Preparation Methods and Applications of CuO-CeO$_2$ Catalysts: A Short Review

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Received: 14 January 2010, Revised: 31 January 2010, Accepted: 1 February 2010

Abstract

The CuO-CeO$_2$ catalytic systems are getting popular for catalyzing very actively the various reactions of environmental, commercial and other importance. In recent years, many methods have been in use for the preparation of versatile CuO-CeO$_2$ catalysts. Reviewing the useful preparation methods of such catalysts is thus the need of the time in view of the globally increasing interest towards all the low temperature redox reactions. This article presents a short review on seventeen different preparation methods of the copper-ceria catalysts, followed by critical discussions on the related redox properties and advancements accomplished with respect to their application aspect, including a systematic compilation of the concerned newer literature in a well-concievable tabular form. © 2010 BCREC UNDIP. All rights reserved.

Keywords: CuO-CeO$_2$ catalysts; preparation methods; potential applications; redox properties

1. Introduction

Liu and Flytzani-Stephanopoulos [1] firstly introduced the catalytic systems based on copper oxide, supported on ceria, for the total oxidation of CO and CH$_4$. Accordingly, this system displayed a substantially high activity and stability related to the oxidation of CO. Complete CO conversion occurred at about 80 °C at a space velocity of 45,000 h$^{-1}$. Thus, in recent years, the high catalytic activity and selectivity of the CuO-CeO$_2$ systems form the basis of their rising popular use in various reactions of environmental, commercial and other importance. Reactions of environmental importance include complete oxidation of CO [1-10], oxidation of hydrocarbon [1,11-14], oxidation of VOC [15-17], NO reduction by CO [18,19], NO reduction by C$_3$H$_6$ [20,21], NO reduction by NH$_3$ [22], three-way catalytic conversion [23], diesel soot oxidation [24-28], SO$_2$ reduction by CO to elemental sulphur [29-32], ammonia decomposition [33,34], phenol oxidation [35-36], etc.

Reactions of commercial importance include production of hydrogen by various processes, such as steam reforming of methanol [37-46], water-gas...
shift (WGS) reaction [47-52] and purification of hydrogen by preferential oxidation of carbon monoxide (CO-PROX) for fuel cells application [53-67], etc.

Reactions of other importance are concerned with the selective oxidation of ammonia to nitrogen [68] and lower hydrocarbon reforming into synthetic gas [69]. Further, CuCeO2 composite catalytic electrodes are used for direct oxidation of various fuels in fuel cells [70-73]. In addition, these binary oxides are also useful for H2O2 decomposition [74] as well as methanol synthesis [75], etc.

To date, there has been frequent most use of CuO-CeO2 systems as additives to reduce the cost of noble metals in the three-way catalysts [23], for the purification of automotive exhaust gas. An excellent activity of the CuO-CeO2 system is on record in the oxidation of CO [1], which is significantly higher than that of the commercially precious forms of metal catalysts [76]. These have been thus widely studied with the aim to possibly replacing the expensive noble metals [1, 2, 53, 77-82].

Abundant availability of Cu and Ce, coupled with their lower costs compared to precious metals, make them strongly competitive. This type of composite catalyst also shows remarkably higher resistance to carbon dioxide, water poisoning, and sulphur compounds [83]. Development of solid oxide fuel cells (SOFC) for operation in the intermediate temperature regime of 600–800 °C with hydrocarbon/methanol/ethanol fuel(s) requires a cathode and an anode possessing high electro-catalytic activity to facilitate O2 reduction and direct oxidation of fuels, respectively. San Ping Jiang [71] reviewed and discussed the progress concerning application of the wet impregnation technique in the development of CuCeO2 composite electrodes for direct oxidation of hydrocarbon in SOFC.

The oxidation catalysts based on CuO-CeO2 can be classified [9] into three types: (i) CuO and CeO2 catalysts [53, 84-88], (ii) CuO catalysts doped with CeO2 (or vice versa) supported on alumina [55, 88-91], and (iii) CuO catalysts supported on mixed CeZr(1-x)O2 oxides [92, 93].

It is a long recognized fact that the properties of the catalysts often depend on their preparation methods. The dispersion and size distribution of metal crystallites, their spatial distribution on the support, the homogeneity of components in a multi-component catalyst, the porosity, surface area, and pore size distribution are the examples of sensitive functions. This sensitivity is with respect to the precursors used and the treatment temperature and atmosphere, as well as other preparation variables, such as pH of the preparation solution or the use of aqueous or organic medium [94], which in turn strongly affect the catalyst activity. In recent years, there has been a significant progress towards understanding the relationship between the preparation method and the final properties of catalysts and catalytic supports. Several methods have been used for the preparation of the versatile CuO-CeO2 catalysts. However, preparation methods of such catalysts have hardly been reviewed so far. Owing to the recurrently expanding interest the world over on the application of copper-ceria catalysts, this brief article is an attempt to review the various useful preparation methods of these copper-ceria catalytic systems, and discuss the redox properties related catalytic activities of the CuO-CeO2 catalysts in light of the preparation methods.

2. Methods of Catalyst Preparation

The choice of a laboratory method for preparing a given catalyst depends on the physico-chemical characteristics desired in its final composition. Nevertheless, the preparation methods are dependent on the choice of basic materials, and earlier experiences support considering support towards diverse ways of preparation, even for a given selection of the basic material. Following methods for the preparation of CuO-CeO2 catalysts are on record:

1. Wet impregnation method [2, 71, 80, 93, 94]
2. Co-impregnation method [9, 70]
3. Precipitation deposition method [5, 95]
4. Co-precipitation of Cu and Ce method [3, 37, 96-99]
5. Urea gelation method [84, 100, 101]
6. Urea nitrate combustion method [17, 53, 83, 86, 102, 103]
7. Solution combustion method [18]
8. Citric acid sole-gel method [25, 86]
9. Surfactant assisted method [8]
10. Solvothermal method [79]
11. Leaching method [104]
12. Chelating method [61]
13. Inert gas condensation (IGC) method [105]
14. Electroless method [90]
15. Laser vaporization and controlled condensation [6]
16. Solvated metal atom impregnation method [4], and
17. Combinatorial synthesis of mixed metal oxides [112, 113]
2.1. Wet Impregnation Method

The wet impregnation method is a common procedure to prepare the CuO-CeO$_2$ catalysts. It involves three steps: (i) contacting the support (CeO$_2$) with the impregnating solution of copper precursors (nitrate, sulphate, acetate, etc.) [80, 93] for a certain period of time, (ii) drying the support to remove the imbibed liquid, and (iii) thermal decomposition, followed by activating the catalyst by reduction or other appropriate treatment. But the Cu(II) ions tend to segregate from CeO$_2$ supports in the form of non-active Tenorite (CuO) particles, even for low Cu(II) loadings [2, 94]. A typical procedure followed by Zheng et al. [80] is described here. CeO$_2$ is prepared by serial thermal decomposition of cerous nitrate [Ce(NO$_3$)$_3$.6H$_2$O] in air for 4 h at 400, 500, 600, or 700 °C. The prepared buff particles are in turn denoted as CeO$_2$-A, CeO$_2$-B, CeO$_2$-C and CeO$_2$-D. The prepared CeO$_2$ supports are impregnated with an aqueous solution of Cu(NO$_3$)$_2$.3H$_2$O for 5 h, where after the excess of water is vaporized by heating at 600°C. The materials, thus obtained, are dried overnight by heating at 800°C and serially calcined in air for 3.5 h at 300, 400, 500, 600, or 800 °C. The prepared catalysts are denoted as CuO/CeO$_2$-A, CuO/CeO$_2$-B, CuO/CeO$_2$-C and CuO/CeO$_2$-D. The final loading of CuO for all the samples is 6.3-wt percentage.

2.2. Co-impregnation Method

Co-impregnation is a general technique for the synthesis of supported heterogeneous catalyst, containing active metal, promoter, stabiliser, etc. In this method, typically, copper and cerium precursors (nitrate, sulphate, acetate, etc.) are dissolved in water solution. Afterwards, this solution is added to a catalyst support up to the time required for total impregnation. The catalyst can then be dried and calcined to drive off the volatile components within the solution, depositing the metal, promoter, stabiliser, etc. on the surface of the support. Gonzalo Aguila [9] prepared bimetallic CuO-CeO$_2$ catalysts by co-impregnation of the support Al$_2$O$_3$/ZrO$_2$/SiO$_2$ for the oxidation of CO at low temperature. They inferred that the support has a strong influence on the activity of the different bimetallic catalysts. Interestingly, the SiO$_2$ supported catalyst showed a higher activity. The bimetallic supported catalysts followed the activity sequence: CuO-CeO$_2$/SiO$_2$ > CuO-CeO$_2$/ZrO$_2$ > CuO-CeO$_2$/Al$_2$O$_3$. The co-impregnation process of ceria and Cu appears to play an important role in the performance of the Cu-based composite anodes for direct oxidation of hydrocarbon in SOFC [70].

2.3. Precipitation deposition method

In precipitation, the objective is to achieve a reaction of the type:

Metal Salt (nitrate/sulphate) Solution + NaOH/ KOH/ Na$_2$CO$_3$ + Support (powder) → Metal hydroxide or carbonate on support

Two processes are involved in the deposition: (i) precipitation of solution in bulk and pore fluid, and (ii) interaction with the support surface. Rapid nucleation and growth in the bulk solution is ought to be avoided, as it produces a deposition exclusively outside the support porosity. Use of urea rather than conventional alkalises has proved to be an effective method to obtain a uniform precipitation. Urea dissolves in water but decomposes quite slow at 90°C, giving thereby a uniform concentration of OH$^-$ both in the bulk and pores. Precipitation takes place homogeneously over the support surface [95] and happens to be the preferred deposition route for loading higher than 10-20%. Below this value, impregnation is usually practised.

Kebin Zhou and coworkers [5] prepared the CeO$_2$ supported CuO catalysts by the precipitation deposition method as follows: The ceria are suspended in water. To this suspension, an aqueous solution of Cu(NO$_3$)$_2$ (0.1 M) is added while stirring. During this process, the suspension is kept constant at a pH of about 9.0 by adding 0.25 M NaOH solution. After an additional 60 min of continuous stirring, the precipitate is filtered and washed. The filtrate is then dried overnight at 80°C in air and calcined at 400°C for 4 h. The loading of CuO is 1 wt percentage for both of the catalysts. They claimed that the high-energy, more reactive {001} and {110} planes of CeO$_2$ nanorods were found to generate synergetic effects between CuO and ceria, resulting in significant enhancement of the copper catalyst performance for CO oxidation.

2.4. Co-precipitation method

The synthesis of the mixed Ce(III) and Cu(II) precursors is generally achieved by heterogeneous co-precipitation in basic media [37, 96-98], the inhomogeneities during the formation of solids being an inherent vice of this procedure [3]. Petar Djinovic et al. [99] prepared the CuO-CeO$_2$ precursor by co-precipitation by adding water solution of Na$_2$CO$_3$ drop-wise to the required amount of aqueous solutions of Cu(NO$_3$)$_2$ and Ce(NO$_3$)$_3$ with concurrent vigorous stirring. In this process, the pH of mixed solution is maintained...
below 6.0. The formed precipitate is thoroughly washed with hot distilled water in order to remove undesired sodium ions, and dried overnight in an oven at 110 °C. Final CuO-CeO$_2$ catalyst emerges after decomposing and calcining the precursor at 650 °C.

It is reported that the catalytic performance of these non-noble metal-containing catalysts is comparable with that of other selective CO oxidation catalysts and for water gas shift reaction catalysts respectively, as reported in the literature. Liu and Flytzani-Stephanopoulos [1] prepared CuO-CeO$_2$ via co-precipitation methods for the total oxidation of CO and CH$_4$. The Cu-ceria catalysts exhibit substantially high activity and stability for CO oxidation at a space velocity of 45,000 v/v h$^{-1}$ and complete CO conversion occurs at around 80 °C. The authors explained the increase in activity of these catalysts owing to the stabilization of Cu$^{+1}$ in catalysts, prepared via co-precipitation methods, originated from the interaction between copper clusters and cerium oxide, and addressed to ceria for performing the role of oxygen source.

### 2.5. Urea gelation method

The urea method provides a highly reproducible homogeneous precipitation process, which makes use of the thermal hydrolysis of urea into ammonium carbonate [100]. Matias Jobbagy et al. [101] explored the urea method for a high-yield of CuO-CeO$_2$ catalyst precursors. To start with, solutions containing urea, Ce(NO$_3$)$_3$, and Cu(NO$_3$)$_2$ are aged at 363 K for 5 h, achieving a quantitative co-precipitation in the form of amorphous Cu(II)-Ce(III) basic carbonates, with Cu(II) contents up to 40%. They observed no Tenorite (CuO) segregation after annealing at 873 K and evaluated the possibilities and limitations of the urea method in the synthesis of mixed Cu(II)-Ce(III) particles—as precursors for copper-promoted-CeO$_2$ catalysts. The samples containing around 20% in copper atoms for preferential oxidation of carbon monoxide (CO-PROX) performed as the best.

Liu et al. [84] quantitatively described this method, in which the precursor salts are metal nitrates and the cerium salt is (NH$_4$)$_2$Ce(NO$_3$)$_6$. The preparation procedure consists of mixing the aqueous metal nitrate solutions with urea (NH$_2$CO-NH$_2$); heating the solution to 100 °C under vigorous stirring and addition of de-ionized water; boiling the resulting gel for 8 h at 100 °C; filtering and washing the precipitate twice with de-ionized water at 50-70 °C; drying the cake in a vacuum oven at 80-100 °C for 10-12 h; crushing the dried lump into smaller particles and calcining the powder in a muffle furnace in air at 650 °C for 4 h. A heating rate of 2 °C/min is used in the calcination step. The BET surface areas of the thus prepared catalysts are in the range of 90–100 m$^2$/g after calcinations at 650 °C. The copper content in CuO-CeO$_2$ or in the doped catalysts is 10 wt%.

### 2.6. Urea–nitrate combustion method

In context with the above-mentioned reactions, urea combustion with nitrates is an effective, one-step technique for the preparation of CuO-CeO$_2$ catalysts with favorable characteristics and catalytic properties [17, 83, 86, 102]. The reactions describing the combustion of urea with copper and cerium nitrate salts can be written as follows:

\[
\begin{align*}
\text{Ce(NO}_3\text{)}_3 + (7/3)\text{CO(NH}_2\text{)}_2 & \rightarrow \text{CeO}_2 + (23/6)\text{N}_2 + (7/3)\text{CO}_2 + (14/3)\text{H}_2\text{O} \\
\text{Cu(NO}_3\text{)}_3 + (5/3)\text{CO(NH}_2\text{)}_2 & \rightarrow \text{CuO} + (8/3)\text{N}_2 + (5/3)\text{CO}_2 + (10/3)\text{H}_2\text{O}
\end{align*}
\]

Avgouropoulos et al. [53] described the following urea–nitrate combustion method for the synthesis of CuO-CeO$_2$ mixed oxide catalysts. Accordingly, cerium nitrate [Ce(NO$_3$)$_3$·6H$_2$O], copper nitrate [Cu(NO$_3$)$_2$·3H$_2$O], and urea [CO(NH$_2$)$_2$] are mixed in the appropriate molar ratios in a minimum volume of distilled water to obtain a transparent solution. The initial urea/nitrate molar ratio is adjusted according to the principle of propellant chemistry [103], taking into account that the urea/nitrate stoichiometric molar ratio is equal to $5(3 - x)/6$, where x denotes the Cu/(Cu + Ce) molar ratio. The urea/nitrate ratio varies from stoichiometric (urea/nitrate $= 2.38$) to 5.5, while the Cu/(Cu + Ce) molar ratio is equal to 0.15. In order to determine the optimum copper loading, two additional catalytic samples with the optimum urea/nitrates molar ratio are prepared, with Cu/(Cu + Ce) molar ratio equal to 0.10 and 0.20. The mixed solutions are heated for a few minutes at 80 °C and the resulting viscous gel is introduced in an open muffle furnace, preheated at 400–500 °C, in a fuming cupboard. The gel starts boiling with frothing and foaming, and in a couple of minutes it is ignited spontaneously with rapid evolution of a large quantity of gases, yielding a foamy voluminous powder. The powder
obtained after combustion contains small amounts of carbonaceous residues as well, because the auto-ignition lasts only for a few seconds. In order to burn-off carbon residues, the powder is heated further at 550 °C for 1 h.

2.7. Solution combustion method

Bera et al. [18] described synthesis of fine particle and large surface area Cu-CeO$_2$ catalysts of crystallite sizes in the range of 100–200 Å by the solution combustion method, for NO reduction. In this method, ceric ammonium nitrate and copper nitrate are used as the sources of cerium and copper. Oxalylidihydrizide (ODH, C$_2$H$_6$N$_4$O$_2$) prepared from diethyl oxalate and hydrazine hydrate is used as the fuel. In a typical combustion synthesis, a Pyrex dish (300 cm$^3$), containing an aqueous redox mixture of stoichiometric amounts of ceric ammonium nitrate (5 g), copper nitrate (0.1419 g), and ODH (2.6444 g) in 100 cm$^3$ volume of H$_2$O, is introduced into a muffle furnace preheated to 350 °C. The solution boiled with foaming and frothing and ignited to burn with a flame yields about 1.5 g voluminous oxide product within 5 min. Similarly, Zr, Y, and Ca doped CeO$_2$ oxides are prepared by this method from their respective metal nitrates and ODH fuel. These oxides are prepared in an open muffle furnace kept in a fuming cupboard. Exhaust is kept on during the firing. The reaction can be controlled by carrying out the combustion in an open atmosphere. By choosing proper sizes of the container and muffle furnace larger quantity of the catalysts (up to 500 g) can be prepared in a single batch. Since the oxides absorb the moisture, it is necessary to store them in a vacuum desiccator and heat them at 300 °C for 12 h before using.

2.8. Citric acid sol–gel method

Sol-gel method has several promising advantages over precipitation. In general, sol-gel synthesis offers better control over surface area, pore volume and pore size distribution. Hydrophilic colloidal solutions are formed of micelles that remain separated because of electrical charges on their surfaces and in the surrounding solution. These charges create repelling forces which prohibit coagulation of the micelles. Such micelles are produced via chemical reactions of polymerization and poly-condensation. Following preparation details followed by two groups of authors have been illustrated.

Qing Liang et al. [25] prepared CeO, Ce–Zr, Cu–Ce and Cu–Ce–Zr mixed oxides with Ce/Zr and Cu/(Cu + Ce + Zr) molar ratios equal to 5/4 and 1/10. This was accomplished following the citric acid sol–gel method. This involves mixing of nitrates [Ce(NO$_3$)$_3$, ZrO(NO$_3$)$_2$ and/or Cu(NO$_3$)$_2$] in deionized water according to the desired molar ratio. Citric acid is added as the complexing agent with a 1.3:1 ratio of the acid to metal ions including Ce$^{3+}$, Zr$^{4+}$ and Cu$^{2+}$. Appropriate amount of polyglycol is followed in accordance with the weight of 10% citric acid added.

The blended solution is sufficiently mixed in a magnetic stirrer and heated at 80 °C until transparent gel is formed. The resulting gel is dried at 110 °C overnight. The powder received is subjected to decomposition at 300 °C for 1 h and calcined at 500 °C for 3 h under static air in a muffle. According to the authors, CuO-CeO$_2$ mixed oxides, which behave as active and remarkably selective to CO$_2$ while operating at significantly low reaction temperature, seem to be a promising candidate catalyst for the selective soot oxidation. CuO-CeO$_2$–ZrO$_2$ mixed oxides are less active but more thermo-stable.

Marban et al. [86] prepared solid dispersions of copper oxide in ceria following this method. In fact copper(II) nitrate, cerium(III) nitrate and citric acid are dissolved in 5 mL of deionised water in appropriate amounts to get solutions with the following characteristics: 1 M in total metals; s = Cu/(Cu + Ce) molar ratio = 0.065, 0.15 or 0.25; z = citric acid/(Cu + Ce) molar ratio = 1.2. The solution is placed in an oven at 70 °C and left to be dried for two days. A yellow-green rigid meringue is obtained that is heated under air flow at a given heating rate (h.r. = 1, 5 or 10 °C/min) up to the calcination temperature (T$_{calc}$ = 450 or 550 °C), at which it is maintained for 4 h. The calcined material has a cigarette ash consistence and is powdered by gentle dis-aggregation in a glass mortar. Following the same procedure, solid dispersions of cobalt oxide in ceria and manganese oxide in ceria too are prepared. Cobalt(II) nitrate and manganese(II) nitrate, respectively, are used in this process instead of copper(II) nitrate (s = [Co or Mn]/([Co or Mn] + Ce) molar ratio = 0.15; z = citric acid/([Co or Mn] + Ce) molar ratio = 1.2; h.r. = 1 °C/min, T$_{calc}$ = 550 °C).

2.9. Surfactant-assisted method

Cao et al. [8] presented surfactant-assisted method for the preparation of CuO/Co$_x$Zr$_{1-x}$O$_2$ catalysts with different CuO content of nanoparticle assembly. In this method, 6 mmol of cetyltrimethylammonium bromide (CTAB) is dissolved into 200 ml distilled water under
ultrasound irradiation for 15 min at room temperature. To this solution, 8 mmol of Ce(NO$_3$)$_3$·6H$_2$O, 2 mmol of Zr(NO$_3$)$_4$·5H$_2$O and calculated amount of Cu(NO$_3$)$_2$·3H$_2$O are added under vigorous stirring. After stirring for 0.5 h, 0.2 mol/l sodium hydroxide solution is added slowly to the above solution until the pH value of the mixed solution reached 10. At this stage, the mixed solution is further stirred for about 12 h. The final suspended solution is aged at 90 °C for 3 h, washed with hot water, dried in the oven at 110 °C for 6 h, then milled and calcined at 400 °C for 4 h. The content of CuO is 0, 5, 10, 15, 20, 25, 30, 40 mol%, and the corresponding catalysts are denoted as CeZrCu$_{10}$, CeZrCu$_{15}$, CeZrCu$_{20}$, CeZrCu$_{25}$, CeZrCu$_{30}$, CeZrCu$_{40}$, respectively. In order to make clear the influence of the calcination temperature on the catalyst property, a series of CeZrCu$_{25}$ catalysts calcined at different temperatures are prepared in the similar manner.

2.10. Solvothermal synthesis

Xiucheng Zheng and co-workers [79] presented solvothermal synthesis combined with impregnation method. They synthesised CeO$_2$ nano-particles via alcohothermal method and CuO/CeO$_2$ catalysts via impregnation method. The procedure is described as follows: CeO$_2$ is prepared via alcohothermal synthesis method. In a Teflon bottle with an inner volume of 50 ml, 0.87 g Ce(NO$_3$)$_3$·6H$_2$O is dissolved into 40 mL ethanol absolute (0.05 mol/l). Thereafter 0.45 g KOH is slowly added to the above solution under vigorous stirring (10 min). When the gray solution changes to yellow colour (30 min), the Teflon bottle is hold in a stainless steel vessel and the vessel is sealed tightly. The alcohothermal treatment is performed at 180 °C for 5 h under auto-genous pressure in an oven. After the alcohothermal treatment, the autoclave is allowed to cool down to the room temperature. The precipitates are separated by centrifuging, washed with de-ionized water and ethanol absolute, and dried in vacuum at 75 °C overnight to get yellow-white CeO$_2$ nano-crystals. The CuO/CeO$_2$ catalysts are prepared by impregnation of the obtained CeO$_2$ with Cu(NO$_3$)$_2$ aqueous solutions. The prepared samples are dried at 80 °C overnight and then calcined at 300, 400 and 500 °C for 3.5 h in air. The CuO loading was 6 wt%.

2.11. Leaching method

Zhu et al. [104] prepared a series of mesoporous copper cerium bimetal oxides as follows: Stock mixed solution of Cu(II) nitrate and Ce(III) nitrate is prepared by dissolving copper nitrate and cerium nitrate in ethanol. Typically, 0.2 g of KIT-6 silica is dispersed in 3.0 ml of the above ethanol solution, containing stoichiometric amounts of corresponding metal salts. The same is stirred at room temperature for 1 h. Ethanol is removed by evaporation through heating the mixture overnight at 373 K. Afterwards, the resulting powder is heated in a ceramic crucible in an oven at 673 K for 6 h to completely decompose the nitrate species. The impregnation step is repeated with 2.0 mL of the metal salt solution in order to achieve higher loadings. After evaporation of the solvent, the resulting material is calcined at 823 K for 6 h. The silica template is then removed at 323 K through etching twice in 10 ml of 2.0 M NaOH aqueous solution. The meso-porous bimetal oxides are recovered by centrifugation, washed with water and finally dried at 323 K. In all cases, the concentrations of the total metal ions, i.e., [Cu(II)]/ [Ce(III)] are kept constant at 0.7 M. The molar percentage ratio of Cu(II) to total metal, i.e., X = [Cu(II)]/[Ce(III) + Cu(II))] x 100, varies between 5 and 50. They claimed that the catalysts reported in this work showed comparable or even superior activities to literature data for catalytic CO oxidation.

2.12. Chelating method

Zhigang Liu et al. [61] studied different methods used to prepare CuO-CeO$_2$ catalysts for preferential oxidation of CO in excess of hydrogen. They showed that the chelating method enhances the formation of defects of ceria and produces a synergistic effect between the cycle of Cu$^{1+}$/Cu$^{2+}$ and that of Ce$^{3+}$/Ce$^{4+}$. The later is beneficial to the improvement of the performance of CuO-CeO$_2$ catalysts for the preferential oxidation of CO. The preparation method is as follows: The CuO-CeO$_2$ catalyst is prepared by chelating method and denoted as 5CuC-CH. The solution of cetyltrimethyl-ammonium bromide (C$_{19}$H$_{42}$BrN) is added in drops into the mixture of 0.055 mol/L Ce(NO$_3$)$_3$ and 0.008 mol/L Cu(NO$_3$)$_2$ solutions with vigorous stirring, and the sol-gel obtained is aged for 30 minutes at ambient temperatures. It is important to note that the solvent used in the experiment is ethanol and not water. The sol-gel is then dried at 100 °C for about 5 h and then heated at 500 °C for 2 h. As a reference, the CuO-CeO$_2$ catalyst is synthesized by coprecipitation method according to the literature [55] and denoted as 5CuC-CP. KOH (0.362 mol/L) is used as precipitator and added to the mixture of 0.055 mol/L Ce(NO$_3$)$_3$ and 0.008 mol/L Cu(NO$_3$)$_2$ solutions,
and the pH value of supernatant liquid is kept at 12.5. The two catalysts are crushed and sieved to 60–80 mesh. The loading of Cu in the catalysts is 5 wt%.

2.13. Inert gas condensation method

By employing the inert gas condensation (IGC) technique, almost any metal can be used to produce composites with a wide range of different compositions [105]. It also provides the possibility to alter the nano-sized morphology, the crystallinity, and particle size [106]. Yet another advantage of the IGC method is that, because of the nature of vapour-condensation growth process, a larger portion of internal interfaces and grain boundaries with a high degree of cleanliness between the metals can be obtained [107]. These are the prerequisites for obtaining highly active catalysts. Skårman et al. [106] followed this method, which is described as follows: The catalyst powders of CuOx/CeO2 are synthesized by inert gas condensation (IGC) utilizing resistive heating evaporation. Pure metallic cerium and copper granules are used as source materials and evaporated simultaneously in two or three resistively heated tungsten crucibles. After pumping down to UHV conditions (<10⁻⁹ Torr), the chamber is filled with a low pressure of inert helium gas. The evaporated metallic monomers are cooled by collisions with the “cold” inert helium gas atoms and aggregated into clusters from collisions between monomers. The produced particle size can be manipulated by the gas pressure or by the evaporation rate. Helium pressures of 0.5, 1.0, 5.0, and 10.0 Torr were tested. The aerosol of particles is transported via self-induced thermal convective flux to a cylindrical liquid N₂-cooled rotating coldfinger, where it is continuously collected [108]. After the evaporation the UHV is restored and then slowly back-filled with oxygen to a final pressure of 1.0 Torr. The oxidized material is scraped off from the coldfinger and characterized in this as-prepared powder form. The treatment and storage in gastight glass cylinders are maintained identical for all samples. More information about the advantages and limitations of the IGC method can be obtained elsewhere [106, 109].

2.14. Electroless method

Shiau et al. [90] prepared catalysts by the electroless plating process, which is described as follows: Before conducting electroless deposition, γ-Al2O3 support is pre-treated with nitric acid to remove any impurities, and activated by palladium chloride solution to provide palladium nucleating centres on surface of γ-Al2O3. The activated γ-Al2O3 is finally contacted with copper solution for copper plating. In the copper solution, formaldehyde is added as reducing agent for the oxidation–reduction reaction. The plating bath is maintained at 70 °C and the pH is adjusted to 12.5. The plated γ-Al2O3 is filtrated and washed with distilled water, where after it is dried at 110 °C for 24 h. The first catalyst, namely EI, is prepared by electroless plating Cu onto γ-Al2O3 and then impregnating Ce followed by drying and calcinations. The second one, namely IE, is prepared by impregnating Ce first, followed by electroless plating Cu onto the support. The third one, namely CI, is prepared by co-impregnation of Cu and Ce onto γ-Al2O3. Since the first two catalysts (EI and IE) contain a small amount of Pd, which is required to activate the substrate during the electroless-plating course, Pd (0.012 wt%) is also added into CI catalyst to get an equal basis. The fourth catalyst, namely pure ECu, is prepared by electroless plating Cu onto γ-Al2O3. All the catalysts contain 5 wt% Cu and 10 wt% Ce (except pure ECu).

2.15. Laser vaporization and controlled condensation (LVCC)

Sundar and Deevi [6] studied CO oxidation activity of Cu–CeO2 nano-composite catalysts prepared by laser vaporization and controlled condensation. They described the method as follows: Desired ratio of metallic copper (2 µm) and ceria particles (1 µm) is mixed and pressed in a mechanical press to form the targets for LVCC experiments. The LVCC process involves pulsed laser vaporization of a target in a chamber under a selected gas mixture. The chamber consists of two parallel plates separated by a quartz ring of 5 cm height. Before the start of experiment, the chamber is evacuated several times and finally filled with argon gas. The top plate is maintained at room temperature and the bottom plate is maintained at a desired higher temperature using an electrical heater. The temperature gradient between the bottom and top plates results in a steady convection current, which can be enhanced under high-pressure (103 Torr) and large temperature gradient (ΔT~200 °C) conditions. The metal vapour is generated by pulsed laser vaporization using the second harmonic (532 nm) of an Nd-YAG laser (100 mJ/pulse, 10⁻⁸ s pulse). Ablation of the target material with the laser results in the formation of atomic, molecular and ionic species. These species react in the gas phase, in a region close to the
target, to form the corresponding nanosized materials. These species are carried by the convective flow generated due to the temperature gradient within the chamber, and deposited on the cold plate of the chamber.

2.16. Solvated metal atom impregnation method (SMAI)

The procedure for preparing Cu/CeO₂ catalysts by SMAI method is described by Zhang et al. [4] as shown below:

\[
\text{Cu}(\text{atom}) + (\text{C}_2\text{H}_5\text{CH}_3)(\text{vapor}) \rightarrow (\text{C}_2\text{H}_5\text{CH}_3)_2(\text{Cu})_n \rightarrow \text{CuO}_2
\]

The dehydrated CeO₂ is used as support and dehydrated and degassed toluene is used as the solvating medium. The preparation of the precursor solution of bis (toluene) copper (0) is carried out in the static metal atom reactor. In a typical experiment, approximately 1 g of copper chop (99.9%) is evacuated under a dynamic vacuum of less than 1.33x10⁻² Pa over a period of about 1 h. After finishing the co-condensation, the co-condensation is warmed up to -78 °C and melted down to the bottom of the reactor. The bis (toluene) copper (0) complex prepared in this way is extremely air sensitive and thermally unstable, which decomposes into copper (0) and toluene at about -100 °C. The precursor solution is transferred to the pre-cooled (-78 °C) CeO₂ through a stainless steel tube. The CeO₂ (20 g) is impregnated with solvated Cu atom (cluster) solution for 5 h at -78 °C under stirring. Then the Cu-toluene /CeO₂ slurry is gradually warmed to room temperature. A syringe removes the colourless excess toluene and the Cu/CeO₂ catalyst is dried under vacuum at room temperature for several hours. The dry sample is stored and handled in a nitrogen-filled glove box. CuO/CeO₂ catalyst is produced by oxidizing the CuO/CeO₂ catalyst in the reaction cell (in oxygen) at 200 °C for 3 h. The authors also prepared CuO/CeO₂ catalyst via conventional impregnation method using Cu(NO₃)₂ solution (to give a copper loading the same as the sample prepared via SMAI). Prepared catalysts are comparatively studied for low temperature CO oxidation.

2.17. Combinatorial synthesis of mixed metal oxides

Combinatorial synthesis is a powerful approach for the study of advanced materials. It is based on high-throughput experimentation, where libraries of potential catalysts are prepared and investigated in a parallel or an automated sequential manner to speed up development and discovery of materials with desired properties. Several reviews of catalyst development provide in-depth background into the technology [110, 111, 112].

One application of combinatorial synthesis of catalyst to soot oxidation has been reported by Reichenbach et al. [113]. A polymerizable complex method (PCM) of powder processing is applied to the combinatorial synthesis of Cu₁₋ₓCeO₂, for CO oxidation. In PCM, metal ions (nitrates) are dissolved in solution with a chelating agent (citric acid) and a polyhydroxyl alcohol (ethylene glycol). The metal ions are chelated by citric acid and are evenly distributed throughout the solution. Upon heating, the water or solvent evaporates, and the ethylene glycol undergoes polyesterification. Thus, a polymer resin is formed with the metal ions homogeneously distributed throughout. The resin is then essentially heated to higher temperatures for helping resin decomposition and formation of oxide powders. Because the PCM is a liquid mix process, metal ions are mixed on a molecular level, thus requiring lower processing temperatures and shorter processing times than comparable solid-state processes. The oxide powders produced in this manner have a higher surface area than those produced by solid-state methods. In this approach, inkjet dispensing technology is used to deposit PCM libraries of compositions combinatorially into “wells” on a metal plate. The solutions are then reacted in parallel in a furnace below 500 °C, with the result being an array of oxide catalysts “caps” of varying compositions.

3. Redox properties of CuO-CeO₂ catalysts

Copper catalyst has been found to be an excellent base metal catalyst for CO oxidation [114]. However, pure copper catalyst is less active and stable than the precious metal catalysts. Carbon monoxide oxidation involves surface oxygen and oxygen vacancy participation. The oxygen mobility of metal oxide catalysts also has something to do with catalyst activity [115, 116]. Cerium oxide is an outstanding oxygen ion conduction material and possesses redox properties, capable of activating the metal-oxygen bond of the active phase and/or of releasing
nascent oxygen with high reactivity. It is well accepted that the high activity of CuO/CeO₂ is attributed to the quick reversible Cu²⁺/Cu⁺ redox couples of highly dispersed copper species [105, 117]. Meanwhile, the redox properties of ceria are generally regarded to play key roles in governing the catalytic behaviours by assisting the Cu²⁺/Cu⁺ couples through Ce⁴⁺/Ce³⁺ cycles [118]. The ease of the Ce⁴⁺/Ce³⁺ redox cycle leads to outstanding oxygen storage capacity (OSC), coupled with the high mobility of oxygen in the crystal structure are two important properties of CeO₂. As a result of that, these oxides are capable of “adsorbing” oxygen reversibly [119], a property that is used in catalytic converters of automobiles as a source of oxygen when the effluent from the engine has a reducing nature [120]. Under real operating conditions, where the engine regime depends on the traffic conditions, the exhaust gases can be either in oxidant or reducing condition. Hence the use of ceria is specifically advantageous, due to its capability to store oxygen under oxidant conditions and to give it back under reducing conditions. The high activity of the CuO-CeO₂ system is attributed to the strong metal-support interactions (SMSI) between Cu species and the CeO₂ support. This interaction causes the reduction of the support and of the small CuO clusters to occur at low temperature. In this way, adsorption of CO produces an easy reduction of the catalyst’s surface with the generation of CO₂ at low temperature. Enhanced catalytic activity in oxidation reactions is believed to be connected to synergistic redox effect of Cu on CeO₂ and vice versa [121].

However, the use of ceria as an active catalyst support is limited by its strong tendency to sintering under high temperature conditions. It is shown that by doping ceria with zirconium oxide, the thermal stability of the material is significantly increased because of the formation of a solid solution which inhibits the sintering at high temperature [122-124]. The enhanced reducibility of ceria-zirconia solutions has sometimes been associated with the ability of the solid solutions to maintain high surface areas; however, recent thermodynamic studies have shown that even bulk oxygen is released much more easily in the mixed oxide [125]. The enthalpy change for oxidation of reduced oxides is found to be -520 kJ/mol O₂ for ceria-zirconia solutions (having a range of compositions), compared to an enthalpy change of -760 kJ/mol O₂ for pure ceria. The introduction of zirconium ions increases the formation of structural defects, which enhances the oxygen storage capacity [126-129]. Indeed, for pure ceria the oxygen exchange between the gas phase and the support is limited only to surface oxygen (homogeneous exchange), while the increased oxygen mobility obtained by doping ceria with zirconium extends the participation also to the bulk oxygen (heterogeneous exchange). Consequently, CuO/CeO₂-ZrO₂ catalysts present an increased reducibility in comparison to ceria-supported systems, due to the promotion also of the bulk ceria to the reduction at low temperature [76, 130, 131].

4. Activity of CuO-CeO₂ catalysts

CuO-CeO₂ catalytic systems have been examined for several processes as mentioned above. All these processes involve oxidation-reduction steps, which are promoted by the presence of ceria in comparison to traditional copper-based systems. The catalysts’ activity of CuO-CeO₂ systems has been discussed for the following applications:

4.1 Environmental pollution control-related applications
4.1.1 CO, HC and NOₓ pollution control

Carbon monoxide, usually emitted from many industrial process, transportation and domestic activities, is the major air pollutant. In addition to CO, hydrocarbons, and NOₓ are also vehicular exhaust pollutants. The three-way catalytic converter has effectively reduced emissions of these pollutants from automobiles. However, higher cost of noble metal catalyst used in current catalytic converters and recent regulations on emission control of vehicles, present a large challenge and opportunity for development of low cost alternatives such as transition metal oxide catalysts [132]. Cu–CeO₂ systems are identified as one of the promising catalysts to substitute for noble metal catalysts for vehicular emission control because of their high activities toward NO and CO and hydrocarbon oxidation [133].

The Cu-ceria catalysts showed substantially high activity and stability for CO oxidation [1], at a space velocity of 45,000 v/v h⁻¹. Complete CO conversion occurred at about 80 °C. Liu and Flytzani-Stephanopoulos [1] explained the increased activity of these catalysts by the stabilization of Cu⁺ in catalysts prepared via co-precipitation methods, originating from the interaction between copper clusters and cerium oxide, and addressing ceria to perform the role of oxygen source.

Oxidation of hydrocarbon, reduction of NO by NH₃ as well as CO and hydrocarbon occurs over 5%
Cu/CeO₂ catalyst in the low temperature window of 150–350 °C [18]. The exhaust purification reactions are represented as follows:

\[
\begin{align*}
\text{CO oxidation:} & \quad \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 \\
\text{HC Oxidation:} & \quad \text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{NO Reduction by CO:} & \quad \text{CO} + \text{NO} \rightarrow \text{CO}_2 + \text{N}_2 \\
\text{NO Reduction by HC:} & \quad 26\text{NO} + 2\text{C}_4\text{H}_{10} \rightarrow 13\text{N}_2 + 10\text{H}_2\text{O} + 8\text{CO}_2 \\
\text{NO Reduction by NH}_3 & \quad \text{NH}_3 + \text{NO} \rightarrow \text{H}_2\text{O} + \text{N}_2
\end{align*}
\]

The CuO-CrOₓ catalyst is regarded as the most active base metal catalyst for CO oxidation at high temperatures prior to the discovery of the present composite catalyst. Reaction kinetics analysis shows that relative reaction rate constants at 150 °C for the composite catalyst 9.4x10⁴ [1] is 5 times more than that for the CuO-CrOₓ catalyst [134]. The activation energies for the composite catalyst, 78 kJ.mol⁻¹, is also lower than that of the CuO-CrOₓ catalyst, 91 kJ.mol⁻¹. In a recent work [135] the present authors reported the strong interaction between CuO and CeO₂ closely related to the preparation routes and calcinations temperature playing a crucial role in the CO oxidation over the CuO–CeO₂ catalysts. The ranking order of the preparation methods of the catalyst in CO oxidation activity followed: sol-gel > urea nitrate > wet impregnation > thermal decomposition > co-precipitation.

4.1.2 Emission control from diesel engines

Diesel engines are the workhorses for industrial, commercial and personal transportation and also play a vital role in power generation. However, they have a serious drawback of relatively high emissions of particulate matter (PM) or soot and nitrogen oxides (NOₓ). Reduction of emissions is of prime importance for both environmental [136] and health concerns [137]. Concerns on health and environmental effects, and the tightening of diesel emissions regulations have driven research and development on control technologies for the control of harmful diesel exhaust pollutants. Among several technologies proposed to control emissions of soot, the catalytic combustion of soot is one of the most promising methods [138]. Effluent gases of the engines have a temperature range of 150-400°C, and consequently it is necessary to develop catalysts active at those temperature levels [138-140]. CuO-CeO₂ composite catalysts show excellent performance for the combustion of soot and are cited in the bibliography [24-28].

Wu et al. [27] synthesized Cu–Ce–Al mixed oxides by depositing Al₂O₃ powders in Cu–Ce gel and treating at 800 °C in air for 10 h. The modification of Al₂O₃ obviously increases the textural stability of the catalyst and improves the dispersion of CuO and CeO₂, which induces a lower soot oxidation temperature and a higher simultaneous NO reduction. Reddy and Rao [28] evaluated bimetallic (CuO–CoO/CeO₂–ZrO₂ and CuO–NiO/CeO₂–ZrO₂) catalysts for soot oxidation. They reported that the CuO–CoO/CeO₂–ZrO₂ combination exhibited an excellent catalytic activity (T₁/₂ = 363 °C) and nearly 100% selectivity towards CO₂. The high activity and stability of the catalyst could be attributed to solid solution formation, facile reduction and oxygen vacancies as well as the size of the metal particles along with their specific surface area.

4.1.3 VOC oxidation

Volatile organic compounds (VOCs), emitted from a variety of industrial processes and transportation activities, are considered as an important class of air pollutants. Catalytic oxidation is one of the most developed techniques used for the elimination of VOCs. CuO–CeO₂ mixed metal oxides comprise a promising family of catalysts and have been found effective catalysts in VOC oxidation. Larsson and Andersson [141] have studied the oxidation of ethanol and ethyl acetate over CuO/TiO₂ and CuO–CeO₂/TiO₂ catalysts. Cu-Ce-Ti-O catalysts show good performance for feeds both without and with water vapour. Hu et al. [16] have worked on the high activity of a CuO–CeO₂ (10 at. % Cu) catalyst in benzene oxidation. CuO–CeO₂ mixed oxides prepared by a combustion method [17] have higher surface areas than the corresponding pure oxides and are efficient total oxidation catalysts allowing destruction of ethanol and ethylacetate with minimal formation of undesired byproducts (acetaldehyde) at all conversion levels.

4.1.4 SO₂ reduction to elemental sulphur

Strong synergism of the composite catalyst has been demonstrated for SO₂ reduction, which is another major air pollutant, emitted by several industrial processes, such as power plants and automobiles. Scrubbing with an adsorbent material and Claus process are commercial technologies for SO₂ removal. The former generates solid waste, while the latter produces elemental sulphur that can be used to make sulphuric acid. However, Claus process involves a multi-step and complex reactor system. High throughput reactors for one-step, direct conversion of SO₂ into elemental sulphur.
sulphur is highly desirable for treatment of SO$_2$-laden industrial streams [142]. Cu- or Ni-modified ceria are active and selective catalysts for SO$_2$ reduction by CO to elemental sulphur [30]. Reduction of SO$_2$ to elemental sulphur is represented as follows:

\[
CO + SO_2 \rightarrow CO_2 + S
\]

4.1.5 Selective catalytic oxidation of ammonia

As is known, ammonia is a toxic inorganic gas with a pungent odor under ambient conditions, and is potentially harmful to public health [143, 144]. Therefore, the removal and the control and prevention, of the ammonia emission from air and waste streams are important in view of the environmental concerns. The selective catalytic oxidation (SCO) of ammonia in a stream to molecular nitrogen and water is one method for solving problems of ammonia pollution [145]. The catalytic oxidation of ammonia has been reported to precede the exothermic reaction as follows:

\[
4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O
\]

Chang-Mao Hung [33] has shown that SCO for ammonia by a bimetallic CuO/CeO$_2$ nanoparticle catalyst promotes the oxidation of NH$_3$. The SCO process was found to be more effective at lower temperatures. This work shows that the SCO process has the potential to treat highly concentrated streams of NH$_3$, helping industrial plants to meet discharge regulations.

4.2. Hydrogen production - related applications

Water-gas-shift reaction, steam reforming of methanol/ethanol and hydrocarbon, partial oxidation of hydrocarbons, preferential oxidation of CO in hydrogen rich gases, etc. is unit catalytic processes for hydrogen production. Although catalytic processes for hydrogen production from hydrocarbon fuels have been in commercial use for a long time, strong momentum propelled by high cost of energy and promise of fuel cells as a more efficient energy conversion process have recently rejuvenated and relegated research interest to hydrogen production technologies. Widespread use of fuel cells requires availability of hydrogen gas on demand at low costs. Hydrogen production-related reactions are as follows:

- Steam reforming of CH$_3$OH:
  \[
  CH_3OH + H_2O \rightarrow CO_2 + H_2
  \]
- Partial oxidation of HC:
  \[
  CH_4 + O_2 \rightarrow CO + H_2
  \]

The Cu-ceria composite catalysts show strong synergism for all these above mentioned reactions. Sedmak et al. [83] demonstrated that it is possible to increase the CuO/CeO$_2$ catalytic performances in CO-PROX by using a sol-gel preparation method. On these systems, characterization analysis evidenced the absence of interstitial copper ions, present in the samples prepared by co-precipitation, but CuO phase was finely dispersed on the surface of large CeO$_2$ crystallites [98]. These high dispersed copper clusters are believed to play a key role in the enhancement of activity of these catalysts. Thus, in contrast with Liu et al. [146] who supposed that the stabilizing effect of ceria on certain redox states of copper is the main reason for better catalytic performances, Martinez-Arias et al. [78] propounded that the facile redox interplay between the two components is the key factor of high catalyst performances.

In 2001 Avgouropoulos [147] tested CuO/CeO$_2$ systems for the reaction of CO oxidation in H$_2$ rich streams. A sample containing low copper concentration (6wt%) and relatively low surface area (16m$^2$/g), prepared via co-precipitation method, showed catalytic performances higher than noble metals based catalysts traditionally used for this application with 95% conversion at 200°C and 60% selectivity. Moreover, these systems showed a very high selectivity (namely 80%) in a wide range of temperature (up to 150 °C corresponding to 80% selectivity). Sedmak [82] tested CuO/CeO$_2$ systems prepared via sol-gel method for the CO-PROX reaction obtaining a significant increase of the catalyst activity with 100% conversion at 100°C and 40% selectivity. A higher activity of catalysts prepared via sol-gel is also observed for the catalytic wet oxidation of the phenol, application in which the system is four time more active and 25% more selective than those prepared via co-precipitation methods. Also CuO/CeO$_2$ catalysts, prepared by urea-nitrate combustion method, have been tested in CO-PROX without showing remarkable improvements [53], but on the contrary a high dependence of the catalyst performances on the urea/nitrate ratio. Wang [148] proposed for CO-PROX systems based on copper and supported on ceria doped with samaria. The presence of a cation Sm$^{3+}$ in the support generates in the ceria structure a charge defect which must be compensated with the vacancy formation. An increase of the vacancy concentration increases the
**Table 1.** Recent literature review at a glance on CuO/CeO₂ catalyst development for various reactions: (A) Reactions of environmental importance

<table>
<thead>
<tr>
<th>CO Oxidation</th>
<th>Catalyst Pnm. Method</th>
<th>Exptal Operating parameter</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu-CeO₂, copptn, bulk &amp; impreg supported, 2 at.% Cu-CeO₂, Caln. temp. = 650-860°C</td>
<td>Fixed-bed reactor, 150 mg cat, 2% CO, 16% O₂-N₂; Total gas flow rate = 100 scm, SV = 42000 h⁻¹</td>
<td>Novel total oxidn. Cat., Activity higher than Cu-based cats, super-rion to Pt-cats, due to synergistic effect between CuO-CeO₂. T₉₀% = 100°C. Resistant to H₂O vapour.</td>
</tr>
<tr>
<td>2</td>
<td>CuO/CeO₂, co-pprtn, Cu-loading 0.5-1.5%, decompen. temp. = 400-950°C</td>
<td>150 mg cat, 2.4% CO, 1.2% O₂-N₂, total gas flow rate = 80 scm.</td>
<td>15%Cu &amp; 650°C are optimum, impregn is better. CeO₂ promotes the redn of CuO, CuO/CeO₂ catalysts behaviour different w.r.t. pure CuO.</td>
</tr>
<tr>
<td>3</td>
<td>CuO/CeO₂ (3.58-7.12wt% Cu) co-pprtn &amp; impregn, Caln 200-1000°C</td>
<td>Flow mircoreactor, 30-300°C, 0.5 g cat(38-63µm), feed 5% CO, 20% O₂-N₂, 0.027mol/g</td>
<td>Optimum caln 400°C, T₉₀% = 72°C, low temp deactivation is reversible, while at high temp irreversible.</td>
</tr>
<tr>
<td>4</td>
<td>CuO/CeO₂ SMAI &amp; Co-impregnation</td>
<td>Fixed-bed micro-reactor, 0 – 120°C, 1 atm., 1% CO-air, 67 ml/min, s.v = 20000ml/h⁻¹ g⁻¹</td>
<td>5% Cu/CeO₂ (SMAI) is better than 5% Cu/CeO₂ (Cl)</td>
</tr>
<tr>
<td>117</td>
<td>CuO/CeO₂, a) copptn, b) deposition-pptn, c) impregnation methods</td>
<td>Feed, CO/O₂/He = 1:1:98, catal 250 mg, 2.5-10 wt% Cu, temp range 25-120°C</td>
<td>Activity order: a &gt; b &gt; c, Optim-um Cu 10 wt% for co-pprtn T₉₀% = 85°C.</td>
</tr>
<tr>
<td>5</td>
<td>CeO₂ nanoparticle &amp; nano-rod by pprtn &amp; hydro-thermal resp., 1% CuO-CeO₂ by pptn method</td>
<td>0.4 g cat, 1% CO, 2% O₂, 97% N₂, s.v = 120000 h⁻¹, heated at 2°C up to 200°C</td>
<td>CuO/CeO₂ nanorods indicate more synergetic effect and were more active (T₉₀% = 150°C) than nanoparticles (T₉₀% = 150°C)</td>
</tr>
<tr>
<td>6</td>
<td>Cu-CeO₂ nano LVCC</td>
<td>25 mg cat, 4% CO, 20% O₂ air, 1 L/min, heated at 15ºC/min</td>
<td>20%Cu-CeO₂ gives lowest LOT during the 2nd run</td>
</tr>
<tr>
<td>90</td>
<td>Cu/CeO₂-Al₂O₃: Electro-less plating, impregn, Co-impregn, 5wt%Cu, 10 wt% Ce</td>
<td>Cat 0.6 g, temp. RT = 200°C, feed 120 ml/min, 2% CO, 2% O₂ &amp; 12% H₂O-He</td>
<td>Electroless plating is the best method, a-phase Cu species is active phase for CO oxidn, 650°C is optimum caln temp.</td>
</tr>
<tr>
<td>8</td>
<td>CuO/CeO₂-ZrO₂ surfactant-assisted method</td>
<td>Temp.110-210°C,200mgcat,10%CO-air,36.6ml/min,SV=11,000ml.h⁻¹g⁻¹</td>
<td>25mom% CuO loading, calcined at 400°C shows Mesopore size distribution &amp; highest activity.</td>
</tr>
<tr>
<td>9</td>
<td>2% Cu, 8% Ce, co-impregnation supported cats. Caln temp=500°C</td>
<td>2%CO,3%O₂,feed=100ml/min, 0.2g cat, temp. 40-300°C</td>
<td>Activity CuO-CeO₂/SiO₂ &gt; CuO-CeO₂/ZrO₂ &gt; CuO-CeO₂/Al₂O₃ T₉₀% = 130°C for the best catalyst.</td>
</tr>
<tr>
<td>10</td>
<td>CuO/Ce₁₋ₓTixO₂, surfactant-assisted co-precipitation, Cu 6%, Caln 500°C</td>
<td>1g cat, 40-60 mesh, 1%CO, 5%O₂-N₂, SV = 30000 h⁻¹, 30-100°C for fresh cat, 40-160°C for aged cat</td>
<td>Higher dispersion of Cu on the support Ce₁₋ₓTixO₂ than on pure CeO₂, strong interaction bet’ Cu and support makes higher activity and thermal stability.</td>
</tr>
<tr>
<td>135</td>
<td>CuO-CeO₂ sol-gel, urea nitrate, wet impregn, thermal depcomp, co-precipitation.</td>
<td>100 mg cat, temp 30-300°C, press – atm, 2.5% CO in air, total feed rate 60 ml/min.</td>
<td>The ranking order of the preparation methods: sol-gel &gt; urea nitrate &gt; wet impregnation &gt; thermal decomposition &gt; co-precipitation.</td>
</tr>
</tbody>
</table>

**Oxidation of hydrocarbon & VOC**

| 11           | CeO₂-xZrO₂CuOₓ, Co-pprtn, Caln 400-1000°C, | Micro flow reactor, feed 1mol% alkane, 8% O₂-H₂, (for CH₄ 4%O₂), 100 ml/min, WHSV = 50000 h⁻¹ | Zr stablises redox activity, Cu dopant promotes activity. C₂H₆ C₃H₈ C₄H₁₀ iC₄H₁₀ T₉₀% 523 489 461 454°C |
| 12           | CuO-CeO₂ impregnation, 5% Cu loading, Caln 500°C, 140-220 mesh size | Fixed-bed reactor, 0.5 g cat, Feed=4000ppm toluene-air GHSV = 4500-13500h⁻¹, temp = 300-400°C | Order of activity: apour > p-xylene > benzene, water aapor or CO₂ inhibited activity, T₉₀% = 240°C. |
| 13           | CuMnO₂–CeO₂, Mn/(Mn + Ce)=0.5, molar, co-pprtn & deposition pptn, Cu = 2.54 wt% | Cat 200mg (40-60mesh), feed 200ppm C₂H₆, 20% O₂–H₂, 100ml/min, GHSV = 30000ml g⁻¹ h⁻¹ | Cu generates surface O₈ species for C₂H₆ adsorption & enhanced activity. |
| 14           | CuO-CeO₂ surfactant-assisted co-pprtn, Cu/Ce = 3/7 atomic, Caln 500°C, | Fixed reactor, 600mg cat (20-60 mesh), feed 0.5% C₂H₆, 5% O₂-N₂, SV = 30000 ml h⁻¹ | Mesoporous texture & surface areas >115 m²/g, CuO-CeO₂ cat shows excellent activity for CO oxidn via a carbonyl intermediate over Cu⁺ site. |
| 15           | CuO–CeO₂Al₂O₃, impregnation method, Caln. temp. = 550°C. | Cat = 120ml, Total feed = 40 l/min, GHSV = 20000 h⁻¹, temp 50-250°C for CO oxidn, 150-300°C for ethanol, ethyl acetate. | CuO–CeO₂Al₂O₃ is more active than CuO-Al₂O₃ for oxidation of CO but the effect of ceria is small for ethyl ace-tate and ethanol combustion. |
| 16           | Mesoporous CuO–CeO₂, pptn method, Caln 600°C | Cat=100mg(40-60mesh), feed: 1000ppm C₂H₆-air 180ml/min, 100-450°C, GHSV=36000g/h | Simple cat prep run, high s.a. (164.5m²/g), pore 1-10nm, excellent activity for oxidation of benzene, T₉₀% = 230°C. |
| 17           | CuO–CeO₂ urea combustion method, urea(Cu/Ce)=1.67-2.33, Cu(Cu-Ce) > 0,25, Caln. 550°C | Cat=80mg (90-180 µm), feed=50ml/min, W/F=0.072 g.s.ml⁻¹, S.V=5x10⁴ h⁻¹, VOC conc in airEtOH (1600), ethyl acetate (1800), toluene(600ppm) | CuO-CeO₂ mixed oxides have higher surface areas than the corresponding pure oxides, & complete VOC conversion at lower temps compared to the single oxides occurred. |
NO reduction

<table>
<thead>
<tr>
<th>Ref</th>
<th>Catalyst Pepn. Method</th>
<th>Exptal Operating parameter</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>5%Cu/CeO2, solution combustion method</td>
<td>TPR, NO/NH3=6/4 &amp; 1/1 molar, 0.2 g cat.</td>
<td>T100%&lt; 230°C by both NH3 &amp; CO T100%&lt; 350°C by n-C6H10</td>
</tr>
<tr>
<td>20</td>
<td>Cu/CeO2&amp;Cu/Cr/CeO2: 0-10wt% Cu, 25-75wt % Cr, impregnation.</td>
<td>Fixed bed reactor, 1 atm, 400°C, NO 20000 ppm, C3H8 20000 ppm, F/W= 10800mlg⁻¹ h⁻¹</td>
<td>Best cat Cu4%/Cr3%/CeO2 in SCR-C3H6 under net oxidizing conditions.</td>
</tr>
<tr>
<td>19</td>
<td>CuO/CeO2·TiO2 Impregnation method Can temp 500°C</td>
<td>120mg cat (20-40 mesh) feed: 6%NO, 6%CO·He, SV= 5000h⁻¹</td>
<td>Optimum composition: 12%CuO, 10%CeO2·TiO2 T100% = 350°C</td>
</tr>
<tr>
<td>21</td>
<td>(a)Cu4%/Ag1%/CeO2 &amp; (b)Cu4%/Ag1%/CeO2·ZrO2·Np, impregnation, caln = 550°C</td>
<td>NO 20000ppm, C3H8 20000 ppm, F/W=30000 mlg⁻¹h⁻¹ feed = 500ml/min, temp. range 250-550°C</td>
<td>Cat (b) showed better activity in temp region (250–350°C), optimum NO conversion, 82.89% is attained at reaction temp=415.38°C</td>
</tr>
<tr>
<td>22</td>
<td>Ce17Cu36HM, NH4+ form of mordenite by ion exchange-ange method, cal 500°C</td>
<td>500ppm NO, 500ppm NH3, 5%O2, 5%H2O, SV=150000h⁻¹, deactivation 20000ppm HCl, 150-450°C</td>
<td>CeCuHM is HCl-tolerable SCR catalyst</td>
</tr>
<tr>
<td>23</td>
<td>Cu4.7%Rh(0-2000ppm) on Al2O3, CeO2- Al2O3, CeO2- ZrO2, Copption-impregnation, Caln=650°C</td>
<td>TWC activity was measured in simultaneous conversion of CO, NOx and C3H6, cat 30-50mg, SV=25000ppm HCL, 150-450°C</td>
<td>Reaction order: CO oxidn&gt;C3H6 oxidn&gt;NO reduction. Cu is active though less than Rh. Support OSC favour the oxidn reactions &amp; NO conversion</td>
</tr>
<tr>
<td>24</td>
<td>Cu–Ce/Zr = 5/4 &amp; Cu/(Cu + Ce + Zr) = 1/10. Citric acid sol–gel using nitrate salts.</td>
<td>TPO, soot/cat = 1/10, tight &amp; loose contacts, 110 mg, heated at 20 °C min. 1000ppm NO + 9.5% O2 in N2 flow 500ml/min.</td>
<td>Cu-Ce best catalyst for tight contact. NO facilitates oxidn. Ti =300, Tmax= 324, T50% =350°C</td>
</tr>
<tr>
<td>25</td>
<td>Cu–Ce/Zr = 5/4 &amp; Cu/(Cu + Ce + Zr) = 1/10. Citric acid sol–gel using nitrate salts.</td>
<td>TPO, soot/cat = 1/10, tight &amp; loose contacts, 110 mg, heated at 10°C min. 9.5% O2 in N2 flow 500 ml/min.</td>
<td>CuO–CeO2–ZrO2 cats were less active but more thermally stable, tight contact, Ti =300, Tmax= 324, T50% =360°C.</td>
</tr>
<tr>
<td>26</td>
<td>Cu/CeO2, K/CeO2, Cu, K/ CeO2, ppton &amp; co-impregnation</td>
<td>TPO soot/cat = 1/10, tight &amp; loose contacts, 110 mg, heated at 10°C/min. 1000 ppm NO + 10% O2 in N2 flow 500 ml/min.</td>
<td>Cu, K/CeO2 catalysts show excellent activity, Ti =300, Tmax= 312, T50% =350°C.</td>
</tr>
<tr>
<td>27</td>
<td>Cu–Ce &amp; Cu–Ce–Al, citric acid sol gel, Cu:Ce = 1:9 molar, (Cu+Ce):Al = 2:1 Caln 500 &amp; 800°C</td>
<td>TPO soot/cat = 1/10, tight &amp; loose contacts, 110 mg, heated at 10°C/min. 1150 ppm NO + 9.6% O2 in N2 flow 500 ml/m.</td>
<td>AL2O3 increases stability and dispersion of CuO &amp; CeO2, lowers soot oxidn temp &amp; increases NO reduction</td>
</tr>
<tr>
<td>28</td>
<td>Cu–CoO/CeO2–ZrO2, CuO–NiO/ CeO2–ZrO2, Wet Impregnation using nitrate salts.</td>
<td>TGA, Soot/cat = 1/4, tight contact, 100 mg , Heated at 10 °C/min in air</td>
<td>CuO–CoO (5wt% each) CeO2–ZrO2 an excellent cat Ti =227, T50% = 363°C</td>
</tr>
</tbody>
</table>

Three way catalyst

<table>
<thead>
<tr>
<th>Ref</th>
<th>Catalyst Pepn. Method</th>
<th>Exptal Operating parameter</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>Cu–Ce/Zr = 5/4 &amp; Cu/(Cu + Ce + Zr) = 1/10. Citric acid sol–gel using nitrate salts.</td>
<td>TPO, soot/cat = 1/10, tight &amp; loose contacts, 110 mg, heated at 20 °C min. 1000ppm NO + 9.5% O2 in N2 flow 500ml/min.</td>
<td>Cu-Ce best catalyst for tight contact. NO facilitates oxidn. Ti =300, Tmax= 324, T50% =350°C</td>
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<td>30</td>
<td>Cu–Ce/Zr = 5/4 &amp; Cu/(Cu + Ce + Zr) = 1/10. Citric acid sol–gel using nitrate salts.</td>
<td>TPO, soot/cat = 1/10, tight &amp; loose contacts, 110 mg, heated at 10°C min. 9.5% O2 in N2 flow 500 ml/min.</td>
<td>CuO–CeO2–ZrO2 cats were less active but more thermally stable, tight contact, Ti =300, Tmax= 324, T50% =360°C.</td>
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<td>31</td>
<td>Cu/CeO2, K/CeO2, Cu, K/ CeO2, ppton &amp; co-impregnation</td>
<td>TPO soot/cat = 1/10, tight &amp; loose contacts, 110 mg, heated at 10°C/min. 1000 ppm NO + 10% O2 in N2 flow 500 ml/min.</td>
<td>Cu, K/CeO2 catalysts show excellent activity, Ti =300, Tmax= 312, T50% =350°C.</td>
</tr>
<tr>
<td>32</td>
<td>Cu–Ce &amp; Cu–Ce–Al, citric acid sol gel, Cu:Ce = 1:9 molar, (Cu+Ce):Al = 2:1 Caln 500 &amp; 800°C</td>
<td>TPO soot/cat = 1/10, tight &amp; loose contacts, 110 mg, heated at 10°C/min. 1150 ppm NO + 9.6% O2 in N2 flow 500 ml/m.</td>
<td>AL2O3 increases stability and dispersion of CuO &amp; CeO2, lowers soot oxidn temp &amp; increases NO reduction</td>
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<td>33</td>
<td>Cu–CoO/CeO2–ZrO2, CuO–NiO/ CeO2–ZrO2, Wet Impregnation using nitrate salts.</td>
<td>TGA, Soot/cat = 1/4, tight contact, 100 mg , Heated at 10 °C/min in air</td>
<td>CuO–CoO (5wt% each) CeO2–ZrO2 an excellent cat Ti =227, T50% = 363°C</td>
</tr>
</tbody>
</table>
Table 1.A. (cont.)

<table>
<thead>
<tr>
<th>SO2 reduction</th>
<th>SO2 redn by CO: whsv = 0.09 g/s/ml, 1%SO2-2%CO-He. SO2 redn by CH4: 1%SO2-0.5%CH4-He, whsv = 0.36g s/ml</th>
<th>La-doped cat is a highly active for SO2 redn by CO &amp; CH4. Cu increases the selectivity to S0 by catalyzing the total oxidn of CH4</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%CuCe(50%Zr)O2, 5%CuCe (4.5%La)O2, urea gelation/copption method, caln 650°C</td>
<td>1%SO2–2%CO–10.7%H2O–He, 0.09 g s/ml, 1% SO2–2%CH4–He, 0.18 g s/ml, 250–700°C, 1 atm press.</td>
<td>Cu-modified catalysts are active &amp; selective for SO2 redn by CO. NO in feed enhances both the SO2 conversion &amp; S0 yield.</td>
</tr>
<tr>
<td>5%Cu-Ce(10%La)O2, 15%Cu-Ce(10%La)O2 urea gelation/co-ption, Caln 650°C for SO2-CO &amp; 720°C for SO2-CH4</td>
<td>TGA reactor, SO2/N2 gas mixture (3600 ppm), 90 ml/min, heated at 20°C/min, RT-760°C, adsorpn gain of wt. was noted</td>
<td>De-Sox performance of prep’d cat was higher than conventi-onal ones. The improved adsorption capacity is due to interaction between Cu-ceria</td>
</tr>
<tr>
<td>CuO–CeO2-sorbent-catalyst, hexa-decylamine surfactant/impregn method</td>
<td>200mg cat, SO2/CO reaction: total feed 160 ml/min &amp; GHSV 25600 h⁻¹, for SO2/NO/CO reaction: total feed 200ml/ min &amp; GHSV= 32000 h⁻¹</td>
<td>Highly active and stable redox catalyst able to completely reduce NO and SO2 simultaneously by CO at a high GHSV= 32000 h⁻¹ to N2 and elemental sulfur</td>
</tr>
</tbody>
</table>

Decomposition of ammonia

| CuO-CeO2=6:4, copption caln 500°C. | fixed-bed reactor, 220–260°C, 1 atm, feed 1000ppm NH3, 4% O2–He, GHSV 92000ml/h.g, 150–400°C. | 98% NH3 removal and high selectivity toward N2 achieved at 400°C. |
| CuO–Ce=6:4, copption, caln 500°C | fixed-bed reactor, temp 150–400°C, 1g cat, 1000ppm NH3–4%O2, ghsv=92000ml/ (gh) | L–H kinetic model with first order reaction represent the NH3 oxidation, apparent E = 27.8 kJ/mol |

Oxidation of phenol

| 5wt%Cu–1wt%Ce/AC, impregn. method, caln 250°C | Batch ads expt for isotherm at 30°C, phenol oxdn in TG/MS, fixed bed reactor for ads-oxdn cycles | Cu–Ce/AC good catalyst–sorbent for phenol ads & cat dry oxdn, adsorptn. capacity =209 mg/g in fresh & stabilizes to 78mg/g after 9 consecutive ads–oxdn cycles. |
| CuOx/Co3O4Zr0.35O2 | Autoclave, 0.75g cat, 250ml of 1000mg/l phenol, 5.05 Mpa air at 150°C, pH=7.0 | CuOx/Co3O4Zr0.35O2 most effective in view of catalytic activity and CO2 selectivity |
### Table 1. Recent literature review at a glance on CuO/CeO$_2$ catalyst development for various reactions: (B) Reactions of commercial importance

<table>
<thead>
<tr>
<th>Reactions of commercial importance</th>
<th>Catalyst System</th>
<th>Reaction Conditions</th>
<th>Results/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam reforming of methanol (SRM)</td>
<td>CuO/CeO$_2$, coppton, calcn</td>
<td>450°C, reduction 350°C with 10%H$_2$</td>
<td>fixed-bed reactor, 220–260°C, 1 atm, 0.3 g cat &lt;70 mesh,</td>
</tr>
<tr>
<td>Oxidative reforming of methanol (OSRM)</td>
<td>CuO/CeO$_2$/Al$_2$O$_3$, coppton, calcn</td>
<td>500°C, reduction 300°C with 5% H$_2$</td>
<td>fixed-bed microreactor, 180–280°C, 1 atm, 500 mg, 0.45-0.55mm size</td>
</tr>
<tr>
<td>Urea combustion</td>
<td>CuO–CeO$_2$, urea combustion</td>
<td></td>
<td>fixed-bed microreactor, 0.3g cat, total flow=70ml/min, W/F=0.257 gs/ml, 5%MeOH, H$_2$O/CH$_3$OH = 0.1</td>
</tr>
<tr>
<td></td>
<td>CuO–CeO$_2$, urea combustion</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CuO–CeO$_2$/γ-Al$_2$O$_3$ impregnation, washcoated platelets</td>
<td></td>
<td>10-channel microreactor, MeOH/ H$_2$O ratio=1/1.1, 1 bar press</td>
</tr>
<tr>
<td></td>
<td>CuO/CeO$_2$ &amp; Cu/CeO$_2$/ZrO$_2$, coprecipitation method</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CuO/CeO$_2$/ZnO/Al$_2$O$_3$ = 30/10/20/40% by wt., copption</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CuO/CeO$_2$ (20–90at% Cu), co-ppton, nitrate precursors,</td>
<td></td>
<td>0.5g cat, 150-210µm, Temp 160-300°C, 1 atm, H$_2$O/MeOH = 1.5–, CuO/CeO$_2$ highest &amp; stable activities at 300°C for both SRM &amp; OSRM. Cu$^0$ is active catalyst species formed &lt; 180°C</td>
</tr>
</tbody>
</table>

### Water gas shift reaction (WGSR)

<table>
<thead>
<tr>
<th>Method</th>
<th>Catalyst System</th>
<th>Reaction Conditions</th>
<th>Results/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO by urea gelation (ug) &amp; template-assisted (ta) method, Cu-Pd-CeO$_2$ by wet impregn (wi) &amp; deposition ppton (dp)</td>
<td>CeO$_2$</td>
<td>0.5ml cat, 210°C, GHSV 17760 h$^{-1}$, feed for wgs 0.2%CO, 10% CO$_2$, 40% H$_2$O-Ar, for O$_2$ assisted wgs 1%O$_2$(air) added</td>
<td>Activity order: Cu-Pd on CeO$_2$ (ug)&gt; CeO$_2$(ta), wi &gt;dp, Cata (ug) shows 100% CO conve-rsion in O$_2$ assisted wgs with extremely high H$_2$ concn.</td>
</tr>
<tr>
<td></td>
<td>CuO/CeO$_2$ (20–30 wt%Cu &amp; 0.5–1 wt% Pd) in the OWGS reaction</td>
<td></td>
<td>Catalyst containing 20–30 wt.% Cu was found to be more active compared to that containing lower Cu loading of about 1 wt% Cu in ceria, both Cu$^0$ &amp; O vacancies in ceria involved in generation of the active sites</td>
</tr>
<tr>
<td></td>
<td>CuO/CeO$_2$ (20-90at% Cu), co-pton, nitrate precursors, 1mol/l NaOH precipitant, calcn 500°C</td>
<td></td>
<td>Activity of cat increased with Cu loading &amp; synergy of Cu &amp; ceria was confirmed. Optimum Cu loading 80 at%, cat showed stability at 360°C</td>
</tr>
</tbody>
</table>
### Table 1.B. (Cont.)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Composition</th>
<th>Preparation Method</th>
<th>Feed, Temperature, and Reactant Molar Fractions</th>
<th>CO Conversion, H2O, and CO2 Productivity, Temp, and Power-law Expression</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>53</td>
<td>CuO-CeO2</td>
<td>Urea nitrate</td>
<td>50-100mg cat, temp 40-280°C, feed 50-100ml/min, W/F=0.03-0.144gs/ml, 1% CO, 1.25% O2, 50% H2-He</td>
<td>100% selective, feed temperature range 45-90°C</td>
<td>Ref. 1</td>
</tr>
<tr>
<td>54</td>
<td>CuO-CeO2, pttion</td>
<td>Calm 500°C</td>
<td>166-176°C for a feed of 1% CO, 1% O2, 50% H2, 20% H2O, 13.5% CO2, He, SV = 42 g h/m3</td>
<td>CO content reduced &lt; 10 ppm, catalyst showed a slow, reversible deactivation, but the activity restored on heating at 300°C under an inert flow.</td>
<td>Ref. 1</td>
</tr>
<tr>
<td>55</td>
<td>CuO-CeO2</td>
<td>sol-gel method</td>
<td>Cat 37-251 mg, temp 45-155°C, feed 100 ml/min</td>
<td>100% selective in the temp range from 45 to 90°C</td>
<td>Ref. 1</td>
</tr>
<tr>
<td>56</td>
<td>CuO-CeO2, CuO–CeO2–ZrO2, &amp; CuO–ZrO2, CuO (1–10 wt%), pttion</td>
<td>Feed:74.17% H2, 0.49%CO, 23.26%CO2, 2.08% CH4, 2.5–10 liters/h</td>
<td>Activities order: CuO–ZrO2&lt; CuO–CeO2–ZrO2, optimim CuO=5 wt%, deactivation of H2O diminished &gt;150°C</td>
<td>Activity order: b &gt; c &gt; a &gt; d, method b) gives easily reducible well dispersed CuO species strongly interacting with ceria.</td>
<td>Ref. 1</td>
</tr>
<tr>
<td>57</td>
<td>CuO-CeO2</td>
<td>sol-gel method</td>
<td>Cat 15 mg, temp 50-200°C, feed 300 ml/min, 300 ppm CO &amp; 300 ppm O2 – He, SV=83000h-1</td>
<td>CO conversion and selectivity value over 90% at temp. around 165°C.</td>
<td>Ref. 1</td>
</tr>
<tr>
<td>58</td>
<td>CuO–CeO2, chelating method</td>
<td>Temp: 50–250°C, Cat: 0.05–0.12 g, feed:50–100 ml/min, 1% CO, 1.25% O2, 50% H2-He</td>
<td>Au/ceeria showed higher acti-vity than CuO/CeO2 at temp &lt;120°C, while CuO/CeO2 were able to operate at higher temps, with better selectivity.</td>
<td>Doping Zr into CeO2 increased the mobility of lattice oxygen &amp; activity comparable with, &amp; its selectivity was much larger than, that of the noble catalyst 5%Pt/Al2O3.</td>
<td>Ref. 1</td>
</tr>
<tr>
<td>59</td>
<td>CuO/CeO2</td>
<td>coprecipitation, calcn. 500°C</td>
<td>Temp: 25–250°C, feed: 1.5 g h/mol</td>
<td>Activity depends on the prep method &amp; Cu loading, 1 wt% Cu gives 100% CO conversion at 100°C</td>
<td>Ref. 1</td>
</tr>
<tr>
<td>60</td>
<td>CuO-CeO2</td>
<td>chelating method/ coprecipitation, calcn. 500°C</td>
<td>50-200mg cat, feed:0–50% H2, 0.5% O2, 0.2% O2, 2.0% CO-Ar, SV=120000 ml/g,h, temp: RT-150°C</td>
<td>chelating method is superior than coprecipitation method, CO conversions at 120°C are 99.6% and 88.6%, resp.</td>
<td>Doping Ni into CeO2 enhanced the mobility of lattice oxygen &amp; activity comparable with, &amp; its selectivity was much larger than, that of the noble catalyst 5%Pt/Al2O3.</td>
</tr>
<tr>
<td>61</td>
<td>CuO-CeO2</td>
<td>chelating method/ coprecipitation, calcn. 500°C</td>
<td>Temp: 50-100°C, feed 50-100 ml/min, 1% CO, 1.25% O2, 50% H2-He</td>
<td>Activity depends on the prep method &amp; Cu loading, 1 wt% Cu gives 100% CO conversion at 100°C</td>
<td>Ref. 1</td>
</tr>
<tr>
<td>62</td>
<td>CuO-CeO2</td>
<td>deposition–pption (DP) &amp; modified deposition–pption (MDP)</td>
<td>Temp: 25–250°C, feed: 1.5 g h/mol, 1% CO, 1.25% O2, 50% H2-He</td>
<td>Activity depends on the prep method &amp; Cu loading, 1 wt% Cu gives 100% CO conversion at 100°C</td>
<td>Doping Ni into CeO2 enhanced the mobility of lattice oxygen &amp; activity comparable with, &amp; its selectivity was much larger than, that of the noble catalyst 5%Pt/Al2O3.</td>
</tr>
<tr>
<td>63</td>
<td>CuO-CeO2</td>
<td>Urea thermal</td>
<td>Cat. 30mg temp.100-300°C, feed: 2% H2-N2, feed 60ml/ min, 2.8%CO, 3.5%O2–N2</td>
<td>More active and selective than a commercial Pt/Al2O3. Activity increases as the Cu content increases</td>
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<tr>
<td>64</td>
<td>CuO-CeO2</td>
<td>coprecipitation method</td>
<td>50mg cat, feed: 50% H2, 1% O2, 1% CO, 1% CuO, 1% CO2, 1% H2O-Ar</td>
<td>Pr doping enhanced activity, the CO-PROX conversion &gt; 99% at 120°C</td>
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</tr>
<tr>
<td>65</td>
<td>CuO-CeO2</td>
<td>coprecipitation method</td>
<td>Cat.-50 mg; 100 mg, flow rate 100 ml (STP)/min, feed gas 1% CO, 1% O2, 50% H2-He</td>
<td>CO oxidation orders: 0.91, 0.37 &amp; 0.62 w.r.t. partial press of CO, CO2 and H2O, resp, E for CO &amp; H2 oxidn:94.4 and 142 kJ/mol, resp</td>
<td>Optimum CuO=7wt%, WI method is better than DP, resulting higher activity</td>
</tr>
<tr>
<td>66</td>
<td>CuO-CeO2, wet impregn (WI) &amp; deposition pption (DP) methods</td>
<td>Optimum CuO=7wt%, WI method is better than DP, resulting higher activity</td>
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<td>Ref. 1</td>
</tr>
<tr>
<td>67</td>
<td>CuO-CeO2(20at%Cu), copption</td>
<td>200-300mg cat, feed: 2000-6000ml/min, 500-3000ppm CO, 500-4500ppm O2, 20%CO= 0.33-3, 0–70%H2, 0-15%CO2, 0-2%CH4, 0-15% H2O, temp: 90-300°C</td>
<td>H2 in feed had little influence on the CO conversion, CO2 and H2O decreased the activity, power-law expression gave a good fit in limited concn ranges, reaction orders depend on the reactant molar fractions.</td>
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<td>Ref. 1</td>
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<tr>
<td>No.</td>
<td>Catalyst System &amp; Preparation Method</td>
<td>Reaction Conditions</td>
<td>Remarks</td>
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<tr>
<td>69</td>
<td>Cu$_0$.7Fe$_2$.O$_4$/Ce–ZrO$_2$, co-</td>
<td>1g cat, feed: 15% CH$_4$, 30ml/min, Ar 30ml/min with H$_2$O p=31.1kPa, temp: 900 &amp; 700°C</td>
<td>Ce/Zr=3/1 molar shows highest activity for syngas prodn, ten repeated cycles, the cat showed the greatest durability</td>
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</tr>
<tr>
<td>71</td>
<td>Ni-free 20wt%Cu-10wt%CeO$_2$-YZ anode</td>
<td>direct oxidation of n-butane at 700°C in SOFC</td>
<td>Wet impregn: An alternative method for fabrication of high performance and nanostrucured electrodes of SOFC has been critically reviewed</td>
<td></td>
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</tr>
<tr>
<td>72</td>
<td>Cu–CeO$_2$–ScZ &amp; Cu–CeO$_2$–yZ fuel cell anodes by coimpregn method, caln: 450°C, 20wt.%Cu–10wt.%CeO$_2$, 15wt.%Cu–12wt.%CeO$_2$, 15wt.%Cu–15wt.%CeO$_2$.</td>
<td>H$_2$ redn of electrodes at 800°C, Electrochemical impedance spectroscopy in H$_2$ and ethanol steam was measured at open circuit voltage with amplitude of 20 mV over 0.008 Hz to 100 KHz</td>
<td>maximum power density of single cell reached 604 mW cm$^{-2}$ and 408 mW cm$^{-2}$ at 800°C in H$_2$ and ethanol steam resp., and cell obtained stable output in ethanol steam over an operation period of 50 h.</td>
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</tr>
<tr>
<td>73</td>
<td>Cu or Cu–Ni with CeO$<em>2$, Ce$</em>{0.9}$Gd$_{0.1}$O$_2$.</td>
<td>CH$_4$ oxidn: TPO, temp: RT-900°C, direct oxidation of CH$_4$ in solid oxide fuel cell</td>
<td>Potential application of cats examined as anodes of SOFC for direct oxidation of hydrocarbons, CH$_4$ oxidn order: CuNi–CG &gt; CuNi–CT &gt; CuNi–C</td>
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</tr>
<tr>
<td>74</td>
<td>Pure and Li$_2$O-doped CuO/CeO$_2$, impregn method, caln 500°C</td>
<td>Activity tests for H$_2$O$_2$ decomposition at 30°C, 50mg cat, 0.5ml H$_2$O$_2$ in 10ml H$_2$O.</td>
<td>Activity of CuO/CeO$_2$ cats increased by increasing both heat treatment time and dopant content, 10wt% CuO is optimum for pure Cu/Ce cat</td>
<td></td>
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</tr>
<tr>
<td>97</td>
<td>10-40 wt% Cu/CeO$_2$, copptn, pre-reduced cat, methanol synthesis</td>
<td>Fixedbed reactor, 0.5g cat, 33% CO, 67%H$_2$, (3.6 l/h, 2MPa), 195°C</td>
<td>Activity at 195°C is comparable with commercial Cu-Zn catalyst at 230-250°C</td>
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</tr>
<tr>
<td>75</td>
<td>3 wt% Cu/Ce$<em>{0.8}$Zr$</em>{0.2}$O$_2$, deposition ptpn, caln 600°C, methanol synthesis</td>
<td>Cat: 0.15g, feed: H$_2$ &amp; CO, H$_2$/CO=3, 60ml/min, temp: 200-250°C, press: 3Mpa</td>
<td>3 wt% Cu/Ce$<em>{0.8}$Zr$</em>{0.2}$O$_2$ is four fold active than that of 3 wt% Cu/ZrO$_2$ in methanol synthesis</td>
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</table>
oxygen ion mobility in the structure, thus enhancing the redox properties of the system. In relation to the CO-PROX reaction, the catalyst activity increases compared to CuO/CeO₂ catalysts prepared via coprecipitation methods but the selectivity decreases.

Table 1 provides a list of representative literature survey on composite catalysts for the above mentioned reactions. The Cu-ceria composite catalysts show strong synergism for all these reactions. These seemingly different reactions have two common fundamental attributes. First, all the reactions involve one oxidizing molecule and another reducing molecule. Second, all these reactions involve transfer of oxygen atom from one molecule to the other.

5. Conclusions

This review summarizes the advances in the preparation methods of CuO-CeO₂ catalysts for many potential applications for various reactions of environmental, commercial and other importance. This catalyst system of particular pore structures, or compositions, crystal structures or high hydrothermal stability depends on the preparation methods. The choice of a laboratory method for preparing a given catalyst depends on the physico-chemical characteristics desired in the final composition for specific application. The authors of the present paper reported ranking order of the preparation methods of the catalyst in CO Oxidation activity as: sol-gel > urea nitrate > wet impregnation > thermal decomposition > co-precipitation.

The CuO-CeO₂ catalysts exhibit versatile applications owing to the large interest in all the low temperature redox reactions. The high activity of CuO-CeO₂ is attributed to the quick reversible Cu²⁺/Cu⁺ redox couples assisted by Ce⁴⁺/Ce³⁺ cycles. The CuO-CeO₂ catalysts show excellent performances in comparison to traditional copper-based systems because of the following properties: (i) outstanding activity in CO oxidation as: sol-gel > urea nitrate > wet impregnation > thermal decomposition > co-precipitation.

Aknowledgements

The authors gratefully acknowledge the receipt of financial support for this work from the Department of Science & Technology, Government of India, under the SERC (Engg. Science) Project Grant NO.SR/S3/ME/ 027/2006.

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