Synthesis of Nanocrystalline CeO_2 with High Surface Area and Mesoporosity Using Template-Assisted Precipitation Method

Tran Thi Thuy[1]*, Nguyen Duy Hieu[1], Vuong Thanh Huyen [1,2]

[1]*Hanoi University of Science and Technology – No. 1, Dai Co Viet Str., Hai Ba Trung, Ha Noi, Viet Nam*
[2]*Leibniz-Institut für Katalyse e.V., Albert-Einstein-Str. 29a, 18059 Rostock, Germany*

Abstract

Nanocrystalline ceria with high surface area and mesoporosity was prepared by template-assisted precipitation method. The method of preparation was facile, using low-cost reagents and could be performed on a large scale. Cerium oxide support was characterized by Brunauner – Emmett - Teller (BET), X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. The optimal conditions for cerium oxide synthesis were using cerium nitrate precursor, adjusting the final pH solution to 11.4 by NH_4OH and ethylene diamine (EDA) and calcination at 550 °C in air for 3 hours. With these conditions, nanocrystalline CeO_2 was obtained with high surface area of 159.5 m^2/g.

1. Introduction

Ceria (CeO_2) is an important catalyst component, as a role of a support/ carrier. High surface area ceria is extremely useful for increasing catalytic activity in several low-temperature applications such as emissions control, water gas shift (WGS), CO oxidation, and volatile organic compound (VOC) combustion/ destruction. Ceria has been the subject of thorough investigations, mainly because of its use as an active component of catalytic converters for the treatment of exhaust gases. However, ceria-based catalysts have also been developed for different applications in organic chemistry. The redox and acid-base properties of ceria, either alone or in the presence of transition metals, are important parameters that allow to activate complex organic molecules and to orient their transformation selectively [1].

The most important property of CeO_2 is as an oxygen reservoir, which stores and releases oxygen via the redox shuttle between Ce^{4+} and Ce^{3+} under oxidizing and reducing conditions, respectively. Ceria also improves the dispersion of supported metals and metal oxides and consequently their activity [2, 3].

Recently, highly dispersed vanadia supported on ceria turned out to be active also for low-temperature (LT) selective catalytic reduction of NO_x by NH_3 (NH_3-SCR) with remarkable resistance to SO_2 [4]. Highly dispersed vanadia supported on CeO_2, turned out to be active also for LT NH_3-SCR [1-5]. The prior art reporting on synthesis of high surface area ceria showed that the template-assisted precipitation method had been used (Table 1).

Table 1. Prior art reporting high surface area ceria

Method, precursor, reference	S_{BET} ($m^2 g^{-1}$)
Urea gelation method, $(NH_4)_2Ce(NO_3)_6$[7]	215
Micro-emulsion method, $Ce(NO_3)_3$ [8]	118
Alkoxide sol-gel, $Ce(NO_3)_3$ [9]	180
Surfactant-template method, $CeCl_3$ [10]	200
Sol-gel, $Ce(NO_3)_3$ [6]	61

As can be seen from the Table 1, some works obtained the high surface area ceria, but only at low temperature (400 – 450°C). When the calcining temperature increased to 550°C, with longer dwelling time, it was difficult to obtain the high surface area support and porosity [6].

Mesoporous nano-CeO_2 with high surface area was prepared using surfactant CTAB, with $Ce(NO_3)_3$ as the precursor and NaOH as the precipitating agent. The surface area of CeO_2, in excess of 200 m^2g^{-1} was obtained after calcination at 400°C [7]. However, this method had been used lower calcination temperature 400°C compared to 550°C of our research. Moreover, NaOH is a strong inorganic base. If it was used as precipitating agent, sodium couldn't be removed during the filtering and heat treatment. In our research, NH_4OH, EDA or urea were used as

---

* Corresponding author: Tel.: (+84) 977.120.602
Email: thuy.tranthi3@hust.edu.vn

precipitating agents. These compounds will be easy to decompose during the calcination.

Therefore, in the present work, synthesis of CeO_2 with high surface area and porosity by template-assisted precipitation method has been focused on.

2. Experiments

The CeO_2 nanoparticles were prepared by template-assited precipitation method as shown in the Figure 1. Cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$, Acros, 99.5%), cerium chloride ($CeCl_3.7H_2O$, Sigma, ≥99.9%) and cetyltrimethylammonium bromide (CTAB, Sigma >99%) were used to prepared two sets of CeO_2 precursors. The first set of CeO_2 precursors were prepared by dissolving $Ce(NO_3)_3 \cdot 6H_2O$ and CTAB in water with the stoichiometric ratio Ce^{3+}: CTAB of 1:0.6. The second set of CeO_2 precursors were synthesized by using 1:1 stoichiometric molar ratio of $CeCl_3.7H_2O$ and CTAB mixed in water.

The precipitation of CeO_2 precursors were promoted by different precipitants including sodium hydroxide (NaOH, Sigma), ammonium hydroxide (NH_4OH, Sigma), urea (ammonium titanyl oxalate monohydrate, Acros, 98%), ethylenediamine (EDA, Sigma, ≥99.5%) and the mixture of NH_4OH and EDA. The precipitants were added dropwise and the final pH of solutions were adjusted up to a value between 10 and 13. Afterwards, the precipitations were dried at 120°C for 10 hours and then calcined in air at 550°C for 3 hours.
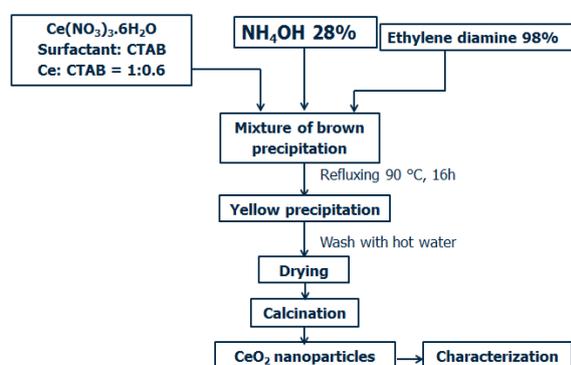
Fig. 1. Schematic overview of CeO_2 synthesis using template-assisted precipitation method

XRD powder patterns were recorded in the 2 Theta range from 5–80° by a theta/theta diffractometer (X'Pert Pro, Panalytical, Almelo, Netherlands) equipped with an X'Celerator RTMS Detector using Cu Kα radiation. Specific surface areas were determined by nitrogen adsorption at -196°C using the single-point BET procedure (Gemini III 2375, Micromeritics).

The transmission electron micrograph (TEM) observation was performed with a JEOL ARM200F instrument equipped with a JED-2300 energy-dispersive X-ray spectrometer (EDXS) for chemical analysis.

3. Results and discussion

CeO_2 nanoparticles were prepared with different recipes. The results were shown in Table 2. The starting materials were cerium nitrate or cerium chloride. The molar ratio between metal ion and CTAB has been varied from 0.6 to 1. CTAB surfactants are amphiphilic molecules. It is easy for the amphiphilic molecule groups to form a variety of ordered polymers in a solution, such as liquid crystals, vesicles, micelles, microemulsion, and self-assembled film [12]. From the perspective of material chemistry, it is generally thought that the interaction between liquid crystal phase of surfactants and organic-inorganic interface plays a decisive role in the morphology of mesoporous materials [13].

The calcining temperature was used based on the previous work [6]. After calcining at 550°C for 3h in air, the CeO_2 nanoparticles were submitted to BET measurements. It was noticed that the cerium nitrate precursor (sample Ce4) allowed to obtain the CeO_2 nanoparticle with high surface areas (159.5 $m^2 g^{-1}$). It may due to the role of EDA, which acts as a precipitator as well as a ligand to complex with Ce^{3+} [14, 15].

EDA has a significant role in the formation of CeO_2 nanoparticles by adjusting the pH of the hydrolysis and controlling the precipitation of CeO_2 precursors. EDA forms complexes with Ce^{3+} through two nitrogen atoms. It is a bidentate ligand. NH_3 is a monodentate ligand. It binds to a metal ion through only one atom (nitrogen atom). Here, a stronger ligand, EDA is introduced to form $[Ce(NH_2CH_2CH_2NH_2)_2]^{3+}$ thereby control the release of isolated Ce^{3+}. During the gelation there is a shift in pH which results in precipitation. The addition of EDA also can increase the viscosity of the solution and slows downs the diffusion coefficient of the building blocks [16, 17]. Therefore, EDA decreases the hydrolysis rate thus making the precipitation of hydroxide more difficult. Otherwise, EDA is a stronger base (pKa = 9.69) than NH_3 (pKa = 9.25).

The role of EDA can be seen in the results of Ce4 and Ce8 samples (Table 2). The pH values of the final solutions are slightly difference (11.4 and 11 respectively), the surface area of the CeO_2 has been obtained much higher. Here, the extra EDA has been added to raise the pH value from 11 to 11.4.

Table 2. Specific surface area (S_{BET}) of different CeO_2 precursors

Sample name	Precursor, molar ratio	Precipitators, pH	S_{BET} (m²g⁻¹)
Ce1	$Ce(NO_3)_3$:CTAB = 1:0.6	NaOH, 13	2.5
Ce2	$CeCl_3$:CTAB = 1:1	NaOH, 13	52.0
Ce3	$CeCl_3$:CTAB = 1:0.6	EDA, 13	6.0
Ce4	$Ce(NO_3)_3$:CTAB = 1:0.6	EDA, NH_4OH, 11.4	**159.5**
Ce5	$CeCl_3$:CTAB = 1:1	EDA, 11	115.0
Ce6	$CeCl_3$:CTAB = 1:1	NH_4OH, 11.1	97.2
Ce7	$CeCl_3$:CTAB = 1:1	NH_4OH, 11.4	111.2
Ce8	$Ce(NO_3)_3$:CTAB = 1:0.6	EDA, NH4OH, 11	66.6
Ce9	$CeCl_3$:CTAB = 1:1	Urea	7.9
Ce10	$CeCl_3$:CTAB = 1:1	EDA, NH_4OH, 11.3	77.3
Ce11	$CeCl_3$:CTAB = 1:1	EDA, NH_4OH, 10.8	77.9
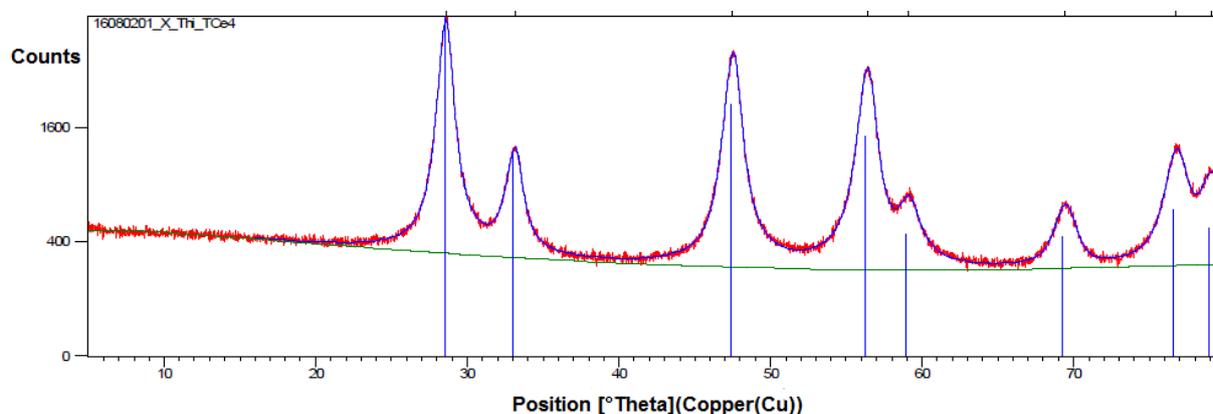
Fig 2. X-ray powder diffractograms observed for the sample Ce4.

Table 3. Calculation the average crystallite size followed the Scherrer's equation based on XRD data

d-spacing [Å]	Pos. [°2Th.]	Height [cts]	Area, [cts*°2Th.]	Integral Breadth [°2Th.]	Crystallite Size only [Å]	Average, nm
3.12113	28.577(6)	2084(8)	3779.29	1.813187	50.7549	4.7266648
2.70066	33.14(1)	660(5)	1221.51	1.850435	50.1965	
1.91216	47.512(7)	1718(7)	3460.92	2.014423	48.16879	
1.63086	56.371(6)	1524(10)	3234.94	2.122363	47.45177	
1.56207	59.09(2)	296(6)	758.1	2.563135	39.76128	

The XRD patterns of the sample Ce4 was shown in Figure 2. XRD patterns of CeO_2 supports show the characteristic peaks of the cubic fluorite structure. As can be seen in Figure 2, the three strongest diffraction peaks (at 3.12113, 1.91216, 1.63086 Å) of the CeO_2 sample correspond to the cubic ceria crystal facets (111), (220) and (311), respectively [15].

The average of crystalline size of CeO_2 nanoparticles of sample Ce4 was 4.7 nm. This data was obtained from XRD measurements. It is based on the Scherrer's equation.

Particle Size = $(0.9 \times \lambda)/ (d \cos\theta)$

Where λ = 1.54060 Å (due to the XRD equipped with an X'Celerator RTMS Detector using Cu Kα radiation.

The XRD data to calculate the average crystallite size following the Scherrer's equation was shown on Table 3.

From BET measurements for the CeO_2 nanoparticle, it was possible to note that the pore volume V_p= 0.2724 cm^{3}g^{-1} and pore size R_p = 3.15nm. The data was shown in Figure 3 and Figure 4.
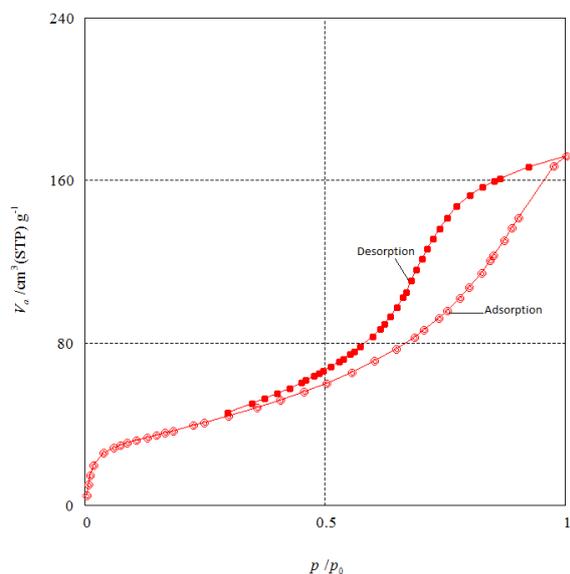
Fig. 3. The quantity adsorbed V_a as function of relative pressure (isotherm liner plot) of the Ce4 sample.
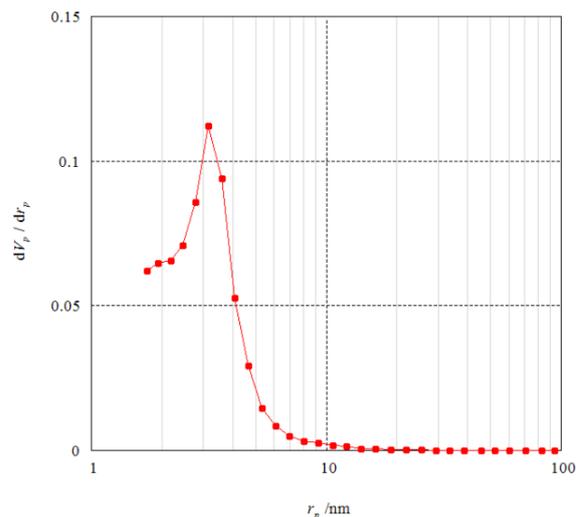
Fig. 4. The derivative vapor pressure (dV_p/dr_p) as a function of pore size of the Ce4 sample.

This proved that CeO_2 nanoparticles with high surface area and mesoporosity were successfully synthesized by template-assisted precipitation method.

TEM images for CeO_2 nano particles are shown in Figure 5. As can be seen in the TEM image for Ce4 sample, the crystalline CeO_2 size varied from 3 to 5 nm (the dark domain represents CeO_2 in the Figure 5 (a)). The pore size was above 3 nm, covered by CeO_2 (the bright domain represents CeO_2 in the Figure 5(b)). These results were found to be in good agreement with XRD and BET data.

| (a) | (b) |
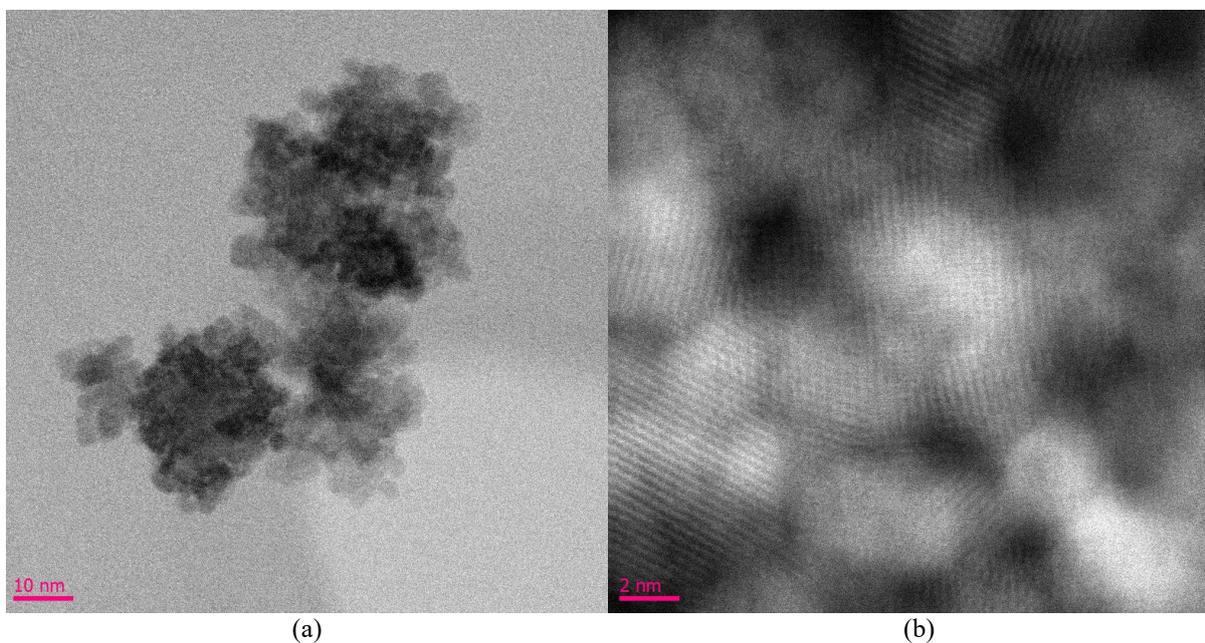
Fig. 5. Transmission electron micrographs of the Ce4 sample at two different magnifications.

4. Conclusion

Template-assisted precipitation method has been used successfully to synthesize nanocrystalline CeO_2 support with markedly high surface area ($159.5 m^2 g^{-1}$) and mesoporosity (pore volume of $0.2724 cm^3 g^{-1}$ and pore size of 3.15nm). The optimal conditions for cerium oxide synthesis were using cerium nitrate precursor using surfactant CTAB with stoichiometric ratio Ce^{3+}: CTAB of 1:0.6, adjusting the final pH solution to 11.4 by NH_4OH and ethylene diamine (EDA) and calcination at 550°C in air for 3 hours. The role of surfactant CTAB had been proved in the templatate-assisted precipiation method. The TEM results were found to be in a good agreement with the XRD and BET data.

References

[1] A. Trovarelli, Catalysis by ceria and related materials, Imperial College Press, London (2002).

[2] L Vivier, D Duprez, Ceria-based solid catalysts for organic chemistry, ChemSusChem, 3 (2010) 654-678.

[3] J Kašpar, P Fornasiero, M Graziani, Use of CeO_2-based oxide in the three-way catalysis, Catalysis Today, 50 (2) (1999) 285-298.

[4] A. Trovarelli, Catalytic properties of ceria and CeO_2-containing materials, Catalysis Reviews, 38(4) (1996) 439-520.

[5] C. Fink, A. Hagemeyer, Z. Hogan, A. Volpe, High surface area cerium oxide, Current Catalysis, (2016) 5(3) 182-202.

[6] TH. Vuong, J. Radnik, M. Schneider, H. Atia, U. Armbruster, A. Brueckner, Effect of support synthesis methods on structure and performance of VO_x/CeO_2 catalysts in low-temperature NH3-SCR of NO, Catalysis Communications, 84 (2016) 171-174.

[7] Yuejuan, W., Jingmeng, M., Mengfei, L., Ping, F., & Mai, H. (2007). Preparation of high-surface area nano-CeO2 by template-assisted precipitation method. Journal of rare earths, 25(1), 58-62.

[8] ES. Bickford, S. Velu, C. Song, Nano-structured CeO_2 supported Cu-Pd bimetallic catalysts for the oxygen-assisted water–gas-shift reaction, Catalysis Today, 99 (3-4) (2005) 347–357.

[9] A. Bumajdad, MI. Zaki, J. Eastoe, L. Pasupulety, Microemulsion-based synthesis of CeO_2 powders with high surface area and high-temperature stabilities, Langmuir, 20 (2004) 11223-11233.

[10] N. Phothammachai, M Rumruangwong, E.Gulari, A.M.Jamieson, S.Jitkarnka, S.Wongkasemjit, Synthesis and rheological properties of mesoporous nanocrystalline CeO2 via sol–gel process, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 247 (1-3) (2004) 61-68.

[11] MN. Guo, CX. Guo, LY. Jin, YJ. Wang, JQ. Lu, MF. Luo, Nano-sized CeO_2 with extra-high surface area and its activity for CO oxidation, Materials Letters, 64 (2010) 1638-1640.

[12] M. F. Islam, E. Rojas, D. M. Bergey, A. T. Johnson, and A. G. Yodh, High weight fraction surfactant solubilization of single-wall carbon nanotubes in water, Nano Letters, 3(2) (2003) 269–273.

[13] H.-P. Lin and C.-Y. Mou, Structural and morphological control of cationic surfactant-templated mesoporous silica, Accounts of Chemical Research, 35(11) (2002) 927–935.

[14] T.T. Thuy, S Hoste, GG Herman, N Van de Velde, K De Buysser, I Van Driessche, Novel water-based cerium acetate precursor solution for the deposition of epitaxial cerium oxide films as HTSC buffers, Journal of Sol-gel Science and Technology, Vol. 51(1) (2009) 112-118.

[15] T.T. Thuy, V Narayanan, N Van de Velde, K De Buysser, P Lommens, GG Herman, V Cloet, I Van Driessche, A nitrilo-tri-acetic acid/ acetic acid route for the deposition of epitaxial cerium oxide films as HTSC buffer layers, Journal of Solid State Chemistry, Vol. 183(9) (2010) 2154-2160.

[16] M Kurian, C Kunjachan, Effect of lattice distortion on physical properties and surface morphology of nanoceria framework with incorporation of iron/zirconium, Nano-Structures & Nano-Objects, 1, (2015), 15-23.

[17] Sun, C., Li, H., & Chen, L. (2012). Nanostructured ceria-based materials: synthesis, properties, and applications. Energy & Environmental Science, 5(9), 8475-8505.