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# Calcination temperature and molar ratio effects of nanosized CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> synthesized within reverse micelles of surfactant/cyclohexane/ water microemulsion

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A porous composite of ceria and lanthana/g-alumina was prepared by inverse microemulsion method. The precursor is heated at several calcination temperature between 823 to 1123 K. Also, the effect of different molar ratio of Ce: La on the crystallization was studied. The study of X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and temperature programmed reduction (TPR) suggested that well crystalline nanosized particles are obtained. The product samples possess mesoporosity with broadly distributed pores between 14 to 22 nm diameter. Surface area increases by increasing the calcination temperature. Also, the particle size of the composite samples decreases with an increasing in molar ratio of Ce: La.

Key words: Reverse micelle, Cerium oxide, Lanthanum oxide, Aluminum oxide, Triton X- 114, Calcination temperature.

# Introduction

Preparation of materials within reverse micelles belong to the family of wet synthesis procedures [1, 2], known of a number of advantages comparing to the traditional high-temperature solid-state processing methods, such as excellent control of the final powders stoichiometries with possibilities of obtaining homogeneity and mixing on narrow particle sizes, atomic scale, negligible contamination of the product during the homogenization of the starting compounds, low aging time, low energy consumption and simple equipment. A number of research have been studied on parameters of reverse micelle synthesis of nano-particles, with a controlled and manipulated data using a variety of design procedures, include: surfactant to co-surfactant [3], water to surfactant [4-6], surfactant effect [7], ionic strength and molar ratio [8-10], aging time [11], temperature [12] and solvent effect [13]. However, due to the signs of frequent uniqueness and significant narrowness of limiting conditions in the processes of reverse micelle preparation of materials, deep question have recently been raised upon the problem of justifying the generalization of relationships between the obtained particles and particular parent microemulsion systems [14]. Moreover, it was found out that the preparation conditions significantly affect the structural properties and the crystallization of individual metal oxide mixtures [15-24]. It is known that the surface structure on small metal nanocrystals may vary drastically and, as a consequence, their size distribution

may play a critical role in structure-sensitive catalytic reaction [25].

A growing interest in aluminum, lanthanum and cerium oxides results from their wide use in variable physicochemical applications. For example, g-alumina is employed as a gas desiccant and in the processes of oil purification and reforming of ethanol [26]. Alumina also plays an important role as a filling compound for different composite ceramics. Lanthanum oxide, for instance, sesquioxide (La<sub>2</sub>O<sub>3</sub>) is also a component of various composite materials both as a main constituent or an additive. Lanthana additive improve chemical, optical and mechanical properties. Ceria (CeO<sub>2</sub>) is one of the oxides which are mostly used to progress the performance of alumina. CeO<sub>2</sub> is a multifunctional rare earth oxide with various chemical and physical properties. Ceria can affect the structural stability and thermal stability of alumina, the degree of dispersion of a metal catalyst supported on an alumina catalyst carrier [27]. Thus, CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are used in many ways for catalytic processes.

This paper reports on the synthesis of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles based on the sol-gel process controlled within reverse micelles of non-ionic surfactant Triton X-114 in cyclohexane for the first time. Besides the presentation of a new preparation approach of metal mixed oxides, this work focuses on the study of the effect of different calcinations temperature and different molar ratio of Ce : La on the crystallization, the crystallite-growth of formed nanocrystalline phases and the phase composition, since according to the literature data mentioned above the preparation route plays the key role. A quantitative X-ray diffraction phase content was also carried out.

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# **Experimental**

Cerium (III) nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O, Sigma Aldrich), lanthanum nitrate (La(NO<sub>3</sub>)<sub>3</sub>, Sigma Aldrich), aluminum isopropoxide (Al(C<sub>3</sub>H<sub>7</sub>O)<sub>3</sub>,Sigma Aldrich), cyclohexane (HPLC grade, Sigma Aldrich), nonionic surfactant Triton X-114 ((1,1,3,3-tetramethylbuthyl) phenyl-polyethylene glycol, C<sub>29</sub>H<sub>52</sub>O<sub>8.5</sub>, Sigma Aldrich), absolute ethanol (water content max. 0.2 vol%, Sigma Aldrich) and double distilled water were used as precursors for the synthesis.

Ceria, lanthana and alumina mixed oxides powders were prepared via sol-gel processing controlled within reverse micelles of nonionic surfactant Triton X-114 in cyclohexane that Fig. 1 shows the flow chart for the preparation of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. Cyclohexane was used as organic solvent. Ceria, lantana and alumina mixed oxides powder with various  $(CeO_2 + La_2O_3)$ :  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> molar ratios (0.2 : 0.8, 0.5 : 0.5 and 0.8 : 0.2):3 were prepared. In the first step of preparation the ceria and lantana sol was prepared: cerium (III) nitrate hexahydrate (0.1302 g) and lanthanum nitrate (0.5196 g) (for Ce : La; 0.2:0.8) was dissolved in absolute ethanol (4.5 ml) under vigorous stirring. In the second step, cyclohexane (24.6 ml) was mixed with Triton X-114 (21.6 ml) and distilled water (0.6 ml) followed by the addition of ceria and lanthana sol. The sol was stirred for 30 min. In the final step, aluminum isopropoxide (0.90 ml) was fluently injected



Fig. 1. Schematic diagram of synthesize of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> $/\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles by reverse microemulsion method.

into the mixture. The precursor micellar ceria and lanthana/y-alumina sol with different molar ratios of Ce : La was stirred for 30 min. Then, the homogeneous transparent sol was poured into Petri's dishes in a thin film layer and then dishes were left standing on air up to the conversion of the sol into the gel. In general, the precursor ceria-lanthana-alumina sols were prepared keeping the molar ratio of cyclohexane: Triton X-114: H<sub>2</sub>O: Al(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>: (Ce(NO<sub>3</sub>)<sub>3</sub>.  $6H_2O + La(NO_2)_3$ . 6H<sub>2</sub>O) at 16.5 : 3 : 3 : 1 and the used amount of absolute ethanol was 4.5-7.5 ml, depending on the amount of dissolved molar ratio of Ce:La. The gelation period of individual ceria-lanthana-alumina sols differed quite a lot: it was from 48 h to 2 weeks which showed a strong dependence on ambient temperature and humidity. Finally, the gels were thermally treated in air at 62 3 K for 5 h and calcined from 823 to 1123 K for 5 hrs.

#### Characterization

Surface area of the samples were determined by N<sub>2</sub> adsorption/desorption isotherm at 77 K, using the BET (Brunauere, Emmette and Teller) analysis method, in a Tristar Micromeritics 3000 flow apparatus. BET surface area was obtained according to BET method at relative pressure between 0.005 and 0.09. The total pore volume was calculated based on the adsorbed nitrogen volume at the highest relative pressure, while the average pore size diameter was determined by the Barrett, Joyner and Halenda at 523 K overnight. X-ray powder diffraction analysis of the samples were carried out with Philips 3100 diffractometer (Koninklijke Philips Electronics N.V., Eindhoven, the Netherlands) using Cu K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.15406$  nm). The powders were spread evenly on a 2 mm thick quartz plate. Crystallite size analysis of samples was calculated from full width at half maximum (FWHM) using Scherer's equation. Deby Scherer relation is given as;

$$d = \frac{0.9\lambda}{\beta \cos \theta} \tag{1}$$

where d is the average crystallite size,  $\lambda$  is the full width at half maximum,  $\lambda$  is the X-ray wavelength (1.542 Å) and  $\theta$  is the angle of diffraction.

Imaging of the powders was completed using a Hitachi S-4700 scanning electron microscope (Hitachi Ltd., Tokyo, Japan). The powder samples were imaged by dispersing them on carbon tape followed by sputter coating with platinum. Transmission electron microscope (TEM) observation was made at an accelerating voltage of 200 kV by placing the powder on a copper grid in order to obtain the morphology and size of the powders. The average size of the particles was estimated from the TEM micrograph using standard image analysis software (IMAGE J).

Temperature-Programmed Reduction (TPR) studies were carried out in a Micrometrics TPR/TPD 2900 instrument equipped with a W-Au thermal conductivity detector and connected to an Olivetti mod. 330-28 acquisition data station at a heating rate of  $10 \text{ °C.min}^{-1}$ . The reducing agent used was a H<sub>2</sub>/Ar mixture (5% vol.). The amount of hydrogen consumed was determined upon integration of the areas under the peaks, after calibration of the instrument with CuO (from Merck).

# **Results and Discussions**

Fig. 2 shows the XRD patterns of the ceria and lanthana/y-alumina precursor with different calcinations temperature (823-1123 K) in air for 5 hrs and different molar ratio of Ce : La (0.2 : 0.8, 0.5 : 0.5 and 0.8 : 0.2) on the crystallization. After heating the precursor at 823 K in air for 5 hrs, the powder is nearly amorphous. Increasing the calcinations temperature to 1123 K, the crystallinity increases and all phases has been identified. With increasing the temperature, the diffraction peaks become sharper indicating the growth of the particles. Also, Fig. 3 shows the XRD patterns of ceria and lanthana/g-alumina with different molar ratios of Ce: La calcined at 1123 K for 5 hrs. Each crystalline phase was identified using JCPDS. With increasing Ce : La molar ratio in samples, major diffraction peaks of CeO<sub>2</sub> shifted to lower  $2\theta$  value. In addition, XRD peak intensity and crystalline phase of nano-catalysts were affected by the variation of Ce : La molar ratio. In the Ce: La (0.2:0.8) molar ratio, a slight shift of diffraction peaks of cubic CeO<sub>2</sub> to lower angle was only observed without phase splitting. In the Ce: La (0.5:0.5 and 0.8:0.2) molar ratios, on the other hand, XRD peaks resulting from the formation of solid solution with cubic phase were gradually developed with increasing Ce : La molar ratio.

Fig. 4 shows the TEM images of nanoparticles synthesized with different molar ratio of Ce:La and the particle size distribution is included as inset. The digitized images were imported into the program, Image J and the population of particles with respect to mean particle diameter was determined. 34 particles were measured from TEM micrograph to establish particle size distribution histograms. The histograms



**Fig. 2.** The XRD patterns of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> $/\gamma$ -Al<sub>2</sub>O<sub>3</sub> at different calcination temperatures; (a) at 823, (b) 973 and (c) 1123 K.



**Fig. 3.** The XRD patterns of  $CeO_2$  and  $La_2O_3/\gamma$ -Al<sub>2</sub>O<sub>3</sub> with different Ce : La molar ratio at 1123K: (a) 0.2:0.8, (b) 0.5 : 0.5 and (c) 0.8 : 0.2.

were created using Image J with binning widths of 5 nm. The mean sizes and standard deviations resulted from Image J are 20.7 and 4.6 nm, respectively.

Surface area, average particle size and pore volume were determined by XRD, BET and  $N_2$  adsorption/desorption measurements that is shown in Table 1. The



Fig. 4. TEM images of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with different Ce : La molar ratio at 1123 K; (a) 0.2 : 0.8, (b) 0.5 : 0.5 and (c) 0.8 : 0.2.

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<b>Table 1.</b> Chemical and physical properties of CeO <sub>2</sub> and La <sub>2</sub> O <sub>3</sub> / $\gamma$ -
Al <sub>2</sub> O <sub>3</sub> with different molar ratios determined by XRD, BET and
N <sub>2</sub> adsorption- desorption measurements.

Supports $CeO_2 + La_2O_3)/\gamma - Al_2O_3$	Average diameter (XRD) (nm)	Particle size (TEM) (nm)	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume $(cm^3g^{-1})$
(0.2 + 0.8)/3	22	35	79	0.354
(0.5 + 0.5)/3	17	28	83	0.429
(0.8 + 0.2)/3	14	23	96	0.495

 Table 2.
 Molar ratio and phase composition of samples determined by SEM-EDX and XRD measurement.

$\begin{array}{c} Supports \\ (CeO_2 + La_2O_3) / \\ \gamma \text{-}Al_2O_3 \end{array}$	$\begin{array}{c} Measured \\ molar ratio \\ (CeO_2 + La_2O_3) / \\ \gamma \text{-}Al_2O_3 \\ (SEM\text{-}EDX) \end{array}$	Phase composition
(0.2 + 0.8)/3	0.22:0.79/2.82	γ-Al <sub>2</sub> O <sub>3</sub> , La <sub>2</sub> O <sub>3</sub> , CeO <sub>2</sub>
(0.5 + 0.5)/3	0.46:0.53/3.12	γ-Al <sub>2</sub> O <sub>3</sub> , La <sub>2</sub> O <sub>3</sub> , CeO <sub>2</sub>
(0.8 + 0.2)/3	0.82:0.23/2.75	γ-Al <sub>2</sub> O <sub>3</sub> , CeO <sub>2</sub> , La <sub>2</sub> O <sub>3</sub>

average particle size obtained from TEM is bigger than that observed from X-ray diffraction lines-broadening analysis. This may be due to the agglomeration of fine particles [28], which occurs not during the chemical synthesizing procedure, but during the isolation of the particles from their parent microemulsion. Table 2 shows molar ratios and phase composition of samples that were determined by SEM-EDX and XRD measurements.

The SEM micrographs are shown in Fig. 5. By increasing the molar ratio Ce:La, the particle size decrease gradually. TEM images (Fig. 4) also provide similar information obtained from SEM images.

TPR measurements were carried out to investigate the reducibility of samples and to observe the interaction between metal oxides. Fig. 6 shows the TPR profiles of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with different Ce : La molar ratio. The Ce : La (0.2 : 0.8, 0.5 : 0.5 and 0.8 : 0.2) molar ratios of catalysts are shown in Fig. 6. However, the broad reduction speaks starting from around 673 K appeared within the range of 923-1723 K. Furthermore, continuous H<sub>2</sub> consumption was observed even after the appearance of main reduction peaks. It is interesting to



Temperature (°C)

**Fig. 6.** The TPR profiles of  $CeO_2$  and  $La_2O_3/\gamma$ -Al<sub>2</sub>O<sub>3</sub> with different Ce : La molar ratio; (a) 0.2 : 0.8, (b) 0.5 : 0.5 and (c) 0.8 : 0.2.

note that the reduction peak position shifted to lower temperature with increasing Ce : La molar ratio in catalysts. It was reported [29] that phases CeO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub> showed a double reduction peaks at 923 to 1723 K. It is found that continuous H<sub>2</sub> consumption at high temperature might cause the sample sintering during the reduction process. It is considered that the shift of reduction peaks of catalysts with 0.4, 0.6 and 0.8 molar ratios to lower temperature with decreasing Ce/La molar ratio can be explained by the fact that highly concentrated Ce<sup>4+</sup> with redox feature enhances the oxygen mobility and oxygen storage capacity [30]. The low-temperature tailing observed in the Ce/La 0.4, 0.6 and 0.8 molar ratio samples might be related to the reduction of CeO<sub>x</sub> species weakly interacted with lantanium oxide.

# Conclusions

A porous composite of ceria and lanthanum/galumina was successfully carried out by inverse microemulsion method. The product samples prepared at different calcination temperature and different molar ration of Ce : La with broadly distributed pores between 14 to 22 nm pore diameter. Increasing the calcinations temperature to 1123 K, the crystallity increased and all the phases were identified. The BET surface area



**Fig. 5.** SEM images of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with different Ce : La molar ratio at 1123 K; (a) 0.2 : 0.8, (b) 0.5 : 0.5 and (c) 0.8 : 0.2.

decreased by increasing the calcinations temperature. Also, the particle size of the composite samples decreased with increasing molar ratio of Ce : La.

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