

The SEM micrographs of the samples were obtained using the scanning electron microscope (Model: TESCAN VEGA3), the SEM micrographs of the samples (CeO_2 oxide) were carried out at the thin-film laboratory, University of Biskra.

The photocatalytic activities of Nano-particles CeO_2 powders were valued by the decomposition of MR in water. The optical system for the photocatalytic reaction was a 4*4 W lamps with a maximum emission at 360 nm for the uv range and 7 W for the visible. The photocatalytic reaction procedures were as follows: MR solutions (20 mL, 10 mgL^{-1}) containing 0.01 g of CeO_2 powders were put in a glass beaker. Prior to irradiation, the suspensions were magnetically stirred without UV irradiation for 30 min to establish adsorption/degradation equilibrium. The distance between the liquid surface and the light source was about 8 cm. During irradiation, 5 mL suspension was successively taken from the reaction cell at given time intervals and separated through centrifugation (4200 rpm, 15 min). The supernate was analyzed by recording variations of the absorption band maximum (523 nm) in the UV–Vis spectra of MR by using a UV–Vis spectrophotometer (Uviline 9400) [16].

III. Results And Discussion

XRD Patterns obtained for the compound under study is shown in the following figures:

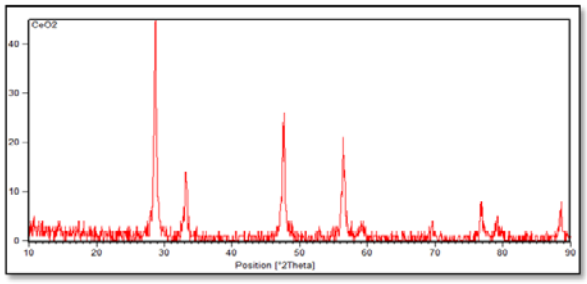

Fig. 1. XRD patterns of CeO_2 prepared by auto-combustion.

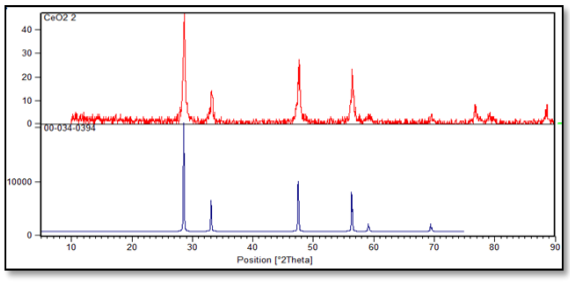

Fig. 2. XRD patterns of CeO_2 prepared by auto-combustion and JCPDS (00-034-0394).

The observed values of the 2θ with JCPDS standards (00-034-0394) for this type of compound (X'pert highscore software) shows us the presence of a single phase, which is the fluorine CeO_2. Fluorine-type phase with cubic symmetry, space group $Fm\bar{3}m$ (225), with lattice parameters: a = b = c = 5,4113 Å and $\alpha = \beta = \gamma = 90$ °[17].

Infrared spectra of samples prepared by various agents of complexation and different methods of synthesis after calcination are shown in the following figure:

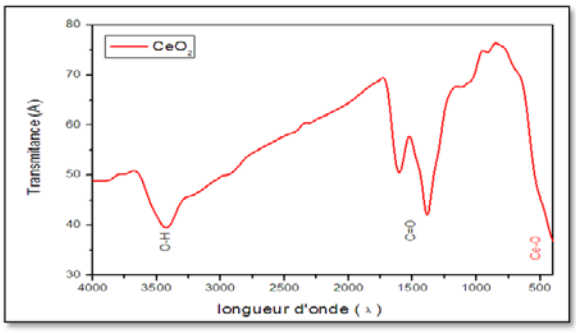

Fig. 3. Infrared spectrum (4000-400 cm^{-1}) of CeO_2 prepared by auto-combustion.

The infrared spectrum of the sample obtained by auto-combustion has a characteristic broad band at 3420 cm^{-1} which depends on the hydroxide elongation vibration (OH) of the water absorbed by the sample or attributed to the (OH) of fuel (glycine). This spectrum also has an intense band around 1605 cm^{-1}, which depends on the carboxyl function (C=O) of glycine. We observe the presence of an intense band around 400 cm^{-1} attributed to the vibrations of the bonds (Ce-O) which confirms the phase formation [18].

In order to measure the grain size distribution, powders of the oxides obtained are used. The granulometric measurements are carried out in a liquid way. The powder is suspended in 700 ml of distilled water by adding 0.5 g of sodium diluent (dispersant) and is ultrasonic dispersed for 15 minutes. Particle size analysis of the self-combustion prepared CeO_2 powder is shown above. The result is displayed in the following figure:

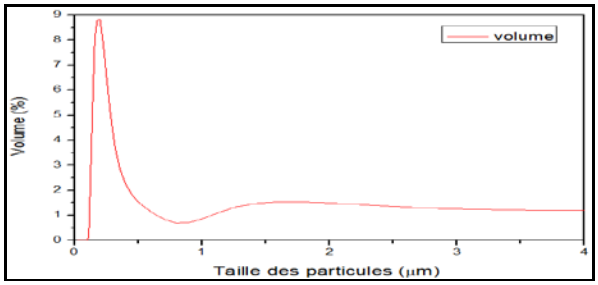

Fig. 4. Particle size distribution of CeO_2 prepared by auto-combustion.

One mode of particle distribution of the sample is shown; the peak is centered at 200 nanometer of the volume distribution is 8.82% [19].

The sample morphology analysis obtained was performed by a SEM apparatus model: TESCAN VEGA 3. The following figures show the SEM images of the sample CeO_2 prepared by auto-combustion:

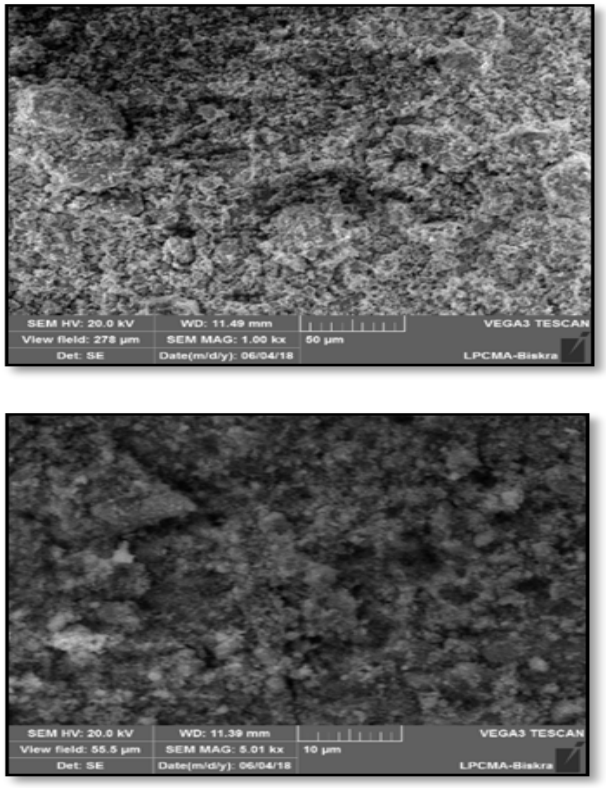

Fig. 5. SEM images of CeO_2 prepared by auto-combustion.

CeO_2 powders synthesized by auto-combustion are a little agglomerated giving almost spherical grains [20].

Before performing the spectrophotometric analyzes, centrifugation was performed to ensure the separation of the heterogeneous MR/CeO_2 solution. A visible lamp with (7 w) and a fixed concentration of CeO_2/MR at: 0.5 mg / 1 ml was used. The absorbance was measured every 15 min for 1 hour [20-21].

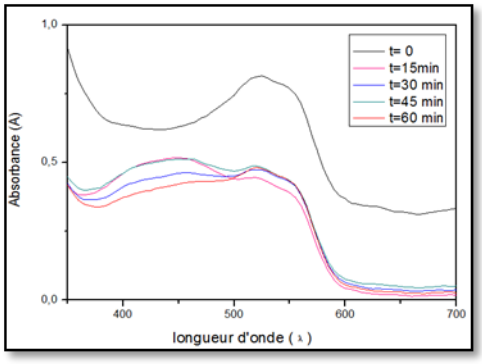

Fig. 6. Uv-visible spectra of MR photodegraded under visible light, using CeO_2.

Under the effect of visible lamp (7w), a decrease in the absorbance of MR by CeO2 catalyst over time was observed. The absorbance of the starting of the MR was 0.815 and after 1 hour it became 0.393. The results are summarized in the following table:

TABLE I. EVOLUTION OF MR ABSORBANCE DURING DEGRADATION (VIS)

T (min)	0	15	30	45	60
A (λ=523nm)	0,815	0,459	0,434	0,411	0,393

In the second part, Ultraviolet lamps with (4 * 4 w) were used and a fixed concentration of CeO_2/MR at: 0.5 mg / 1 ml was used. The absorbance was measured every 15 minutes for 1 hour.

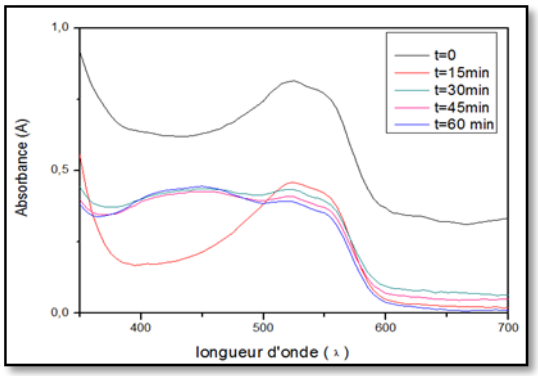

Fig. 7. UV -Visible spectra of MR photodegraded under UV light, using CeO_2.

Under the effect of UV lamps (4*4w), a decrease in the absorbance of MR by CeO_2 catalyst over time was observed. The absorbance of the starting of the MR was 0.815 and after 1 hour it became 0.443. The results are summarized in the following table:

TABLE II. EVOLUTION OF MR ABSORBANCE DURING DEGRADATION (UV)

T (min)	0	15	30	45	60
A (λ=523nm)	0,815	0,481	0,474	0,466	0,433

IV. CONCLUSION

The Nano-particle CeO_2 powders can be synthesized by the auto-combustion method using corresponding metal nitrates as oxidizers and glycine as fuel. The combustion can be considered as a thermally induced autocatalytic anionic redox reaction of the gel. After combustion, the gel is directly transformed into a single-phase CeO_2 powders with spongy aspect. The Nano-particle CeO_2 powders exhibited a good activity in the degradation of MR under UV and visible light irradiation. The degradation percentage of MR after 1 h on CeO_2 powders was about 50%, indicating good photocatalytic activity of the obtained CeO_2 powders.

REFERENCES

[1] Li, M., Schnablegger, H. and Mann, S., 1999. Coupled synthesis and self-assembly of nanoparticles to give structures with controlled organization. Nature, 402(6760), p.393.

[2] Taubert, A., Palms, D., Weiss, Ö., Piccini, M.T. and Batchelder, D.N., 2002. Polymer-assisted control of particle morphology and particle size of zinc oxide precipitated from aqueous solution. Chemistry of materials, 14(6), pp.2594-2601.

[3] Al-Yassir, N. and Le Van Mao, R., 2007. Catalysts for the thermo-catalytic cracking (TCC) process: Interactions between the yttria in yttria-doped alumina aerogel and the mono-oxide MoO_3, CeO_2, and bi-oxide MoO_3–CeO_2 species. Applied Catalysis A: General, 332(2), pp.273-288.

[4] Atkinson, A., Barnett, S., Gorte, R.J., Irvine, J.T.S., McEvoy, A.J., Mogensen, M., Singhal, S.C. and Vohs, J., 2011. Advanced anodes for high-temperature fuel cells. In Materials For Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group(pp. 213-223).

[5] Fu, X.Q., Wang, C., Yu, H.C., Wang, Y.G. and Wang, T.H., 2007. Fast humidity sensors based on CeO_2 nanowires. Nanotechnology, 18(14), p.145503.

[6] Feng, Q., Zhang, Z., Ma, Y., He, X., Zhao, Y. and Chai, Z., 2012. Adsorption and desorption characteristics of arsenic onto ceria nanoparticles. Nanoscale research letters, 7(1), p.84.

[7] Y.W. Zhang, R. Si, C.S. Liao, C.H. Yan, Facile alcohothermal synthesis, size-dependent ultraviolet absorption, and enhanced CO conversion activity of ceria nanocrystals, J. Phys. Chem. B 107 (2003) 10159–10167.

[8] H.X. Mai, L.D. Sun, Y.W. Zhang, R. Si, W. Feng, H.P. Zhang, H.C. Liu, C.H. Yan, Shape-selective synthesis and oxygen storage behavior of ceria nanopolyhedra, nanorods, and nanocubes, J. Phys. Chem. B 109 (2005) 24380–24385.

[9] T.S. Sreeremya, K.M. Thulasi, A. Krishnan, S. Ghosh, A Novel, Aqueous route to fabricate ultrasmall monodisperse lipophilic cerium oxide nanoparticles, Ind. Eng. Chem. Res. 51 (2012) 318–326.

[10] K.B. Zhou, X. Wang, X.M. Sun, Q. Peng, Y.D. Li, Enhanced catalytic activity of ceria nanorods from well-defined reactive crystal planes, J. Catal. 229 (2005) 206–212.

[11] Qu, X., Xie, D., Gao, L., & Du, F. (2014). Synthesis and photocatalytic activity of TiO_2/CeO_2 core–shell nanotubes. Materials Science in Semiconductor Processing, 26, 657-662.Eason, G., Noble, B. and Sneddon, I.N., 1955. On certain integrals of Lipschitz-Hankel type involving products of Bessel functions. Phil. Trans. R. Soc. Lond. A, 247(935), pp.529-551.

[12] Bang, N. D., & Hue, H. T. T. (2009). Synthesis of nano-particles of CeO_2 by auto-combustion method. Vietnam Journal of Chemistry, 47(3), 385.

[13] Djani, F. (2016). Etude physicochimique du système $LaMM'O_3$ à base de métaux divalents et trivalents (Doctoral dissertation, Université Mohamed Khider-Biskra).

[14] Lavat, A. E., & Baran, E. J. (2003). IR-spectroscopic characterization of $A_2BB'O_6$ perovskites. Vibrational spectroscopy, 32(2), 167-174.

[15] F. Djani, M. Omari, A. Martinez-Arias, Synthesis, characterization and catalytic properties of La (Ni, Fe)O_3–NiO nanocomposites, Journal of Sol-Gel Science and Technology, vol. 78, no 1, 2016, p. 1-10.

[16] PRIMO, Ana, et al. Efficient visible-light photocatalytic water splitting by minute amounts of gold supported on nanoparticulate CeO_2 obtained by a biopolymer templating method. Journal of the American Chemical Society, 2011, 133.18: 6930-6933.

[17] Tamizhdurai, P., et al. "Environmentally friendly synthesis of CeO $_2$ nanoparticles for the catalytic oxidation of benzyl alcohol to benzaldehyde and selective detection of nitrite." Scientific Reports 7 (2017): 46372.

[18] R.C.Deus, M.Cilense, C.R.Foschini, M.A.Ramirez, E.Longo, A.Z. Simões, Influence of mineralizer agents on the growth of crystalline CeO_2 nanospheres by the microwave-hydrothermalmethod, Journal of Alloys and Compounds. 550 (2013) 245251.

[19] Quik JT. Fate of nanoparticles in the aquatic environment: removal of engineered nanomaterials from the water phase under environmental conditions. [Sl: sn]; 2013.

[20] Djani, Faical, Ikram Noureddine, and Arturo MARTINEZ ARIAS. "characterization of $La_{1-x}Sr_xMnO_3$ ($0 \leq x \leq 0.2$) nanopowders synthesized by different methods." university politehnica of bucharest scientific bulletin series b-chemistry and materials science 80.1 (2018): 101-112.

[21] Ravishankar, Thammadihalli Nanjundaiah, et al. "Synthesis and characterization of CeO_2 nanoparticles via solution combustion method for photocatalytic and antibacterial activity studies." ChemistryOpen 4.2 (2015): 146-154.