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Preparation nano CeO_2 from Binh Dinh monazite ore by acid method and applying to environmental treatment

Cao Van Hoang[1,*], Nguyen Thi Dieu Cam[1], Nguyen Ngoc Hoa[2], Nguyen Van Luong[1], Nguyen Dinh Doc[1], Nguyen Quang Bac[3], Dao Ngoc Nhiem[3]

[1] Qui Nhon University, 170 An Duong Vuong, Quy Nhon City, Binh Dinh Provine, 55000, Viet Nam
[2] Department of Science and Technology, 208 Dien Hong, Quy Nhon City, Binh Dinh Province 55000, Viet Nam
[3] Institute of Material Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi 10000, Viet Nam
**Email: caovanhoang@qnu.edu.vn*

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ABSTRACT

This article reported the preparation of Nano CeO_2 by acid method from Binh Dinh monazite ore. Obtained CeO_2 was examined by the method of X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), specific surface area analysis by Brunauer-Emmet-Teller (BET) method, UV-VIS. Obtained CeO_2 has particle size 16.7 nm and surface area 30.1 m^2/g.

Introduction

Vietnam is one of the countries that are rich in mineral resources with large reserves. Rare-earth metals ore has reserved about 10 million tons that are scattered in mines in the Northwest and distributed along the coasts of central provinces in the form of black sand.

In recent years, rare earth elements have been increasingly used in many fields. In particular, nano CeO_2 has been synthesized by different methods [1-7]. Because of its superior properties, nano CeO_2 is widely used: as photocatalyst materials, luminescent material manufacturing, and polishing materials, UV absorbent materials. CeO_2 is also used as catalysts to perform reactions such as cracking. Because CeO_2 can be easily converted between two forms of Ce^{+4}/Ce^{+3}, it is capable of catalyzing exhaust gas treatment [1,2].

In this paper, $Ce(OH)_4$ was directly from monazite rich ore from Binh Dinh monazite ore using H_2SO_4 method. Then, nano CeO_2 was the first time prepared from $Ce(OH)_4$ and glycine through a combustion method.

Experimental

Chemical and equipment

Chemicals: Concentrated sulfuric acid, concentrated acid nitrate, glycerin, NH_4OH, NaOH were pure analysis grade and Binh Dinh monazite ore.
Equipment: Heating magnetic stirrer from IRE (Italy), Oven from M400 (Germany), furnace S4800 (USA), and some glassware

Material synthesis

The process of preparing nano CeO_2 from Binh Dinh monazite ore was studied and investigated. The optimal conditions were chosen for Binh Dinh monazite ore to given as figure 1.

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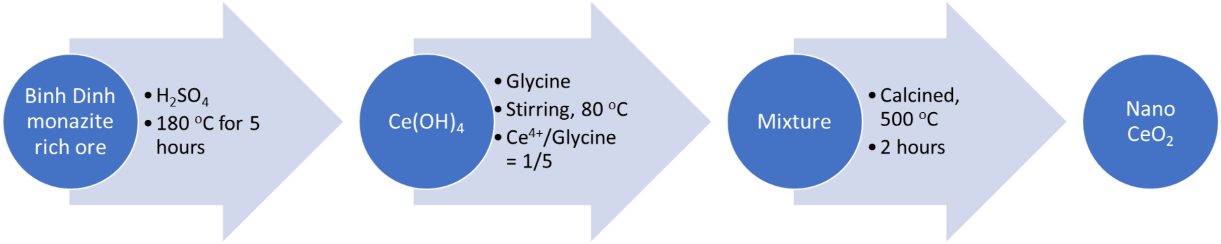

Figure 1: The CeO_2 preparation procedure using glycine combustion method

Ore decomposition process: concentration of acid H_2SO_4 90 %, the ratio of monazite ore/acid = 1/3, decomposition time 5 hours, at 180 °C in a autoclave. The ratio of ore separation solution was 1/13

The process of precipitation formation $Ln_2(SO_4)_3.Na_2SO_4.nH_2O$: ratio of ore:$Na_2SO_4$ (solid) (g/g) = 1:4, optimum temperature 25 °C, optimal time 120 minutes

The process of converting precipitate of $Ln_2(SO_4)_3.Na_2SO_4.nH_2O$ to $Ln(OH)_3$: ratio of ore:NaOH (solid) (g/g) = 1:3, optimum temperature 100°C, optimal time 90 minutes.Effect of the oxidizing agent from Ce^{3+} to Ce^{4+}: acid HNO_3.

Effect of pH to $Ce(OH)_4$ precipitation: Optimal pH 2.5.

Effect of precipitant to $Ce(OH)_4$: 25 % NH_3 solution.

The factors affecting the preparation of CeO_2 from $Ce(OH)_4$: ratio of $Ce(OH)_4$/glycine (mol/mol) = 1:5, pH to form gel = 3, gelation temperature 80 °C, calcination temperature 500 °C for 2 hours.

The process of preparing nano CeO_2 from Binh Dinh monazite ore was included two main stages:

The first stage: Preparation $Ce(OH)_4$ from monazite ore

The finely ground monazite ore was (particles size < 0.074 mm) weighed and put into a 250 mL beaker. Acid H_2SO_4 90 % was added by the ratio of ore(g)/acid(g) = 1/3. Baker was covered by a glass top, placed in a stove from sand, and heated in a fume hood at 250 °C for 5 hours.

The solution was filtered to separate light blue solution contained Ln^{3+}. NaOH was added to the obtained solution by the ratio of ore(g)/NaOH(g) = 1/3. The solution was stirred on stirrer at 100 °C for 90 minutes. The precipitate was filtered (white-gray precipitate), dried at 100 °C. After dried, the hydroxides of rare earth elements were changed from gray-white to yellow.

$Ln_2(SO_4)_3 + 6NaOH = 2Ln(OH)_3 + 4Na_2SO_4$

The hydroxides of rare earth elements were dissolved by HNO_3 solution (the ratio of HNO_3:H_2O = 4:3) at 80 °C for 90 minutes. The solution was changed to orange-red color. The solution was added 25% concentrated NH_3 solution to pH 2.5 to obtain a precipitate of cerium (IV) hydroxide. After filtering and drying at 100 °C, $Ce(OH)_4$ was obtained with light yellow color.

The second stage: Preparation nano CeO_2 from $Ce(OH)_4$

$Ce(OH)_4$ precipitate was completely dissolved by HNO_3 solution (the ratio of concentrated acid HNO_3:water = 4:3) in the ratio of $Ce(OH)_4$(g)/HNO_3(ml) = 1/3, stirred at 80 °C to get a red-orange solution, then removed excess acid from the solution by heating at 80 °C.

The Ce^{4+} solution was slowly added to glycine solution by the ratio of $Ce(OH)_4$ (mol)/glycine (mol) = 1/5 and added distilled water to obtain 80 ml of solution. The pH of the solution was adjusted by HNO_3 acid and NH_3 solution to obtain a solution with pH 3. The solution was stirred continuously and heated on a magnetic stirrer at 80 °C until transparent gel. The viscous solution was obtained. The gel was aged overnight. Then gel was dried at 100 °C until a thin yellow layer (with foam structure) was obtained and then calcined at 500 °C for 2h to obtain CeO_2 product (light brick red color).

Research methods

The formation and crystal phase change of CeO_2 were determined by X-ray Diffraction (XRD) Simens D5000 (Germany).

The morphology and particle size were determined by scanning electron microscopy (SEM) JEOL-5300 (Japan) and transmission electron microscopy (TEM) JEOL-JEM-1010 meter (Japan). The composition analysis of the solid was determined by X-ray energy dispersive spectroscopy (EDS).

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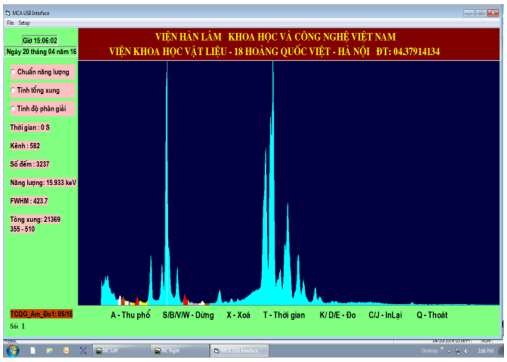
The specific surface area of nano CeO_2 was measured by the BET method (Brunauer-Emmet-Teller) liquid N_2 adsorption at 77 K on ASAP 2010 meter (USA).

Determination of radiation absorption capacity of CeO_2 material was measured by UV-Vis absorption spectroscopy of solid samples on JASCO-V-670 UV-Vis Spectrophotometer.

Results and discussion

Characteristics of Binh Dinh monazite samples

Fine monazite ore was taken from Nam De Gi (Cat Thanh, Phu Cat, Binh Dinh). The compositions of Binh Dinh monazite ore were determined by the X-ray fluorescent method. The results were presented in figure 2 and table 1.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Ngày 20 tháng 04 năm 16
Thời gian : 0 S
Kênh : 582
Số đếm : 3237
Năng lượng: 15.933 keV
FWHM : 423.7
Tổng xung: 21369
355 - 510
TCQG_Am_Đo1: 05/15
Số: 1

Figure 2: The compositions of Binh Dinh monazite ore

Table 1: The compositions of Binh Dinh monazite ore

Metals	Composition (wt.%)
La	20.13
Ce	43.86
Nd	16.43
Pr	4.90
Sm	3.22
Gd	3.10
Eu	0.12
Er	0.37
Ho	0.15
Y	2.37
Tm	0.03
Sc	0.01
Tb	0.33
Dy	1.10
Yb	0.16
Lu	0.02
Ga	3.70
Th	5.96
U	0.01

X-ray diagram (XRD)

Figure 3 showed that peaks appeared at positions 2θ = 28.40 °; 33.14 °; 47.36 °; 56.25 °; 59.09 °; 69.45 °. This was proved that CeO_2 had a crystalline structure, good crystallinity (sharp and high peak). The crystal grain size calculated by the Scherrer formula was 16.7 nm.

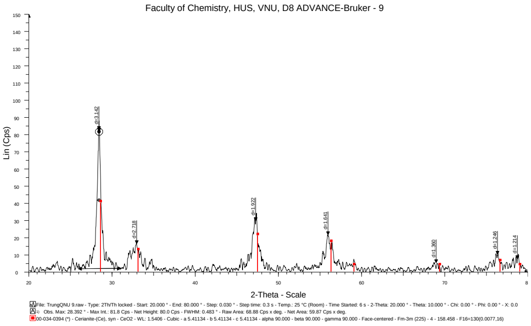

Figure 3: Xray pattern of CeO_2 oxide

Surface morphology of CeO_2 oxide

Figure 4 showed that CeO_2 oxide had nanostructure and fairly uniform, spherical, and clear sizes with a diameter of about an average of 20-50 nm. This size was a favorite for the catalyst process.

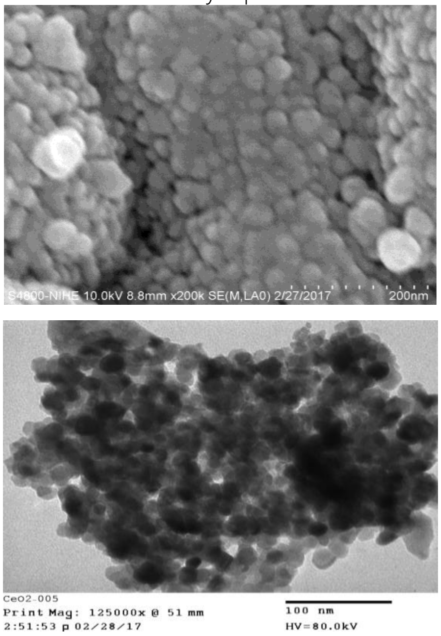

Figure 4: SEM and TEM images of CeO_2 oxide

Result of specific surface area by Brunauer-Emmet-Teller (BET) method

The porous properties and capillary structure of CeO_2 material were investigated by nitrogen adsorption and

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desorption isotherm measurements at 77 K. The result was shown in figure 5.

Figure 5 showed that the shape of the N_2 adsorption-desorption isotherm at 77 K of the CeO_2 oxide belonged to IUPAC class IV. Capillary condensation occurred clearly at a relative pressure of about 0.62. The isotherm had an H3 hysteresis ring. This showed that the CeO_2 material had a medium pore structure (2-50 nm) [8]. The specific surface area of the prepared CeO_2 powder (SBET) calculated by measurement was 30.1 m^2/g. Thus, the synthesized CeO_2 powder was very suitable for application in water and air treatment purposes.

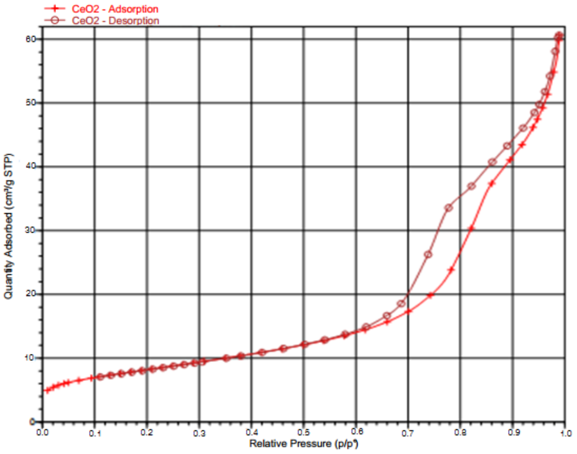

Figure 5: The N_2 adsorption-desorption isotherm of the CeO_2 oxide

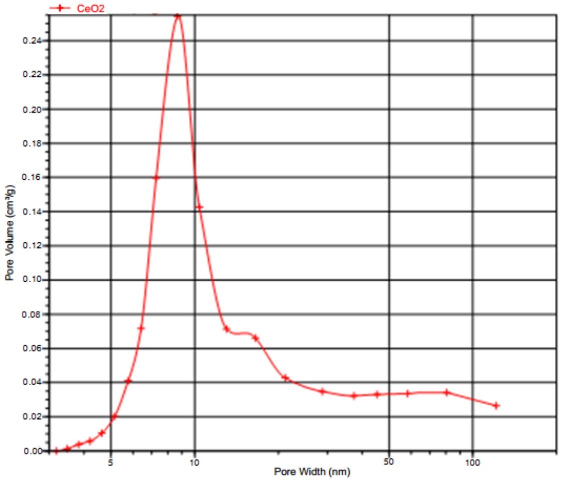

Figure 6: The distribution curve of the capillary size of the CeO_2

Figure 6 shows the pore size distribution curve of the CeO_2 material [9]. A maximum peak corresponded to a pore diameter of about 8 nm.

X-ray energy dispersive spectroscopy (EDS)

Figure 7 showed that the prepared CeO_2 sample consisted of two main elements, Cerium, oxygen, and was pure.

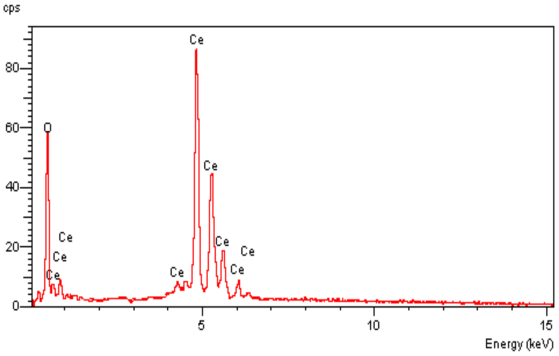

Figure 7: X-ray energy dispersive spectroscopy (EDS) of CeO_2

UV-Vis absorption spectroscopy of a solid sample

Figure 8 showed that an absorption peak in the ultraviolet region was λ_{max} = 340 nm. CeO_2 absorbed excitation light with a wavelength in the ultraviolet region and was a semiconductor with bandgap energy E_g = 3.097 eV. Thus, CeO_2 had a photocatalytic to treat organic pigments in the ultraviolet region.

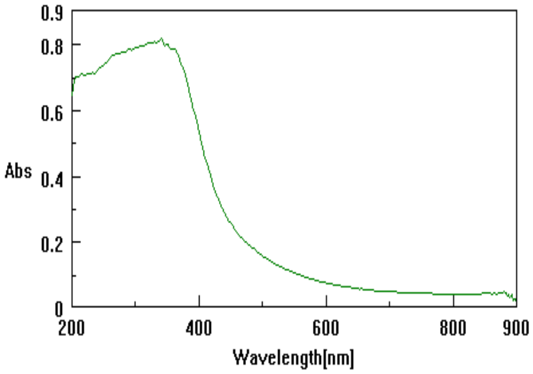

Figure 8: UV-Vis absorption spectroscopy of CeO_2

Investigation of photocatalytic activity of CeO_2

50 mL of 10 ppm methylene blue solution were exactly taken and put into a 100 mL beaker, then added to the solution 0.2 g CeO_2. The solution was stirred in the dark to reach adsorption equilibrium for time = 30 minutes. The reaction solution was stirred continuously at room temperature and illuminated by a UV lamp with wavelength λ = 365 nm placed above the reaction cup at a distance of about 5 cm from the surface of the solution. The remaining methylene blue solution concentration was measured at different reaction times

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t = 10, 30, 60, 90, 120, 150, 180 minutes. The results were shown in table 2 and figure 9.

Table 2: Decomposition efficiency of methylene blue with light time

Time (min)	10	30	60	90	120	150	180
Final concentration (ppm)	5.33	3.76	2.67	1.88	1.16	0.89	0.86
Decomposition performance (%)	46.7	62.4	73.3	81.2	88.4	91.1	91.4

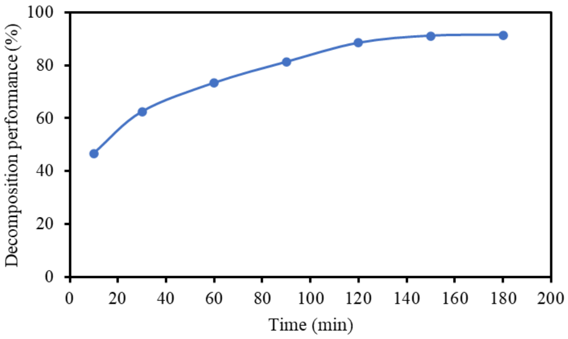

Figure 9: Decomposition efficiency of methylene blue with light time

The results showed that the decomposition efficiency of Methylene Blue increased with illumination time. When the lighting time was 150 minutes, the decomposition efficiency reached over 91 %.

Conclusion

Nano CeO_2 oxide was investigated and prepared by acid method from Binh Dinh monazite ore was Scherrer crystal particle size 16.4 nm with particle size 20-25 nm and specific surface area 30.1 m^2/g.

The photocatalytic ability of nano CeO_2 oxide was evaluated by methylene blue decomposition reaction. The decomposition efficiency of methylene blue was over 91 % after 2.5 hours.

Acknowledgments

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