Research Article

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Catalytic oxidation of CO over CuO/CeO$_2$ nanocomposites synthesized via solution combustion method: effect of fuels

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Abstract: A series of CuO/CeO$_2$ catalysts were successfully synthesized via solution combustion method (SCS) using different fuels and tested for CO oxidation. The catalysts were characterized by energy-dispersive X-ray analysis (EDXRA), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), $N_2$ adsorption-desorption isotherms and H$_2$ temperature-programmed reduction (H$_2$-TPR). It was found that the used fuels strongly affected the characterization and the low-temperature reduction behavior of CuO/CeO$_2$ catalysts. The CuO/CeO$_2$-urea catalyst exhibited higher catalytic activity toward CO oxidation ($T_{50}=120^\circ$C, $T_{100}=159^\circ$C) than the 5 other synthesized catalysts. In addition, the CuO/CeO$_2$-urea catalyst displayed high stability for CO oxidation during five cycles and water resistance. The enhanced catalytic CO oxidation of the synthesized samples can be attributed by a combination of factors, such as smaller crystallite size, higher specific surface area, larger amount of amorphous copper(II) oxide, more mesoporous and uniform spherical-like structure. These findings are worth considering in order to continue the study of the CuO/CeO$_2$ catalyst with low-temperature CO oxidation.

Keywords: CuO/CeO$_2$ nanocomposite, CO oxidation, solution combustion synthesis, fuels

1 Introduction

Many different catalysts have been prepared and tested for CO oxidation. For example, noble metal catalysts, such as gold nanoparticles [1], Pt-CeO$_2$/SiO$_2$ [2], Pt-group-metal [3], Ag/KIT-6 [4], Fe/Ag15 [5, 6] have been demonstrated to be efficient on CO oxidation. It is known that gold nanoparticles are the best catalyst for CO oxidation at room temperature. However, due to limited availability, high cost, and sensitivity to sulfur poisoning of noble metals, more and more researchers are paying attention to new catalysts containing cheaper metals [7, 8]. In recent years, cerium dioxide (CeO$_2$) has been receiving quite a lot of attention because of its availability and high reactivity as a catalyst. The CeO$_2$ demonstrates high oxygen storage capacity, rich oxygen vacancies and the ability to easily switch between Ce$^{3+}$ and Ce$^{4+}$ [9]. In addition, its catalytic activity could be significantly increased if other metal ions, such as Cu$^{2+}$, were doped into the CeO$_2$ structure, which was due to the interaction of cerium with copper ions, causing a partial modification of the oxidation state through the formation of a redox pair (Ce$^{3+}$-Ce$^{3+}$/Cu$^{2+}$-Cu$^{2+}$), this leads to the formation of stabilized Cu$^+$, which are active components involved in the adsorption of CO [10, 11]. The same situation is observed in other similar systems [12, 13]. A large number of CuO/CeO$_2$ were prepared by different methods and tested for the catalytic activity, for example, by co-precipitation [14] with the temperature ($^\circ$C) for 50% CO conversion at $T_{50}=116^\circ$C, by urea gelation/co-precipitation [15] with $T_{50}=85^\circ$C, by solid-state impregnation [16] with $T_{83}=80^\circ$C, by co-precipitation, deposition-precipitation and impregnation [17] with CO total conversion at $85^\circ$C, by sol-gel [18] with $T_{50}=117^\circ$C, by urea-nitrate combustion method [19] with $T_{50}=95^\circ$C. Compared the catalytic CO oxidation of CuO/CeO$_2$ composites to alone oxide CuO [20, 21] with $T_{50}=114^\circ$C or CeO$_2$ [22, 23] with $T_{50}=240^\circ$C, $320^\circ$C and compared to other metal oxides, such Fe$_2$O$_3$ [24] with $T_{50}=230^\circ$C, Mn$_2$O$_3$ [25, 26] with $T_{50}=184^\circ$C, $213^\circ$C, the composites appear to be more activity.
From all the presented kinds of literature, we recognized that SCS possesses the preferential features that distinguish it from all other methods. Firstly, since SCS is a self-sustaining thermal process, so all we need is just to provide the initial heat for the reaction. In addition, the SCS method does not need complex equipment and the synthesis time is also fast. Secondly, in the SCS processes, the majority of the heat develops due to the burning of fuels, which can become a factor to control the desired characteristics of combustion products. Thirdly, the SCS processes generate a large number of gaseous byproducts. Such gases lead to a significant extension of the solid products, which make the powdered products porous and finely dispersed. Thus, due to the promising advantage of low cost and high activity, CuO/CeO₂ catalysts are expected to replace expensive noble metal catalysts in the future.

The basic principles of controlling the composition, size, morphology, and structure of SCS products are to regulate the chemical composition of the fuel, the oxidizer, the ratio between them and the solvents in the preparation step [27]. The work of Varma et al. [28] shows the diversity of the SCS-based method for nanosized materials and its potential commercialization pathways, a lot of SCS-related articles have been reported, but there is very little research on the effect of fuels on this method. Therefore, the purpose of this work is to synthesize the CuO/CeO₂ composites via the SCS method and to investigate the effect of fuels on the characteristics of synthesized products and how it affects the catalytic performance. Such findings can support the progress of CuO/CeO₂ catalysts for low-temperature oxidation of CO. The fuels selected in this work are most frequently used for the solution preparation, as mentioned in the review work of Varma et al. [28]. They are available, inexpensive, low decomposition temperature, and typically dissolved in a solvent with metal nitrate hydrates. The differences from the physical point of view between the used fuels were shown in Table 1, as can be seen, the standard enthalpy of combustion of fuels is different, resulting in their heat supply during combustion will also vary, therefore, the particles of the combustion products can be formed in different sizes. The differences from the chemical point of view between the types of fuel used are based on the difference in the molar mass, which determines the amount of gases that will be generated during the reaction, so the combustion products may be changed in different kinds of structure and morphology of the CuO/CeO₂ composites. In addition, various types of fuel form complexes with metal cations in solutions, as a result of which Cu particles will be dispersed differently on the surface of the CeO₂ lattice and these will definitely affect the catalytic performance of the CuO/CeO₂ catalysts.

### 2 Experimental

#### 2.1 Catalyst preparation

The catalysts were synthesized according to the following redox reactions, the fuels used were urea (CH₄N₂O), citric acid (C₆H₈O₇), ascorbic acid (C₆H₈O₆), glucose (C₆H₁₂O₆), urotropine (C₆H₁₂N₄), and glycine (C₂H₅NO₂):

**Urea:**

\[
8\text{CH}_4\text{N}_2\text{O} + 2\text{Ce(NO}_3)_3 + 2\text{Cu(NO}_3)_2 = 2\text{(CuO/CeO}_2) \quad (1)
\]

+ 8\text{CO}_2 \uparrow + 13\text{N}_2 \uparrow + 16\text{H}_2\text{O} \uparrow

**Citric acid:**

\[
8\text{C}_6\text{H}_8\text{O}_7 + 6\text{Ce(NO}_3)_3 + 6\text{Cu(NO}_3)_2 = 6\text{(CuO/CeO}_2) \quad (2)
\]

+ 48\text{CO}_2 \uparrow + 15\text{N}_2 \uparrow + 32\text{H}_2\text{O} \uparrow

**Ascorbic acid:**

\[
12\text{C}_6\text{H}_8\text{O}_6 + 10\text{Ce(NO}_3)_3 + 10\text{Cu(NO}_3)_2 = 10\text{(CuO/CeO}_2) \quad (3)
\]

= 10\text{(CuO/CeO}_2) + 72\text{CO}_2 \uparrow + 25\text{N}_2 \uparrow + 48\text{H}_2\text{O} \uparrow

**Glucose:**

\[
2\text{C}_6\text{H}_12\text{O}_6 + 2\text{Ce(NO}_3)_3 + 2\text{Cu(NO}_3)_2 = 2\text{(CuO/CeO}_2) \quad (4)
\]

+ 12\text{CO}_2 \uparrow + 5\text{N}_2 \uparrow + 12\text{H}_2\text{O} \uparrow

**Urotrope:**

\[
4\text{C}_6\text{H}_12\text{N}_4 + 6\text{Ce(NO}_3)_3 + 6\text{Cu(NO}_3)_2 = 6\text{(CuO/CeO}_2) \quad (5)
\]
+ 24CO₂ ↑ + 23N₂ ↑ + 24H₂O ↑

Glycine:

\[
16C₂H₄NO₂ + 6Ce(NO₃)₃ + 6Cu(NO₃)₂ \rightarrow 6(CuO/CeO₂) + 32CO₂ ↑ + 23N₂ ↑ + 40H₂O ↑
\] (6)

A detailed description of the synthesis of similar oxide systems is shown in the works [29, 30]. The steps of synthesis are as following (the number of reagents was taken in the stoichiometric ratio): first, the fuel was dissolved in the minimum volume of distilled water; next, cerium(III)-98.0% and copper(II)-99.0% nitrates were added to this solution; after that, the resulting solution was completely dissolved; after that, the solution was stirred until all components were completely dissolved; after that, the resulting solution was placed inside a stainless steel beaker, which was heated on a hot plate in air and maintained until complete evaporation of water from the solution; finally, the reaction mixture foamed, ignited, and burned to form a friable powder (Appendix 1, 2).

The combustion products were calcined at 500°C for 2 hours (heating rate 5°C/min) under an air atmosphere to remove the residual carbon and to obtain the stable catalysts, as were suggested in [31, 32]; then the final powders were analyzed using a complex of physicochemical methods. The obtained samples were named as CuO/CeO₂-urea, CuO/CeO₂-glycine, CuO/CeO₂-ascorbic, CuO/CeO₂-citric, CuO/CeO₂-urotropine depending on the different used fuels.

### 2.2 Characterization methods

The microstructure of the samples, as well as their elemental composition, was analyzed by scanning electron microscopy on a TESCAN VEGA 3 SBH (Czech Republic) – scanning electron microscope, in the detection mode of secondary electrons (“relief mode”).

X-ray diffraction analysis was performed on a RIGAKU SmartLab 3 Diffractometer with monochromatic CuKα radiation (λ=0.15406 nm) in the range of Bragg angles (2θ) from 20° to 100° with a step scanning of 0.01°, a speed of 2°/min. Qualitative X-ray analysis was carried out using a powder X-ray diffraction database, quantitative X-ray analysis was performed using the Rietveld method. The average crystallite size (D) for spherical nanoparticles was calculated according to the Scherer equation:

\[
D = \frac{0.9 \cdot \lambda}{β \cdot \cos(θ)}
\] (7)

where λ – X-ray wavelength, nm; β – full width at half maximum, in radians; θ – Bragg angle, in radians.

Fourier-transform infrared spectra were recorded using Shimadzu IRTracer-100 spectrometer with a resolution of 2 cm⁻¹, using 34 scans per spectrum in the range of 350–4000 cm⁻¹.

The specific surface area, total volume in pores, and pore size distribution of samples were determined using a Micrometrics ASAP 2020 with nitrogen as an adsorbate (N₂ adsorption-desorption isotherms at −196°C (77 K)).

H₂-TPR was performed on Chemosorb (SOLO, Russia) equipped with a thermal conductivity detector. The sample (80 mg) was pretreated in argon flow at 250°C for 30 min, then heated to 800°C at a ramp rate of 10°C/min under a gas flow (60 ml/min) of H₂ (5 vol%) and Ar (95 vol%). CuO was used as an external reference for the calibration of hydrogen consumption. Frozen isopropanol with a temperature of about −90°C was used as a water trap.

### 2.3 Catalytic activity measurements

The catalytic oxidation of CO was carried out in a fixed-bed reactor system (the reactor tube consisted of stainless steel with fittings, the internal diameter of 0.9 cm and length of 47 cm) at the atmospheric pressure. In this work, preliminary preparation of the sample was taken by pressing the catalyst powder into a pellet with a pressure of 110 atm., then the pellet was flapped and put through a sieve to obtain small particles with a diameter of 0.8 mm. Measurements of CO oxidation were evaluated using 4 cm³ of these small particles of catalyst (about 7 grams of each sample). The total gas-air flow rate was 1 liter per minute, which included 0.4% CO. The reaction temperature was controlled using a thermocouple placed on the outer wall of the reactor. The CO concentration in the reactor flow was analyzed using a “Tsvet-100, model 102” gas chromatograph (GC) equipped with a flame ionization detector attached to a column.

Contact time (t) of the gases with catalysts was determined by Eq. (8).

\[
t = \frac{\text{volume of catalyst}}{\text{flow rate of gas}} = \frac{4 \cdot 60}{1000} = 0.24 \text{ sec}. \quad (8)
\]

The CO conversion (x_CO) was calculated based on CO consumption (Eq. (9)). CO conversion from 0% to 100% took about 2 hours.

\[
x_{CO} (%) = \frac{n_{CO}^{in} - n_{CO}^{out}}{n_{CO}^{in}} \cdot 100,
\]

where \(n_{CO}^{in}\) and \(n_{CO}^{out}\) are the corresponding peak area of the GC response at the inlet and outlet CO, respectively.
3 Results and discussion

3.1 Characterization of catalysts

3.1.1 Energy-dispersive X-ray analysis

Figure 1a shows the purity of the CuO/CeO$_2$-urea sample, as evidenced by the presence of 3 elements Ce, Cu, and O in the EDX spectra, the 5 other samples also showed the same result. The synthesis of CuO/CeO$_2$ composites with an atomic ratio of Cu/Ce is 50/50 (or 1:1) according to the balanced chemical equation of each redox reaction presented in Eq. 1-6. The results obtained by EDXA method show the ratio of Cu/Ce is not actually of 50/50 (Figure 1b), but with deviation in the range of 0.1-5.9 at%, which can be explained by its local character (i.e. limited powder areas are analyzed).

3.1.2 Powder X-ray diffraction

The results from XRD patterns of the synthesized samples (Figure 2a) were compared with the Powder Diffraction Standards (JCPDS) of cerium and copper oxides, showing that all samples have obvious diffraction peaks that belong to crystalline CeO$_2$ (cr-CeO$_2$) with a cubic fluorite-type structure [14, 17, 33], but for the copper oxide phase, only a part of peaks is observed (cr-CuO, monoclinic structure) [34], some peaks are lower intensity and the others do not appear, so it can be said that a part of CuO species presents as an amorphous phase (am-CuO) on the catalyst surface. Therefore, we used the Rietveld method to determine the quantity of these phases. The calculated results...
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Figure 3: The average crystallite size of CuO (a) and CeO$_2$ (b). An amount of am-CuO phase in the catalyst changes when using different fuels, the most notable is the case of CuO/CeO$_2$-urea catalyst with the largest number of am-CuO. The change of the phase composition can be explained by the formation of complexes in different forms between fuels and metal cations and due to the different combustion temperatures in the synthesis process, i.e. different standard enthalpy of combustion $\Delta H^\circ_c$ of fuels (Table 1).

The average crystallite size ($D$) was calculated by the Eq. (7) for each phase of the CuO/CeO$_2$ catalysts (Figure 3), the deviation due to the calculation is estimated at $D \pm 2$ nm. Figure 3 indicates the different crystallite size of CuO and CeO$_2$ in the catalysts, remarkably pay attention to case of CuO/CeO$_2$-urea catalyst, the smallest size of CeO$_2$ is formed (6.1 nm), as a result of the presence of the largest amount of am-CuO, which leads to difficulties in association between CeO$_2$ itself particles. Because active sites involved in the adsorption of CO related to copper species on the catalyst surface, which means CuO/CeO$_2$-glycine catalyst with the smallest crystallite size of CuO (7.8 nm) promises to be a good candidate for high catalytic CO oxidation. In addition, the change in the crystallite size of the catalysts proved the different combustion temperatures in the reaction zone of each synthesis by using different types of fuel. Moreover, we have used the XRD results to report a crystallite size distribution of CuO and CeO$_2$, which is presented in Appendix 3.

3.1.3 FTIR spectral analysis

The functional groups on the surface of the prepared catalysts are shown on the FTIR spectra (Figure 4). The wavenumber of peaks in the region of 375-405 cm$^{-1}$ can be attributed to vibrations of $\nu$(Ce-O) bonds [35], and $\nu$(Cu-O) bonds in the region of 465-485 cm$^{-1}$ [36]. Furthermore, adsorbed $\delta$(H-O-H) water bonds (1618-1637 cm$^{-1}$) and $\nu$(O-H) hydrogen bonds (3421-3434 cm$^{-1}$) are also presented on the catalyst surface, which indicates the amount of moisture absorbed by the samples in the air [37]. Also, there are vibrations of $\nu$(C-H) (2854-2971 cm$^{-1}$), $\delta$(H-C-H) (1356-1386 cm$^{-1}$), and $\nu$(C=O) (1085-1095 cm$^{-1}$) bonds, which indicate traces of ethanol used for cleaning experimental instruments and equipment.

3.1.4 Scanning electron microscopy

Figure 5 shows SEM micrographs with a resolution of 2$\mu$m for all catalysts. On the basis of SEM data, it is shown that the type of fuel used displays a strong effect on the morphology of the combustion products: spherical-like struc-
tures [11, 37, 38] were formed for CuO/CeO$_2$-urea, -glycine, -urotropine catalysts; sponge-like morphology is observed when using ascorbic acid, citric acid, and glucose as the fuel. A more uniform morphology was obtained by using urea. All types are formed by isotropic nanoparticles agglomerated in micron-sized structures. The amount of gases generated during the reaction of each 6 syntheses is different as observed by us during the experiment, which may result in the formation of differently porous, foamy products.

3.1.5 Low-temperature nitrogen adsorption-desorption

The porous structure of the CuO/CeO$_2$ catalysts was evaluated by the N$_2$ adsorption-desorption isotherms at −196°C (Figure 6), Figure 6a reveals that all catalysts display type IV curves (according to the IUPAC classification of adsorption isotherms), which are characteristic of adsorbents that are mesoporous materials [7, 39]. Moreover, pore size distributions are established by DFT (density functional theory) calculated from the adsorption branch of the isotherms (Figure 6b) and Barrett-Joyner-Halenda (BJH) method calculated from the desorption branch of the isotherms (Figure 6c). Figure 6b shows that the pore diameter of the samples focuses in the mesoporous range of 23 and 37 nm, whereas the mode diameter obtained by applying the BJH theory is smaller than compared to the DFT result (in the range of 1-5 nm). Figure 6d shows the specific surface area $S_{BET}$ (Brunauer-Emmett-Teller method) and total volume in pores $V_{DFT}$ of the catalysts. The $S_{BET}$ values increase in the series catalysts: CuO/CeO$_2$-glycine < CuO/CeO$_2$-urotropine < CuO/CeO$_2$-citric < CuO/CeO$_2$-ascorbic < CuO/CeO$_2$-urea. The largest specific surface area (21.7 m$^2$/g) belongs to the case of CuO/CeO$_2$-urea sample due to the smaller crystallite size of CeO$_2$, in contrast, compared to the case of CuO/CeO$_2$-glycine catalyst. The more porous on the surface catalyst is discovered by the $V_{DFT}$ values: CuO/CeO$_2$-ascorbic > CuO/CeO$_2$-urea > CuO/CeO$_2$-glycine.
3.1.6 \( \text{H}_2 \)-temperature-programmed reduction

Because of the CuO/CeO\(_2\)-urea catalyst possesses the most perspective characteristics for catalysis, therefore its reducibility is further studied by \( \text{H}_2 \)-TPR profile. The TPR profile shows a single reduction peak at 330°C. This finding indicates a concurrent reduction of the copper oxide species and surface CeO\(_2\) takes place owing to the synergic interaction between CuO and CeO\(_2\). The same situation is found from work [40]. The reduction peak for CeO\(_2\) does not appear, because CeO\(_2\) is favorable to the formation of strongly, easily reducible surface copper species and is overlapped with that of CuO [41].

3.2 Catalytic performance

The catalytic activity of all catalysts is shown in Figure 8a. Among these catalysts, CuO/CeO\(_2\)-urotropine exhibits the
lowest activity with temperature for 50% CO conversion ($t_{50}$) is 153°C, while the CuO/CeO$_2$-urea catalyst is the most active with $t_{50}$ is 120°C (Figure 8b). It can be observed that the catalytic activity of the samples is highly related to their $S_{BET}$, which means that with an increase in the specific surface area, the catalytic activity also increases, but it is not a deciding factor, according to the characteristics of catalysts discussed above, the high catalytic CO oxidation of both CuO/CeO$_2$-urea and CuO/CeO$_2$-glycine catalysts can be explained by the large number of amorphous CuO phase on surface catalyst, the more porous property, the smaller crystallite size of CuO and CeO$_2$, the spherical-like structure and the more uniform morphology. The CuO/CeO$_2$-glucose catalyst possesses the largest crystallite size of both CuO and CeO$_2$, which explains its low activity for CO oxidation.

Compared with the same system of CuO/CeO$_2$ composites derived from in-situ synthesis, mechanical mixing and impregnation methods [42, 43] and through the direct decomposition [41] with the $t_{50}=71, 102^\circ$C, our CuO/CeO$_2$-urea catalyst exhibit high comparative catalytic performance toward CO oxidation, but in the base of present work, if we have already determined the optimal fuel, we can further synthesize the CuO/CeO$_2$ catalysts by changing the ratio of fuel/oxidizer or ratio of CuO to CeO$_2$ in order to obtain the higher specific surface area and the more quantity of surface-active oxygen species of the catalysts, which are the determinants for low-temperature of CO oxidation.

The best catalyst obtained (CuO/CeO$_2$-urea) from the synthesized samples are further investigated its circularity and effect of water vapor. Figure 8c shows that after reused five times, the catalyst still maintains a high catalytic per-
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![XRD pattern of CuO/CeO$_2$-urea catalyst derived from the SCS method before and after CO oxidation (a); crystallite size distribution of CuO and CeO$_2$ nanoparticles obtained before and after CO oxidation (b).](image)

**Table 2:** Characterization of CuO/CeO$_2$-urea catalyst after carrying out the oxidation of CO with five cycles

| CuO/CeO$_2$-urea catalyst | $S_{BET}$, m$^2$/g$^a$ | $V_{DFT}$, cm$^3$/g$^b$ | $D_{P}$, nm$^c$ |
|----------------------------|------------------------|-------------------------|----------------|
| Before CO oxidation       | 21.7                   | 0.031                   | 23 (BJH)       |
| After CO oxidation        | 12.2                   | 0.016                   | 23 (BJH)       |

$^a$Brunauer–Emmett–Teller (BET) specific surface area; $^b$Total volume in pores measured at $P/P_0 = 0.99$; $^c$The pore diameter calculated from the desorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) or Density Functional Theory (DFT) method.

Formance. Moreover, CuO/CeO$_2$-urea has been undergone an experiment in the presence of water vapor with relative humidity (RH) of 70% and the absence of water vapor with RH=7%. The result (Figure 8d) shows that, in the presence of water vapor, the catalyst exhibits a little inactive effect on CO oxidation as concluded of works [22, 23, 25, 26], but after temperatures exceed 130°C, it works normally again.

After carrying out the oxidation of CO with five cycles, the characterizations of the CuO/CeO$_2$-urea catalyst are further studied by XRD and N$_2$ adsorption-desorption isotherms. The results are presented in Figure 9 and Table 2. Figure 9 reveals that after CO oxidation, the phase composition of the composite is still kept the same, the crystallite size of CeO$_2$ is almost no change, but the size of CuO becomes smaller after CO oxidation. The $S_{BET}$ and $V_{DFT}$ values decrease (Table 2) may be due to pressing the catalyst powder into a pellet during sample preparation for CO oxidation.

4 Conclusions

The CuO/CeO$_2$ samples were obtained by the SCS method using different types of fuel. The fuels greatly affect the characteristics of the synthesized catalysts and their catalytic performance. The optimal fuel was determined for the combustion method for synthesizing the CuO/CeO$_2$ catalyst – urea, CuO/CeO$_2$-urea catalyst possesses the preferential properties for CO oxidation, such as a small crystallite size of both CuO, CeO$_2$, a high specific surface area, a large amount of amorphous CuO species, large mesoporous and uniform spherical-like structure. It is advisable to continue studying the optimal conditions for the synthesis of CuO/CeO$_2$ catalysts based on the SCS method to obtain a catalyst with low-temperature CO oxidation, which can be implemented in practical applications in the future.

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Appendix 1: Synthesis of CuO/CeO$_2$ composite in solution combustion method (SCS) used urea as the fuel can be divided into stages: after preheating where free and a portion of the water evaporates the reaction mixture foams (1), then at some temperature, it ignites (2), burns (3) and follows by the cooling stage (4) to form an as-synthesized powder.

Appendix 2: The as-synthesized powders of CuO/CeO$_2$ catalysts derived from SCS method using different fuels: a) CuO/CeO$_2$-urea; b) CuO/CeO$_2$-glycine; c) CuO/CeO$_2$-urotropine; d) CuO/CeO$_2$-ascorbic; e) CuO/CeO$_2$-citric; f) CuO/CeO$_2$-glucose.
Appendix 3: Crystallite size distribution of copper(II) oxide and cerium(IV) oxide in CuO/CeO₂ samples of the (111) diffraction peak.