Preparation, Characterization and Optimization of High Surface Area Ce-La-Cu Ternary Oxide Nanoparticles

Seyyed Ebrahim Mousavi and Hassan Pahlavanzadeh*
Faculty of Chemical Engineering, Tarbut Modares University, Tehran, Iran

Habib Aliebrahim
Faculty of Chemical Engineering, Petrochemical center of Excellency, Amirkabir University of Technology, Tehran, Iran

(Received 9 June 2017; Accepted 30 August 2017; Published 23 September 2017)

In this article, CeO$_2$-La$_2$O$_3$-CuO ternary oxide nanoparticles were synthesized using co-precipitation method. Taguchi experimental design was used for producing high surface area ternary oxides. The effect of precipitating agent and its concentration, percentage of lanthanum and copper, calcination temperature, and calcination time, on the surface area of nanoparticles, were studied. The synthesized nanoparticles were characterized by SEM, BET surface area, XRD, EDX, N$_2$ adsorption isotherm, and BJH pore size distributions. The maximum surface area obtained for these nanoparticles was 99.4 m$^2$/g. Also, performance of ternary oxides was examined in the reactor test, as a catalyst. [DOI: 10.1380/ejssnt.2017.87]

Keywords: Ternary oxide nanoparticles; High surface area nanoparticles; Taguchi method; Cerium-Lanthanum-Copper

I. INTRODUCTION

Ceria-based metal oxide catalysts are of great importance and are widely used in various industrial processes and environmental pollution control reactions. Due to versatile properties of cerium oxide for various applications, the use of binary and ternary combinations of metal oxides (including ceria) has increased in recent years [1, 2].

Various ternary combinations of cerium oxide have been studied in the literatures. Ce-Mn-Al for soot oxidation [2], Ce-Cu-Zr for CO removal from hydrogen-rich gas [3] and catalyst deep oxidation of benzene [4], Ce-Zr-Nd for gasoline engine exhaust reduction [5], Ce-Cu-V for carbon black oxidation [6], Ce-Cu-Zr for methane dry reforming [7], Ce-Au-La for water gas shift reactions [8], Ce-Ni-La for partial oxidation of methane [9], Ce-Ca-Mn for CO$_2$ oxidative coupling of methane [10], Ce-Zr-Al as an oxidation agent [11], and Ce-Ni-Zr for hydrogen storage [12] have been proposed. Given the importance of ternary oxide combinations, cerium-lanthanum-copper ternary oxide was studied in this research. Ternary-gasification catalysts were used as a catalyst in water-gas shift reaction [13–15], and wet oxidation of ammonia solution [16].

Also, Ce-La-Cu and Ce-Zr-Cu tri-oxides have been extensively used for SO$_2$ reduction by CH$_4$ [17]. Moreover, Ce-La-Cu and Ce-La-Ni tri-oxide catalysts have been compared in SO$_2$ reduction by CH$_4$ [18]. The copper-doped catalysts (Ce-La-Cu) showed higher SO$_2$ conversion and sulfur yield [18].

Consequently, Ce-La-Cu tri-oxide is a selective catalyst for SO$_2$ reduction by CH$_4$ to sulfur. The specific surface area of such ternary metal oxide is a key parameter in increasing a catalyst activity, especially in gas-solid reactions. Thus, it is necessary to maximize the specific surface area of Ce-La-Cu tri-oxide by adjusting the effective synthesis conditions, through an experimental design method.

In this study, combinations of Ce-La-Cu, in the form of ternary metal oxide nanoparticles, were prepared and their specific surface areas were maximized using Taguchi experimental design method. First, the effect of precipitating agent and its concentration on surface area of nanoparticles was investigated. Then, the percentage of lanthanum and copper, calcination temperature, and calcination time were determined, by Taguchi method, for maximum specific surface area. Finally, the effect of polyvinylpyrrolidone surfactant and ultrasonic, on the surface area of optimized nanoparticles, were studied.

II. EXPERIMENTAL

A. Materials and Instruments

Cerium nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O), lanthanum nitrate hexahydrate (La(NO$_3$)$_3$·6H$_2$O), copper nitrate trihydrate (Cu(NO$_3$)$_3$·3H$_2$O), sodium hydroxide (NaOH), and urea (CO(NH$_2$)$_2$) were purchased from Merck. The BET specific surface area and adsorption isotherms of the nanoparticles were measured using nitrogen adsorption method, at 77 K, by Autosorb-1MP apparatus from Quantachrome. The BJH pore size distributions were extracted from the above mentioned N$_2$ adsorption isotherms.

X-Ray Diffraction (XRD) patterns were collected by an Equinox 3000 instrument, with working voltage of 40 kV, and scanning range between 10$^\circ$–118$^\circ$, in about 6 minutes with resolution of 0.1$^\circ$. Average crystal sizes of the nanoparticles were calculated using Scherrer’s equation from XRD peaks [19].

The morphology of nanoparticles was observed by Scanning Electron Microscopy (SEM), using Leo 1455VP scanning microscope. Moreover, compositions of metals in the mixed nanoparticles were determined by energy dispersive x-ray fluorescence (EDX) analysis, using a Tescan Vega/II/XMU instrument.

* Corresponding author: pahlavzh@modares.ac.ir
B. Design of Experiments

In general, in experimental studies, Taguchi method employs orthogonal arrays to minimize time and cost. Copper percentage, lanthanum percentage, calcination temperature, and calcination time are the main factors, the effects of which were studied using Taguchi experimental design and their optimum values were determined. L16 Taguchi orthogonal design array was used for maximization of nanoparticles specific surface area [20, 21]. The signal to noise (S/N) ratio method was used to analyze the experimental data.

C. Synthesis

The co-precipitation method in the aqueous solution of metal nitrates was used for nanoparticles preparation. At first, some solutions with certain concentrations were produced. Then, for each type of nanoparticle, solutions (including specific amounts of metals) were combined and stirred for a few minutes to be integrated. Thereafter, the nanoparticles were precipitated using NaOH or urea solution. The precipitate was filtered and washed by distilled water, several times. In the next step, the nanoparticles were dried overnight, at 120°C in an oven. Finally, the nanoparticles were calcined at 600–700°C, for 3–6 hours.

D. Catalyst Performance Tests

Relative performances of the ternary oxides, considered as catalysts, were compared for SO2 reduction by CH4. The system consists of a thermogravimeter (TG) from Rheometric Scientific Inc., and an online Mass Spectrometer (MS) from Leda Mass. The catalyst was used as a slab pellet form and was located on platinum wire basket cell, inside the TG. At first, TG is purged by an inert gas stream (gas 1). Then, the system is heated to the desired temperatures (ramp and isothermals), under a mixture of reaction gases. This reacting gas (gas 2) is a combination of CH4, SO2 and inert streams, at predefined concentrations. SO2 inlet concentration, in the mixture, was adjusted by a mass flow controller, while CH4 was in the excess flow rate. After reaching moderate temperatures, the reaction took place.

As it is evident, SO2 conversion in this system is not complete. Since, there are some gas paths around the pellet in TG, without contact to the catalyst. However, this system is ideal for the study of relative performances of various catalysts by comparing mole fractions of outlet gaseous streams.

III. RESULTS AND DISCUSSION

A. Preparation of Nanoparticles

In the first stage, the effect of precipitating agents, on specific surface area of CuO, was studied (table I). Two precipitating agents, NaOH and urea, with different concentrations, were used for the synthesis of metal oxides.

| Sample   | Precipitating Agent | Surface Area (m²/g) |
|----------|---------------------|---------------------|
| CuO      | NaOH (0.05 mol/lit) | 35.61               |
| CuO      | NaOH (0.1 mol/lit)  | 73.55               |
| CuO      | NaOH (0.2 mol/lit)  | 39.83               |
| CuO      | Urea (0.1 mol/lit)  | 15.41               |
| CuO      | Urea (0.5 mol/lit)  | 21.54               |

TABLE II. BET surface area and average crystal size of single and binary oxide nanoparticles

| Sample      | Calcination Temperature (°C) | BET Surface Area (m²/g) | Average Crystal Size (nm) |
|-------------|-----------------------------|-------------------------|---------------------------|
| CeO₂        | 700                         | 36.5                    | 15.56                     |
| La₂O₃       | 700                         | 38.94                   | 18.28                     |
| Ce(15%La)Oₓ | 650                         | 80.51                   | 7.19                      |
| Ce(15%Cu)Oₓ | 650                         | 48.42                   | 10.62                     |

FIG. 1. XRD patterns of pure and binary metal oxide nanoparticles

For precipitating agent of NaOH, the precipitate was formed quickly. But for urea, high temperature and a long time is required for the precipitate to form. This may be due to lower alkaline strength of urea than NaOH, and thus, higher concentrations of urea than NaOH were used.

As Table I indicates, CuO synthesized by NaOH shows higher specific surface area, with respect to urea as the precipitating agent. Among different concentrations of NaOH, copper oxide, synthesized with 0.1 mol/lit NaOH, has the highest specific surface area. Therefore, 0.1 mol/lit NaOH was chosen as precipitating agent in synthesis of all nanoparticles.

Addition of lanthanum and copper to cerium oxide causes an increase in nanoparticles surface area, while the effect of lanthanum increase is higher, compared to copper (Table II). It is seen that, as the nanoparticles BET surface area increased, the average crystal size obtained from the Scherrer equation decreased and particles became smaller.
TABLE III. Factors and levels employed in Taguchi experimental design

| Factor               | Allocated Letter | Levels          |
|----------------------|------------------|-----------------|
| Copper Percent       | A                | A1 5%           |
|                      |                  | A2 10%          |
|                      |                  | A3 15%          |
|                      |                  | A4 20%          |
| Lanthanum Percent    | B                | B1 5%           |
|                      |                  | B2 10%          |
|                      |                  | B3 15%          |
|                      |                  | B4 20%          |
| Calcination Temperature | C             | C1 600°C        |
|                      |                  | C2 630°C        |
|                      |                  | C3 660°C        |
|                      |                  | C4 690°C        |
| Calcination Time     | D                | D1 3 h          |
|                      |                  | D2 4 h          |
|                      |                  | D3 5 h          |
|                      |                  | D4 6 h          |

XRD patterns of pure and binary metal oxides are shown in Fig. 1. For binary metal oxide nanoparticles, the major peak belongs to cerium oxide. The peaks of minor metal oxides are not seen in XRD pattern, due to its low amount. For the binary metal oxide nanoparticles compared to the pure cerium oxide, the height of the maximum XRD peak increases (higher crystallinity).

EDX spectrum of binary nanoparticles confirms metals ratio in the mixed binary oxides (Ce=80.21% and Cu=19.79% for Ce(15%Cu)O₂, Ce=85.12% and La=14.88% for Ce(15%La)O₂).

In the next step, the effects of copper percentage, lanthanum percentage, calcination temperature, and calcination time were considered as major optimization factors for Ce-La-Cu ternary oxides. Taguchi design method was used for maximizing the surface area of nanoparticles, considering four levels for each factor. The factors and their levels are shown in Table III. Temperature range was considered between 600 to 700°C. Since, at very low calcination temperatures, the formation of metal oxide crystal structure is imperfect, more noise will be seen in XRD graph. For low calcination times, this effect also occurred.

Considering four factors and four levels for each factor, a L₁₆(₄⁴) orthogonal array of Taguchi method was used for the design of experiments. Table IV shows L₁₆ Taguchi design and BET results obtained from the produced Ce-La-Cu ternary oxide nanoparticles.

As Table IV shows, the surface area of ternary oxide nanoparticles were increased greatly, compared to pure cerium oxide. The maximum surface area, equal to 89.78 m²/g, was obtained for sample 11 (Ce(15%La)(15%Cu)O₂).

S/N response graphs, for surface area of Ce-La-Cu ternary oxide nanoparticles, are shown in Fig. 2. The order of effective factors, for producing higher surface area of ternary oxide nanoparticles, is C>B>A>D.

Based on the S/N response graphs, optimum conditions for the highest surface area were found to be 5% copper concentration, 15% lanthanum concentration, 600°C calcination temperature, and calcination time of 3 hours (A at level 1, B at level 3, C at level 1, and D at level 1). Ce-La-Cu ternary oxide nanoparticles, at the optimum condition, were prepared and 99.4 m²/g was obtained for its surface area, which is higher than all other surface areas obtained from the 16 samples. This indicates that optimization has been accomplished successfully.

After optimization of Ce-La-Cu ternary oxide nanoparticles, the effect of polyvinylpyrrolidone surfactant, on the specific surface area of the optimum sample, was studied. Polyvinylpyrrolidone solution (20 g/lit), at various volume ratios, was added to the optimum sample before precipitation, and its effect on the nanoparticles surface area was studied. The results are shown in Table V.

As it can be seen in Table V, addition of surfactant does not have a positive effect on surface area of nanoparticles. At high and low surfactant ratios (2.4 and 0.4), the surface area of nanoparticles is greatly reduced. At moderate ratio of surfactant, the nanoparticles surface area is higher.
TABLE IV. L₁₆ orthogonal array of Taguchi design and the results obtained from experiments

| Sample | A   | B   | C   | D   | Description         | Surface Area (m²/g) | S/N   |
|--------|-----|-----|-----|-----|---------------------|---------------------|-------|
| 1      | A₁  | B₁  | C₁  | D₁  | Ce(5%La)(5%Cu)Oₓ    | 88.53               | 38.94181|
| 2      | A₁  | B₂  | C₂  | D₂  | Ce(10%La)(5%Cu)Oₓ  | 73.3                | 37.30208|
| 3      | A₁  | B₃  | C₃  | D₃  | Ce(15%La)(5%Cu)Oₓ  | 69.08               | 36.78705|
| 4      | A₁  | B₄  | C₄  | D₄  | Ce(20%La)(5%Cu)Oₓ  | 40.31               | 32.10826|
| 5      | A₂  | B₁  | C₂  | D₃  | Ce(5%La)(10%Cu)Oₓ  | 78.39               | 37.88521|
| 6      | A₂  | B₂  | C₁  | D₄  | Ce(10%La)(10%Cu)Oₓ | 62.65               | 35.93842|
| 7      | A₂  | B₃  | C₄  | D₁  | Ce(15%La)(10%Cu)Oₓ | 61.49               | 35.77609|
| 8      | A₂  | B₄  | C₃  | D₂  | Ce(20%La)(10%Cu)Oₓ | 51.83               | 34.29162|
| 9      | A₃  | B₁  | C₃  | D₄  | Ce(5%La)(15%Cu)Oₓ  | 48.55               | 33.72378|
| 10     | A₃  | B₂  | C₄  | D₃  | Ce(10%La)(15%Cu)Oₓ | 27.78               | 28.87464|
| 11     | A₃  | B₃  | C₁  | D₂  | Ce(15%La)(15%Cu)Oₓ | 89.78               | 39.06359|
| 12     | A₃  | B₄  | C₂  | D₁  | Ce(20%La)(15%Cu)Oₓ | 47.03               | 33.4475 |
| 13     | A₄  | B₁  | C₄  | D₂  | Ce(5%La)(20%Cu)Oₓ  | 31.4                | 29.93859|
| 14     | A₄  | B₂  | C₃  | D₁  | Ce(10%La)(20%Cu)Oₓ | 81.28               | 38.19967|
| 15     | A₄  | B₃  | C₂  | D₄  | Ce(15%La)(20%Cu)Oₓ | 48.87               | 33.78085|
| 16     | A₄  | B₄  | C₁  | D₃  | Ce(20%La)(20%Cu)Oₓ | 40.38               | 32.12333|

TABLE V. Effect of polyvinylpyrrolidone on BET surface area of the optimum sample

| Sample | Volume Ratio of Surfactant/Solution | Surface Area (m²/g) |
|--------|-------------------------------------|---------------------|
| Ce(15%La)(5%Cu)Oₓ | 0.4 | 29.46 |
| Ce(15%La)(5%Cu)Oₓ | 0.8 | 80.97 |
| Ce(15%La)(5%Cu)Oₓ | 1.2 | 91.08 |
| Ce(15%La)(5%Cu)Oₓ | 1.6 | 87.79 |
| Ce(15%La)(5%Cu)Oₓ | 2   | 90.91 |
| Ce(15%La)(5%Cu)Oₓ | 2.4 | 69.96 |

FIG. 4. EDX graphs of Ce-La-Cu ternary oxide optimum nanoparticles

but its value is less than the surface area for nanoparticles synthesis without any surfactant.

Another factor, the effect of which was studied on the surface area of optimum nanoparticles, was ultrasonic. The effect of ultrasonic on the synthesis of nanoparticles (at 10, 20 and 30 min) was examined. Table VI shows BET results of these experiments.

As Table VI shows, after being under ultrasonic effect (20 and 30 min) for a long time, surface area of the sample was reduced. Only 10 min after using ultrasonic, the surface area of nanoparticles was increased, compared to the samples not being under ultrasonic effect, but this increase is negligible.

TABLE VI. Effect of ultrasonic on BET surface area of optimum nanoparticles

| Sample | Ultrasonic Time | Surface Area (m²/g) |
|--------|----------------|---------------------|
| Ce(15%La)(5%Cu)Oₓ | 10 min | 100.51 |
| Ce(15%La)(5%Cu)Oₓ | 20 min | 77.69 |
| Ce(15%La)(5%Cu)Oₓ | 30 min | 78.68 |

FIG. 5. SEM of the optimum ternary oxide nanoparticles

B. Characterization of the Optimized Nanoparticles

XRD patterns for cerium oxide and optimum ternary oxide nanoparticles are shown in Fig. 3. As it can be seen, for optimum nanoparticles, the major peak is similar to cerium oxide. But, an increase in the peak width and a decrease in the peak height are seen.

EDX graphs for optimum nanoparticles are presented in Fig. 4. The results of EDX indicate that the percentages of metals in optimized nanoparticle are 3.8%Cu/15.7%La/80.5%Ce.

Figure 5 shows SEM for optimum ternary nanoparticles. As it can be seen, the optimized ternary oxide nanoparticles have almost spherical shapes.

Figure 6(a) shows nitrogen adsorption isotherms for the optimum ternary oxide nanoparticles, and also cerium oxide, obtained by plotting the volume of nitrogen adsorbed against relative pressure (P/P₀). For optimum nanoparticles, N₂ adsorption was greatly increased, in comparison...
with pure cerium oxide. This is because of a great increase in specific surface area of the optimum sample, compared to pure cerium oxide.

Barrett-Joyner-Halenda (BJH) meso-pore size distributions of optimum nanoparticles and pure cerium oxide are compared in Fig. 6(b). Changes in size and volume of pores for optimum nanoparticles are clear in this figure.

Specific surface areas, average crystal sizes, pore volumes of optimum ternary oxide nanoparticles, and pure cerium oxide are compared in Table VII.

As it can be seen in Table VII, specific surface area of optimum ternary oxide nanoparticles has increased 270%, compared to pure cerium oxide. The average crystal size obtained for optimized ternary nanoparticles is 6.94 nm, which is 55% lower than the average crystal size of pure cerium oxide (15.56 nm). Also, total pore volume obtained from BJH model shows 35% increase in optimum ternary oxide nanoparticles, compared to pure cerium oxide.

Increase in total pore volume and decrease in average crystal size of optimum ternary oxide nanoparticles are reasonable, given an increase in its surface area.

### C. Catalysts Activity Comparison Tests

To investigate the effect of increasing specific surface area, the optimized ternary oxide with the highest surface and ternary oxide with minimum surface area (sample 10 in the table IV, Ce(10%La)(15%Cu)O_{x}) were compared in reactor test, as a catalyst. In gas-solid catalytic reactions, specific surface area of the catalyst is an important factor and the above mentioned tests were accomplished for performance comparison.

SO₂ reduction with methane, for production of elemental sulfur, is a new method for toxic SO₂ removal in flue gas.

The reaction between sulfur dioxide and methane is as follows:

\[
\text{CH}_4 + 2\text{SO}_2 \rightarrow 2\text{S} + \text{CO}_2 + 2\text{H}_2\text{O} \tag{1}
\]

This method, in addition to removing sulfur dioxide contaminant, turns it into a usable product.

SO₂ conversions for various catalysts are presented in Fig. 7 versus operating temperature.

As it can be seen at all temperatures, the optimum catalyst shows much higher conversion than the catalyst with minimum surface area, that is completely consistent with their specific surface areas.

This is probably due to the fact that the specific surface area of optimum catalyst is much higher and this factor provides more active sites for reaction; thus, more
reactions can be done.

It is worth noting that, when temperature increases, SO$_2$ conversions for all catalysts are extremely increased. This shows that the reaction is strongly temperature dependent.

Generally, the result of reaction test shows that by surface area optimization of ternary oxide, the catalytic performance is greatly improved.

IV. CONCLUSIONS

High surface area of Ce-La-Cu ternary oxide nanoparticles were prepared by co-precipitation method with NaOH. The optimum conditions of copper percentage, lanthanum percentage, calcination temperature, and calcination time were found by Taguchi L$_{16}$ array design. Results have shown that calcination temperature was the most effective factor to obtain higher surface area. Ce(15%La)(5%Cu)O$_2$ nanoparticles, with specific surface area of 99.4 m$^2$/g and average crystal size of 6.94 nm, were prepared as optimum ternary oxide. Ultrasonic has little effect on surface area of optimum ternary oxide nanoparticles (increased to 100.5 m$^2$/g), but adding polyvinylpyrrolidone surfactant does not have any positive effect.

Also, in the comparison of catalytic performances of ternary oxides, it was found that surface area optimization can greatly improve the performance.

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