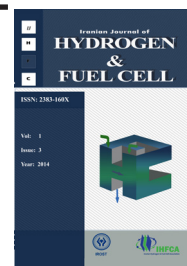


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Optimization of Preparation Factors for Cerium Oxide Synthesis as a Support for CO PrOx Catalyst

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Abstract

Nanocrystalline ceria has been considered as support for carbon monoxide preferentially oxidation. In this study ceria was prepared by precipitation method and the effects of preparation conditions, such as pH of solution (8-10), aging time (1-12 hr), drying temperature (80-120°C), calcination time (2-6 hr) and temperature (400-600°C) were investigated on ceria synthesized powders properties. Nanocrystalline ceria were characterized by thermal gravimetric analysis (TGA), X-ray diffraction (XRD) and ASAP analysis. Calcination temperature and pH of solution have the highest effect on powder specific area. Finally, optimum conditions for the synthesis of cerium oxide in this study are pH = 10, aging time = 6 hr, drying temperature = 120°C, calcination time = 6 hr, and temperature = 500°C. Crystalline size of ceria is lower than 20 nm and in the shape of sphere-like and maximum surface area is 74.45 m²/g. 7%CuO/CeO₂ catalyst was prepared by wetness impregnation method and was tested in catalyst for oxidation of CO in presence of hydrogen (preferentially oxidation, PrOx). The CO conversion and CO₂ selectivity was achieved 57.3 – 98% and 83-40% by temperature increasing from 80-180 °C, respectively.

1. Introduction

In recent years, CeO₂ nanocrystalline plays an important role as a catalyst, support and promoter in many processes, as well as CO oxidation [1], removing of NO_x [2], reforming [3], WGS reaction [4,5], preferential oxidation (PrOx) [6], etc. Several methods for the synthesis of ceria have been studied, such as precipitation (hydrothermal and nonhydrothermal) [7-10], solvothermal [11,12], micro emulsion [13], alcohothermal [14], microwave hydrothermal [15] methods. Among these methods,

due to the advantages of the simple process, easy scale-up and low cost, the precipitation technique has attracted the most extensive attention [16]. For example, Zhou et al. [17] produced CeO₂ particles of about 4 nanometers from cerium nitrate and ammonia. Matijevic and Hsu [18] prepared sub-micron Ce₂O-(CO)₂-H₂O particles from cerium nitrate with urea. Chen and Chen [19] prepared CeO₂ particles from cerium nitrate with hexamethylenetetramine, whereas Li et al. [20] used ammonia carbonate and diethyl amine as precipitating agent. Yamashita et al. [21] produced CeO₂ particles from cerium chloride

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and sodium hydroxide in the presence of hydrogen peroxide under various pH conditions. Uekawa et al. [22] obtained 7–9 nm CeO_2 particles starting from cerium nitrate in the polyethylene glycol solution [16]. On the other hand, the PEMFC's ideal fuel is hydrogen; it can be produced through steam reforming of fossil fuels (such as natural gas, methanol, ethanol ...) followed by the water gas shift reaction. A subsequent WGS reaction reduces the amount of CO to nearly 1% [24]. The PEMFC anode catalyst which are operated at relatively low temperature (80°C) easily poisoned by trace of CO in the hydrogen rich feed gas. The preferential oxidation (PrOx) process is one of the most effective methods for the removal of CO trace from the reformat stream. CO PrOx is a reaction to convert CO in a H_2 rich gas mixture to CO_2 with minimal H_2 consumption.

In this paper, the effect of preparation factors in precipitation method such as pH of reaction, drying temperature, calcination temperature and time were investigated on ceria properties. Maximizing surface area (BET) and minimization of pore diameter of ceria powder were used as an objective function in optimization process. Automatic design and analysis of Taguchi experiments method was used and Qualitek software was used for data analysis. Moreover the effect of aging time was investigated. Finally, the optimum ceria was used as a support for Cu catalyst and were tested in CO-PrOx operation conditions.

2. Experimental

2.1. Preparation of ceria powder

Fig. 1 shows the preparation steps of ceria synthesis. 1M homogeneous aqueous solution of cerium nitrate was prepared by solution of $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ (Loba chemi, 99.9%) powder in deionized water. Then ammonia $[\text{NH}_3]$ (Merck, 25%) was added slowly to reach the desired pH (8–11). The resulting suspension was left to settle for 1 hr. The precipitate was filtered and washed with deionized water.

Finally, the ceria cake dried overnight (in various temperatures = 80, 100 and 120°C). The dried precipitate was calcinated in different times and temperatures ($T_c = 400, 500$ and 600°C and $t_c = 2, 4$ and 6 hr).

The CuO/CeO_2 catalyst was prepared by wetness impregnation method with copper nitrate solution $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$ (Merck, 99.5%) and the optimum ceria sample for catalytic activity of ceria as support in CO-PrOx process. The catalyst was then dried at 120°C for 12 hr and calcinated at 500°C for 4 hr in air.

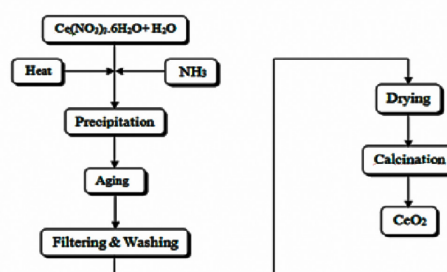


Fig. 1. Preparation scheme for cerium oxide synthesis.

2.2. Design of experiments

There are many parameters which affect the chemical and physical properties of ceria powder. To determine the effects of preparation conditions on the ceria powder synthesis, reaction pH, drying temperature, calcinations temperature and time were considered as the most important parameters. A design of experiment (DOE) method is necessary for the experimental work which involves many inputs to minimise the number of experiments needed to be preformed. The most frequently used methods are partial or full factorial and the Taguchi approach. The method is based on balanced orthogonal arrays. In this work, L9 orthogonal array consisting of 9 experiment trials and 4 columns was used (see Table 1).

The main variables involved in this study and the BET surface area of the final product results are shown in Table 1. Three levels for each variable refer to the maximum and minimum limits that influence the BET surface area of the final product.

Table 1. L₉ Orthogonal array, Factor level in the experiments and results.

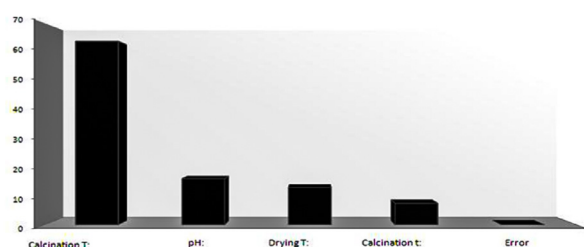
Exp. No.	Parameter Levels				PH	Drying Temp.	Calcination Temp.	Calcination time	Surface Area
	(A)	(B)	(C)	(D)		°C	°C	hr	(m ² /g)
1	1	1	1	1	8	80	400	2	44.68
2	1	2	2	2	8	100	500	4	48.64
3	1	3	3	3	8	120	600	6	38.84
4	2	1	2	3	9	80	500	6	48.71
5	2	2	3	1	9	100	600	2	37.78
6	2	3	1	2	9	120	400	4	48.53
7	3	1	3	2	10	80	600	4	34.02
8	3	2	1	3	10	100	400	6	61.38
9	3	3	2	1	10	120	500	2	61.14

Results of Taguchi experimental method was analyzed by Qualitek-4 program. Effect percent of all factors showed in Table 2 and Fig 2. ANOVA (ANalysis Of VAriance) is used to determine the significant level and contribution of each variable to the surface area of ceria powder. As shown in Table 2, the most parameters affected on BET results were calcinations temperature, pH, drying temperature and time of calcinations, respectively.

Finally, optimum conditions to achieve higher surface area were determined and presented in Table 3.

Table 2. Analysis of variance (ANOVA).

	Factors	DOF	Sum Of Squares	Variance	Pure Sum	Percent
1	pH	2	118.406	59.203	118.406	15.999
2	Drying Temp.	2	95.719	47.859	95.719	12.933
3	Calcination Temp.	2	470.712	235.356	470.712	63.603
4	Calcination time	2	55.233	27.616	55.233	7.463

**Fig. 2. Significant factors and interaction influence.**

To investigate the effect of aging time on precipitation and finally ceria powders properties, after samples synthesized in optimum conditions of pH, drying temperature, calcinations time and temperature (see Table 3), three specimens were prepared by varying

Table 3. Optimum conditions suggested by Qualitek-4.

	Factors	Level Desc.	Level
1	pH	10	3
2	Drying T	120 °C	3
3	Calcination T	500 °C	2
4	Calcination time	6 hr	3

the aging time for precipitation, means 1, 6 and 12 hr.

2.3. Characterization of samples

Thermal gravimetric analysis (TGA) was performed using PL-STA-1640 equipment. Approximately, 15 mg of ceria powder was exposed in air and the temperature was increased from room temperature to 600 °C (increasing rate of 5 °C/min).

Also the XRD patterns were recorded on an X-ray diffractometer (PANalytical X'Pert-Pro) using a Cu K α monochromatized radiation source and a Ni filter in the range $2\theta = 20 - 80^\circ$. The XRD patterns of ceria, sample 4 and ceria synthesized at optimum conditions have been presented in Fig. 3. The crystalline mean particle sizes of ceria catalyst have been determined by the X-ray broadening technique employing the Scherrer formula as:

$$d_{XRD} = \frac{0.9\lambda}{FWHM \cos \theta} \quad (1)$$

Where λ is the X-ray wavelength (1.5406 Å), FWHM (in Rad) is the full width at half maximum of the characteristic peak (111) of CeO₂ and θ is the diffraction angle for the (111) plane.

The surface areas (BET), and mean pore diameter and total pore volume were determined by nitrogen adsorption at 77 K using an automated gas adsorption analyzer (Gimini, Micromeritics).

3. Result and discussion

3.1. Effect of Reaction pH

Reaction pH was one of the important parameters in

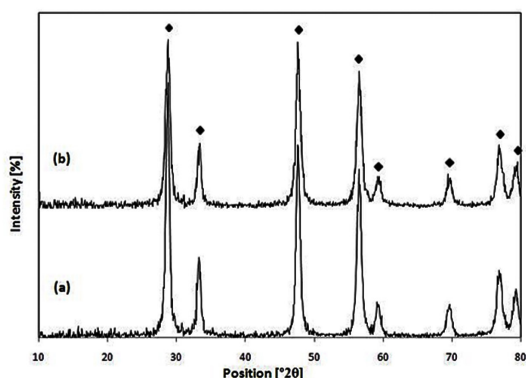


Figure 3. XRD patterns, (a) 4th sample and (b) sample prepared at optimum conditions.

catalyst synthesis that influenced on final powder properties. As the ammonia was added into the precursor solution, the $\text{Ce}(\text{OH})_3$ precipitate was formed immediately, subsequently, the $\text{Ce}(\text{OH})_3$ was oxidized to hydrated $\text{Ce}(\text{IV})$ ions in alkaline environment. Then further hydrolyzed to form $[\text{Ce}(\text{OH})_x(\text{H}_2\text{O})_y]^{(4-x)+}$ complex. Finally, the cerium (IV) hydroxide is deprotonated by water molecules to form cerium oxide (CeO_2) [16].

Simultaneously $\text{Ce}(\text{III})$ oxidation, H_3O^+ released and pH value decreased so to maintain the pH value constant, it is necessary to ammonia addition. In this paper, precipitation of ceria was performed at pH = 8, 9 and 10. Results showed that the cerium oxide surface area increased with increasing the pH.

3.2. Effect of calcination temperature

The influence of the calcination temperature of CeO_2 has been studied on the CeO_2 surface area. The ceria precursor was treated at three different temperatures (400, 500 and 600 °C). TGA results of the precursor demonstrated considerable weight loss between 50 and 450 °C (Fig. 4). No loss of weight was evident above 450 °C. Hence, CeO_2 calcinated powders at 500 °C and 600 °C had a little or no ammonia within the catalyst pores.

As shown in ANOVA's table (see Table 2), calcination temperature is significant parameter in determining the surface area. Two factors seem to determine the

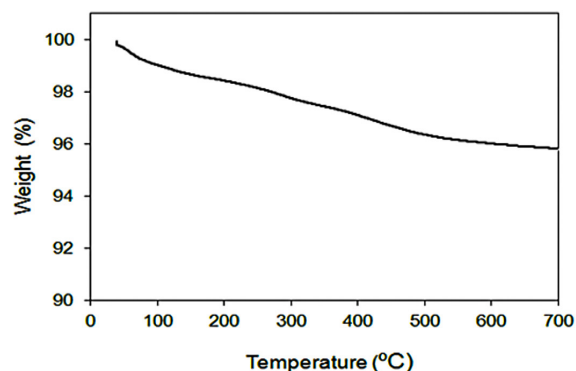


Figure 4. TGA curve for ceria before calcination.

surface area, i.e. pore blocking and particle sintering. Crystalline size decreasing as a result of increasing calcination temperature over the certain point. Calcination temperature above 500 °C would start to result in more severe particle sintering. Therefore an optimum BET is obtained at an intermediate calcination temperature [23]. BET result with calcination temperature of 500 °C (pH= 10, $t_c=2$ hr) was 61.14 m^2/g and it was more than BET obtained at 600 °C.

To verify these results, two more samples have been calcinated at 450 °C and 550 °C in abovementioned conditions of pH and t_c . Fig. 5 shows the BET results of these 4 samples and it was evident that the optimal temperature is 500 °C that was greater than 550 °C too.

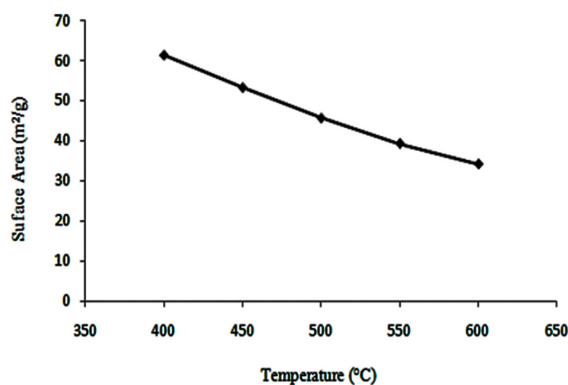


Fig. 5. Effect of calcinations temperature on surface area.

3.3. Effect of calcination time

We have studied the influence of calcination time on

the properties of CeO_2 by synthesis in three different times (2, 4 and 6 hr). The Qualitek results (Fig. 6) showed that higher calcination time, pH, drying temperature and middle calcinations temperature was suitable. The weak result of the calcinated ceria at lower time can be related to the limited time and incompletely ammonia removal, thus preventing of the formation of low crystalline size structure and blocking pores. Removing of these extraneous particles caused low crystalline size, higher BET and subsequently higher catalyst activity.

aging time on ceria properties has been investigated, by increasing of aging time from 1 to 12 hr. crystalline size decreased and subsequently surface area increased by increasing time from 1 to 6 hr, but surface area slowly decreased and pore volume increased by increasing it to 12 hr (see Table 4). More aging time caused bigger crystalline size and less agglomeration, and short time of aging increased the porosity of catalyst [23]. So this seem that the optimum aging time for ceria preparation was 6 hr (in the range of 1-12 hr) with a surface area of $74.45 \text{ m}^2/\text{g}$ and optimum value of mean

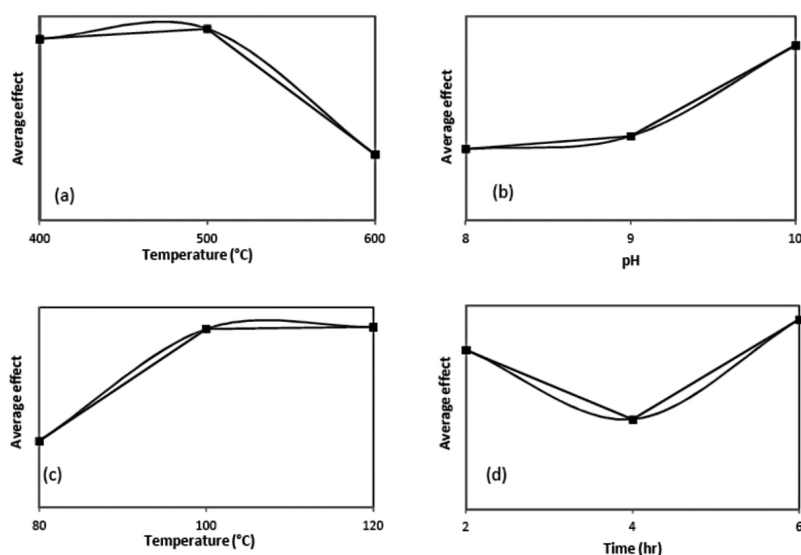


Fig. 6. Average effects of a) calcinations temperature, b) pH of solution, c) drying temperature and d) calcinations time, on the ceria surface area.

3.4. Effect of drying temperature

The ceria precursor after aging step was dried in three different temperatures (80, 100 and 120°C) for 12 hr. Higher surface area related to the sample that dried at higher temperature. Increasing of this temperature and removing of water and some of impurities caused to achieve a higher surface area. It is necessary to declare that the effect of this parameter was negligible.

3.5. Effect of aging time

In addition to the nine experiments which suggested by Taguchi method for 4 parameters, two more samples was prepared in different aging times. The effect of

pore diameter and total pore volume. Fig. 7 (a, b, c, d) depicts the typical SEM images for ceria powders which aged at 1, 6 and 12 hr, respectively. The results for morphology of samples were in agreement with aging time. Fig. 8 showed the adsorption/desorption isotherm of prepared powders at different aging time. With increasing of aging time the small particles dissolve continuously and the large particles grow unceasingly. Therefore, it is helpful to prolong the aging time for the growth and uniformity of the particles [10]. As shown in Fig. 9, pore size distribution were narrower in more aging time, this related to uniformity of the particles, moreover with increase of aging time, pore size distribution peak slowly shifted to the right side, means that pore size has been increased.

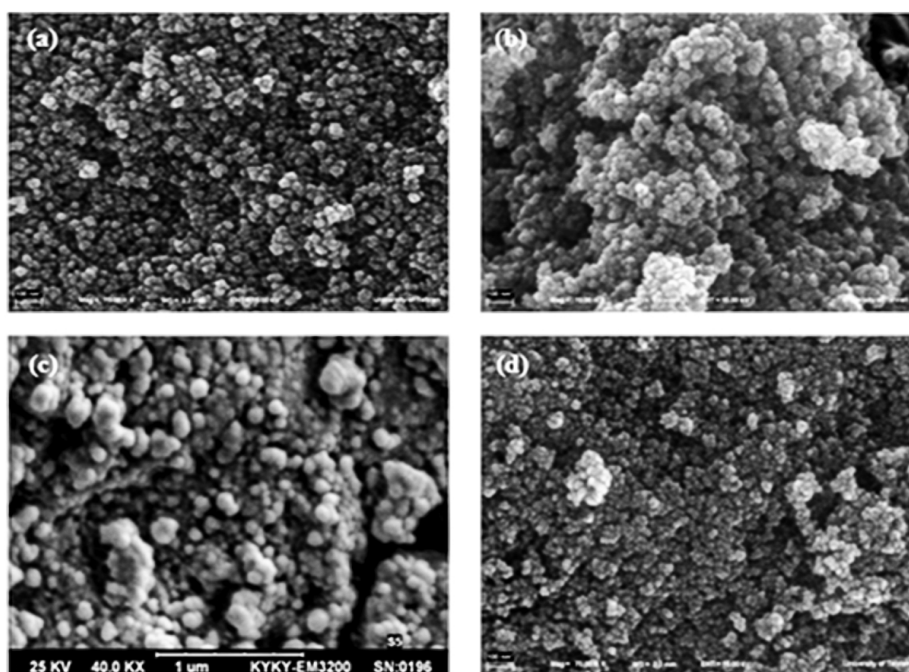


Figure 7. SEM for CeO_2 nano powders prepared at different aging time: Ceria aged at (a) 1 hr; (b, c) 6 hr (2 scales) and (d) 12 hr.

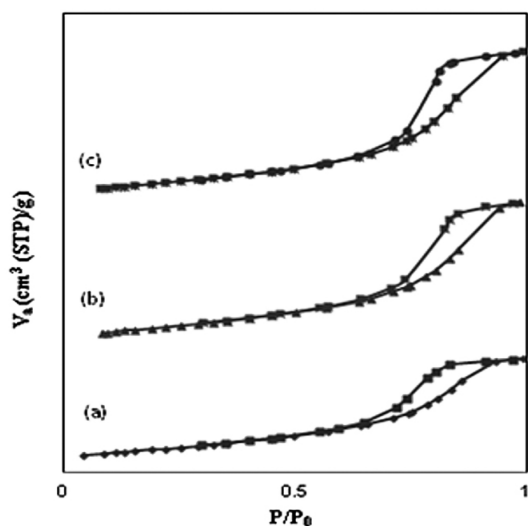


Fig. 8. Adsorption / desorption isotherm of powders prepared at different aging time: Ceria aged at (a) 1 hr; (b) 6 hr and (c) 12 hr.

3.6. Catalytic activity test

Activity test were carried out at temperature range (80-180 °C) for preferential oxidation process, in a fixed-bed quartz reactor (8 mm-ID) with 120 mg

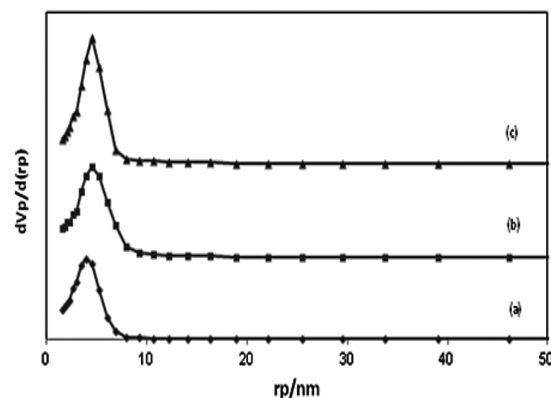


Fig. 9. Pore size distribution of sample prepared at optimum conditions with different aging time: Ceria aged at (a) 1 hr, (b) 6 hr, and (c) 12 hr.

of CuO/CeO_2 in atmospheric pressure. The setup for reaction was discussed in our previous work [25]. Gas feed composition was 2% CO , 2% O_2 , and 96% H_2 and the total flow rate was 40 ml/min corresponding to a space velocity of 20000 h^{-1} . Before the light-off tests the catalysts was pretreated at 400°C for 1 hr in O_2 stream with a flow rate of 20 ml/min. Inlet and outlet gases were analyzed by a Shimadzu-8A

chromatograph equipped with a TCD.

In this process two competing parallel reactions are important, the oxidation of CO and oxidation of H₂ (see Eqs. 2, 3).

The CO conversion and CO₂ selectivity were calculated according to Eqs. 4 and 5. The catalytic activity of Cu catalyst supported on synthesized CeO₂ showed in Fig. 10.

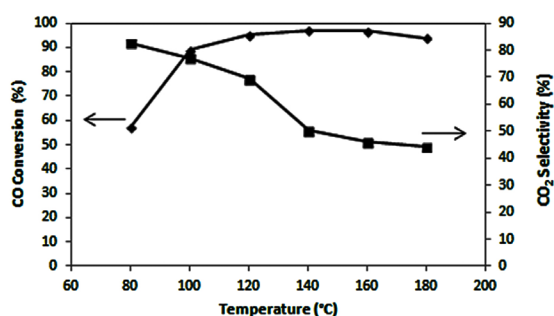


Fig. 10. CO conversion and CO₂ selectivity of 7%Cu/CeO₂ in $\lambda=2$ and GHSV=20000 h⁻¹.



$$\text{CO conversion}(\%) = \frac{[\text{CO}_{in}] - [\text{CO}_{out}]}{[\text{CO}_{in}]} \times 100 \quad (4)$$

$$\text{CO}_2 \text{ selectivity}(\%) = 0.5 \times \frac{[\text{CO}_{in}] - [\text{CO}_{out}]}{[\text{O}_{2in}] - [\text{O}_{2out}]} \times 100 \quad (5)$$

As shown in Fig. 10, using of ceria prepared in optimum conditions as a support for Cu catalyst, increased CO conversion from 57% to 98% by temperature increasing from 80 to 160 °C. CO₂ selectivity has been achieved nearly 83% in low temperature. So we can suggest this catalyst to use in final purification of hydrogen in low temperatures (80-140 °C).

4. Conclusion

Surface area of the prepared CeO₂ can be optimized to higher surface area by varying the preparation conditions include solution pH, aging time, drying temperature, time and temperature of calcination via precipitation method. Optimization was based on Taguchi design method with four factors (pH, T_d, T_c and t_c) and three level of them. The obtained BET surface area results were analyzed by Qualitek-4 program and optimum conditions were estimated.

The sample which synthesized in optimum conditions has BET surface area of 64.43 m²/g. By aging time variation on the optimum conditions, the BET surface area was increased to 74.45 m²/g at 6 hr of aging time. Appropriate activity of copper catalyst supported on this ceria showed the support surface area is the one of important factor in catalytic activity in the CO ProX process.

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Symbols Used

λ	excess of oxygen factor
λ [Å]	X-ray wavelength
ANOVA	ANALYSIS Of VARIANCE
ASAP	Accelerated Surface Area and Porosimetry
BET	Brunauer–Emmett–Teller
D _{XRD} [nm]	Crystalline mean particle sizes
DOE	Design Of Experiment
GHSV [h ⁻¹]	Gas Hourly Space Velocity
FWHM	Full Width at Half Maximum of the characteristic peak
PEMFC	Proton Exchange Membrane Fuel Cell

PROX	Preferentially Oxidation
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetric Analysis
WGS	Water-Gas Shift
XRD	X-Ray Diffraction

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