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Preparation Methods and Applications of $CuO\text{-}CeO_2$ Catalysts: A Short Review

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Abstract

The $CuO\text{-}CeO_2$ 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 $CuO\text{-}CeO_2$ 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.

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Keywords: $CuO\text{-}CeO_2$ 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 occured at about 80 ^{0}C at a space velocity of 45,000 h^{-1}. Thus, in recent years, the high catalytic activity and selectivity of the $CuO\text{-}CeO_2$ 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_3H_6 [20,21], NO reduction by NH_3 [22], three-way catalytic convertion [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

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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, Cu/CeO_2 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 H_2O_2 decomposition [74] as well as methanol synthesis [75], etc

To date, there has been frequent most use of $CuO\text{-}CeO_2$ 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 $CuO\text{-}CeO_2$ systems 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 ^0C with hydrocarbon/methanol/ ethanol fuel(s) requires a cathode and an anode possessing high electro-catalytic activity to facilitate O_2 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 Cu/CeO_2 composite electrodes for direct oxidation of hydrocarbon in SOFC.

The oxidation catalysts based on $CuO\text{-}CeO_2$ can be classified [9] into three types: (i) CuO and CeO_2 catalysts [53, 84-88], (ii) CuO catalysts doped with CeO_2 (or vice versa) supported on alumina [55, 88-91], and (iii) CuO catalysts supported on mixed $Ce_xZr_{(1-x)}O_2$ 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 $CuO\text{-}CeO_2$ catalysts. However, preparation methods of such catalysts have hardly been reviwed 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 $CuO\text{-}CeO_2$ 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 towardss diverse ways of preparation, even for a given selection of the basic material. Following methods for the preparation of $CuO\text{-}CeO_2$ 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 [$Ce(NO_3)_3.6H_2O$] in air for 4 h at 400, 500, 600, or 700 ^{0}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 $Cu(NO_3)_2.3H_2O$ for 5 h, where after the excess of water is vaporized by heating at 600C. The materials, thus obtained, are dried overnight in an oven at 800 C and serially calcined in air for 3.5 h at 300, 400, 500, 600, or 800 ^{0}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 $Al_2O_3/ZrO_2/SiO_2$ 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 SiO2 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_2O_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_2CO_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 alkalis 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. So 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 ^{0}C in air and calcined at 400 ^{0}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 in-homogeneities 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_2CO_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 ^{0}C. Final CuO-CeO_2 catalyst emerges after decomposing and calcining the precursor at 650 ^{0}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 ^{0}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 $(NH_4)_2Ce(NO_3)_6$. The preparation procedure consists of mixing the aqueous metal nitrate solutions with urea (NH_2-CO-NH_2); heating the solution to 100 ^{0}C under vigorous stirring and addition of de-ionized water; boiling the resulting gel for 8 h at 100 ^{0}C; filtering and washing the precipitate twice with de-ionized water at 50-70 ^{0}C; drying the cake in a vacuum oven at 80-100 ^{0}C for 10-12 h; crushing the dried lump into smaller particles and calcining the powder in a muffle furnace in air at 650 ^{0}C for 4 h. A heating rate of 2 ^{0}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 ^{0}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:

$$Ce(NO_3)_3 + (7/3)CO(NH_2)_2 \rightarrow CeO_2 + (23/6)N_2 + (7/3)CO_2 + (14/3)H_2O$$

$$Cu(NO_3)_3 + (5/3)CO(NH_2)_2 \rightarrow CuO + (8/3)N_2 + (5/3)CO_2 + (10/3)H_2O$$

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(NO3)3·6H2O], copper nitrate [$Cu(NO_3)_2 \cdot 3H_2O$], 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 ^{0}C and the resulting viscous gel is introduced in an open muffle furnace, preheated at 400–500 ^{0}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 ^{0}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. Oxalyldihydrazide (ODH, $C_2H_6N_4O_2$) 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_2O, is introduced into a muffle furnace preheated to 350 ^{0}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 and 10% Cu/CeO_2 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 ^{0}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 ^{0}C until transparent gel is formed. The resulting gel is dried at 110 ^{0}C overnight. The powder received is subjected to decomposition at 300 ^{0}C for 1 h and calcined at 500 ^{0}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, 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 ^{0}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 ^{0}C/min) up to the calcination temperature (T_{calc} = 450 or 550 ^{0}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 ^{o}C/min, T_{calc} = 550 ^{o}C).

2.9. Surfactant-assisted method

Cao et al. [8] presented surfactant-assisted method for the preparation of CuO/$Ce_{0.8}Zr_{0.2}O_2$ catalysts with different CuO content of nano-particle 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 $Ce(NO_3)_2 \cdot 6H_2O$, 2 mmol of $Zr(NO_3)_4.5H_2O$ and calculated amount of $Cu(NO_3)_2.3H_2O$ 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 ^{0}C for 3 h, washed with hot water, dried in the oven at 110 ^{0}C for 6 h, then milled and calcined at 400 ^{0}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 $CeZrCu_0$, $CeZrCu_5$, $CeZrCu_{10}$, $CeZrCu_{15}$, $CeZrCu_{20}$, $CeZrCu_{25}$, $CeZrCu_{30}$, $CeZrCu_{40}$, 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 $Ce(NO_3)_2 \cdot 6H_2O$ 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 ^{0}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 ^{0}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 ^{0}C overnight and then calcined at 300, 400 and 500 ^{0}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 $(NO_3)_2$ 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 ^{0}C for about 5 h and then heated at 500 ^{0}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 $Ce(NO_3)_2$ 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 CuO_x/CeO_2 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 N_2-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 decribed as follows: Before conducting electroless deposition, γ-Al_2O_3 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-Al_2O_3. The activated γ-Al_2O_3 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 ^{0}C and the pH is adjusted to 12.5. The plated γ-Al_2O_3 is filtrated and washed with distilled water, where after it is dried at 110 ^{0}C for 24 h. The first catalyst, namely EI, is prepared by electroless plating Cu onto γ-Al_2O_3 and then impregnating Ce followed by drying andcalcinations. 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-Al_2O_3. 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-Al_2O_3. All the catalysts contain 5 wt% Cu and 10 wt% Ce (except pure Ecu).

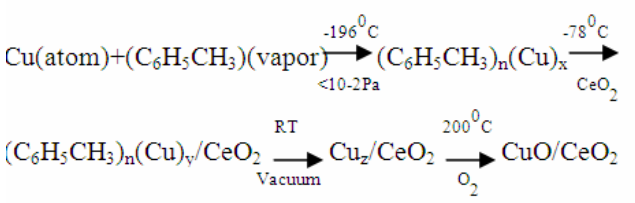
2.15. Laser vaporization and controlled condensation (LVCC)

Sundar and Deevi [6] studied CO oxidation activity of Cu–CeO_2 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 ^{0}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/CeO_2, catalysts by SMAI method is described by Zhang et al. [4] as shown below:



The dehydrated CeO_2 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 aperiod of about1 h. After finishing the co-condensation, the co-condensation is warmed up to -78 ^{0}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 ^{0}C. The precursor solution is transferred to the pre-cooled (-78 ^{0}C) CeO_2 through a stainless steel tube. The CeO_2 (20 g) is impregnated with solvated Cu atom (cluster) solution for 5 h at -78 ^{0}C under stirring. Then the Cu-toluene /CeO_2 slurry is gradually warmed to room temperature. A syringe removes the colourless excess toluene and the Cu/CeO_2 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/CeO_2 catalyst is produced by oxidizing the CuO/CeO_2 catalyst in the reaction cell (in oxygen) at 200 ^{0}C for 3 h. The authors also prepared CuO/CeO_2 catalyst via conventional impregnation method using $Cu(NO_3)_2$ 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 Cu_{1-x} Ce_xO_3, 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 ^{0}C, with the result being an array of oxide catalysts "caps" of varying compositions.

3. Redox properties of $CuO-CeO_2$ 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 some thing 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/CeO_2 is attributed to the quick reversible Cu^{2+}/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 Cu^{2+}/Cu^{+} couples through Ce^{4+}/Ce^{3+} cycles [118]. The ease of the Ce^{4+}/Ce^{3+} 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 CeO_2. 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-CeO_2 system is attributed to the strong metal–support interactions (SMSI) between Cu species and the CeO_2 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 CO_2 at low temperature. Enhanced catalytic activity in oxidation reactions is believed to be connected to synergistic redox effect of Cu on CeO_2 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 O_2 for ceria-zirconia solutions (having a range of compositions), compared to an enthalpy change of -760 kJ/mol O_2 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/CeO_2-ZrO_2 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-CeO_2 catalysts

CuO-CeO_2 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-CeO_2 systems has been discussed for the following applications:

4.1 Environmental pollution control-related applications

4.1.1 CO, HC and NO_x 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 NO_x 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–CeO_2 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 ^{0}C. Liu and Flytzani-Stephanopoulos [1] explained the increased activity of these catalysts by the stabilization of Cu^{+1} 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 NH_3 as well as CO and hydrocarbon occurs over 5%

Cu/CeO_2 catalyst in the low temperature window of 150–350 ^0C [18]. The exhaust purification reactions are represented as follows:

CO oxidation: $CO + O_2 \rightarrow CO_2$
HC Oxidation: $CH_4 + O_2 \rightarrow CO_2 + H_2O$
NO Reduction by CO: $CO + NO \rightarrow CO_2 + N_2$

NO Reduction by HC:
$26NO + 2C_4H_{10} \rightarrow 13N_2 + 10H_2O + 8CO_2$
NO Reduction by NH_3: $NH_3 + NO \rightarrow H_2O + N_2$

The $CuO\text{-}CrO_x$ 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 ^0C for the composite catalyst $9.4x10^4$ [1] is 5 times more than that for the $CuOCrO_x$ catalyst [134]. The activation energies for the composite catalyst, 78 $kJ.mol^{-1}$ is also lower than that of the $CuO\text{-}CrO_x$ catalyst, 91 $kJ.mol^{-1}$. In a recent work [135] the present authors reported the strong interaction between CuO and CeO_2 closely related to the preparation routes and calcinations temperature playing a crucial role in the CO oxidation over the $CuO–CeO_2$ 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 (NO_x). 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 150-400^0C, and consequently it is necessary to develop catalysts active at those temperature levels [138-140]. $CuO\text{-}CeO_2$ 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 Al_2O_3 powders in Cu–Ce gel and treating at 800 ^0C in air for 10 h. The modification of Al_2O_3 obviously increases the textural stability of the catalyst and improves the dispersion of CuO and CeO_2, which induces a lower soot oxidation temperature and a higher simultaneous NO reduction. Reddy and Rao [28] evaluated bimetallic ($CuO–CoO/CeO_2–ZrO_2$ and $CuO–NiO/CeO_2–ZrO_2$) catalysts for soot oxidation. They reported that the $CuO–CoO/CeO_2–ZrO_2$ combination exhibited an excellent catalytic activity ($T_{1/2}$ = 363 ^0C) and nearly 100% selectivity towards CO_2. 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. $CuO–CeO_2$ 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/TiO_2 and $CuO–CeO_2/TiO_2$ 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 $CuO–CeO_2$ (10 at. % Cu) catalyst in benzene oxidation. $CuO–CeO_2$ 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 SO_2 reduction to elemental sulphur

Strong synergism of the composite catalyst has been demonstrated for SO_2 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 SO_2 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 SO_2 into elemental

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_3OH:

$$CH_3OH + H_2O \rightarrow CO_2 + H_2$$

Partial oxidation of HC:

$$CH_4 + O_2 \rightarrow CO + H_2$$

Water-gas-shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Preferential oxidation of CO:

$$CO + O_2 \rightarrow CO_2,\ H_2 + O_2 \neq H_2O$$

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 ($16 m^2/g$), prepared via coprecipitation 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/CeO_2 catalyst development for various reactions:
(A) Reactions of environmental importance

CO Oxidation			
Ref	**Catalyst Pepn. Method**	**Exptal Operating parameter**	**Remark**
1	Cu-Ce-O, copption, bulk & impregn supported, 2 at.% Cu-CeO_2, Caln. temp.= 650-860^{0}C.	Fixed-bed reactor, 150 mg cat, 2% CO, 16% O_2-N_2, Total gas flow rate-100 sccm, SV=42000 h^{-1}.	Novel total oxidn. Cat., Activity higher than Cu-based cats, supe-rior to Pt-cats, due to synergistic effect between CuO-CeO_2. $T_{100\%f}$= 100^{0}C. Resistant to H_2O vapour.
2	CuO/CeO_2, co-pption. & impregn, Cu-loading 0.5-15%, decompn. temp = 400-950^{0}C	150 mg cat, 2.4% CO, 1.2% O_2-N_2, total gas flow rate-80 sccm.	15%Cu & 650^{0}C are optimum, impregn is better. CeO_2 promotes the redn of CuO, CuO/CeO_2 catalysts behaviour different w.r.t. pure CuO.
3	CuO/CeO_2 (3.58-7.12wt% Cu) co-pption & impregn, Caln 200-1000^{0}C	flow microreactor, 30-300^{0}C, 0.5g cat(38-63μm), feed 5% CO, 20%O_2-N_2, 0.027mol/g/h	Optimum caln 400^{0}C, $T_{100\%}$= 72^{0}C, low temp deactvaion is reversible, while at high temp irreversible.
4	CuO/CeO_2 SMAI & Co-impregnation	Fixed-bed micro-reactor, 0 – 120^0 C, 1 atm., 1% CO-air, 67 ml/min, sv = 20000mlh^{-1} g^{-1}	5% Cu/CeO_2 (SMAI) is better than 5% Cu/CeO_2 (CI)
117	CuO/CeO_2, a) copption, b) deposition-pption, c) impregnation methods	Feed, CO/O_2/He = 1:1:98, catal 250 mg, 2.5-10 wt% Cu, temp range 25-120^{0}C	Activity order: a > b > c, Opti-mum Cu 10 wt% for co-pption $T_{100\%}$ = 85 ^{0}C.
5	CeO_2 nanoparticle & nano –rod by pption & hydro- thermal resp., 1% CuO-CeO_2 by pption method	0.4 g cat, 1%CO, 2%O_2, 97%N_2, s.v = 120000h^{-1}, heated at 2^{0}C up to 200^{0}C	CuO/CeO_2 nanorods indicate more synergetic effect and were more active (T_f=150^{0}C) than nanoparticles ($T_{100\%}$=150^0 C)
6	Cu-CeO_2 nano LVCC	25 mg cat, 4% CO, 20% O_2-Ar, 1 L/min, heated at 15^{0}C/min	20%Cu-CeO_2 gives lowest LOT during the 2nd run
90	Cu /CeO_2/ Al_2O_3: Electro-less plating, impgn, Co-impregn,5wt%Cu,10 wt% Ce	Cat 0.6 g, temp. RT- 200^{0}C, feed 120 ml/ min, 2% CO, 2% O_2 & 12% H_2O-He	Electroless plating is the best method, α-phase Cu species is active phase for CO oxidn, 650^0 C is optimum caln temp.
8	$CuO/Ce_{0.8}Zr_{0.2}O_2$ surfactant-assisted method	Temp.110-210^{0}C,200mgcat,10%CO -air,36.6ml/min,SV=11,000ml. $h^{-1}g^{-1}$	25mol% CuO loading, calcined at 400^{0}C shows Mesopore size distribution & highest activity.
9	2% Cu, 8% Ce, co-impregion supported cats. Caln temp=500^{0}C	2%CO,3%O_2, feed:100 ml/ min, 0.2g cat, temp. 40-300^{0}C	Activity $CuO-CeO_2/SiO_2$ >$CuO-CeO_2$/ ZrO_2>$CuO-CeO_2$/ Al_2O_3, $T_{100\%}$=130^{0}C for the best catalyst.
10	$CuO/Ce_{1-x}TixO_2$, surfactant-assisted co-precipitation, Cu 6%, Caln 500^{0}C	1g cat, 40-60 mesh, 1%CO, 5%O_2-N_2, SV= 30000h^{-1}, 30-100^{0}C for fresh cat, 40-160^{0}C for aged cat	Higher dispersion of Cu on the support $Ce_{1-x}Ti_xO_2$ than on pure CeO_2, strong interaction bet' Cu and support makes higher activity and thermal stability.
135	CuO-CeO_2 sol-gel, urea nitrate, wet impregn, thermal decompn, co-precipitation.	100 mg cat, temp 30-300^{0}C, press – atm, 2.5% CO in air, total feed rate 60 ml/min.	The ranking order of the preparation methods: sol-gel > urea nitrate > wet impregnation > thermal decomposition > co-precipitation.
Oxidation of hydrocarbon & VOC			
11	$Ce_{0.76}$ $Zr_{0.19}Cu_{0.05}$ O_2-x, Co-pption, caln 400-1000^{0}C,	Micro flow reactor, feed 1mol% alkane, 8% O_2-He, (for CH_4 4%O_2), 100 ml/min, WHSV=50000h^{-1}	Zr stabilises redox activity, Cu dopant promotes activity. C_2H_6 C_3H_8 C_4H_{10} i C_4H_{10} $T_{90\%}$ 523 489 461 454^{0}C
12	CuO-CeO_2, impregnation, 5%Cu loading, caln 500^{0}C, 140-220 mesh size	Fixedbed reactor, 0.5g cat, feed=4000ppm toluene-air GHSV= 4500-13500h^{-1}, temp:200-400^{0}C	Order of activity: apour > p-xylene > benzene, water apour or CO_2 inhibited activity, $T_{100\%}$=240^{0}C.
13	Cu/MnO_x–CeO_2, Mn/ (Mn + Ce)=0.5, molar, co-pption & deposition pption, Cu = 2.54 wt%	Cat 200mg (40-60mesh), feed 200ppm C_6H_6, 20% O_2-He, 100ml/min, GHSV = 30000ml $g^{-1}h^{-1}$	Cu generates surface O_6 species for C_6H_6 adsorption & enhanced activity.
14	CuO-CeO_2, surfactant-assi-sted co-pption, Cu/Ce=3/7 atomic, Caln 500^{0}C.	Fixedbed reactor, 600mg cat (20-60 mesh), feed 0.5% C_3H_8, 5%O_2-N_2	mesoporous texture & surface areas >115 m^2/g, CuO-CeO_2 cat shows excellent activity for CO oxidn via a carbonyl intermediate over Cu^+ site.
15	CuO_x–CeO_x/Al_2O_3, impre-gnation method, caln. temp. = 550^{0}C.	Cat = 120ml, Total feed = 40 l/min, GHSV = 20000 h^{-1}, temp 50-250^{0}C for CO oxidn, 150-300^{0}C for ethanol, ethyl acetate.	CuO_x–CeO_x/Al_2O_3 is more active than CuO_x-Al_2O_3 for oxidation of CO but the effect of ceria is small for ethyl ace-tate and ethanol combustion.
16	Mesoporous CuO–CeO_2, pption method, caln 600^{0}C	Cat=100mg(40-60mesh), feed: 1000ppm C_6H_6-air 160ml/min, 100-450^{0}C, GHSV=36000/96000h^{-1}	Simple cat prepn route, high s.a. (164.5m^2/g), pore 1-10nm, excellent activity for oxidation of benzene, $T_{100\%}$=230^{0}C
17	CuO–CeO_2 urea combustion method, urea/(Cu-Ce)=1.67-2.33, Cu/(Cu-Ce) > 0.25, Caln. 550^{0}C	Cat=60mg (90-180 μm), feed=50ml/min, W/F= 0.072 g.$s.ml^{-1}$, S.V=5x10^4 h^{-1}, VOC conc in airEtOH (1600), ethyl acetate (1800), toluene(600ppm)	CuO–CeO_2 mixed oxides have higher surface areas than the corresponding pure oxides, & complete VOC conversion at lower temps compared to the single oxides occurred.

Table 1.A. (cont.)

NO reduction			
18	5%Cu/CeO_2, solution combustion method	TPR, NO/NH_3=6/4 & 1/1 molar, 0.2 g cat,	$T_{100\%}$< 230^{0}C by both NH_3 &CO $T_{100\%}$< 350^{0}C by n-C_4H_{10}
20	Cu/CeO_2& Cu/Cr/CeO_2 0-10wt% Cu, 25-75wt % Cr, impregnation.	Fixed bed reactor, 1 atm, 400^{0}C, NO 20000 ppm, C_3H_6 20000 ppm, F/W= 10800mlg^{-1} h^{-1}	Best cat $Cu_{4\%}/Cr_{3\%}/CeO_2$ in SCR-C_3H_6 under net oxidizing conditions.
19	CuO/CeO_2-TiO_2 Impregnation method Can temp 500^{0}C	120mg cat (20-40 mesh) feed: 6%NO, 6%CO-He, SV= 5000h^{-1}	Optimum composition: 12%CuO, 10%CeO_2-TiO_2 $T_{100\%}$ = 350^{0}C
21	(a)$Cu_{4\%}/Ag_{1\%}/CeO_2$ & (b)$Cu_{4\%}/Ag_{1\%}/CeO_{2(75\%)}$-$ZrO_{2(25\%)}$, impregnation, caln = 550^{0}C	NO 20000ppm, C_3H_6 20000 ppm, F/W=30000 mlg^{-1}h^{-1} feed = 500ml/min, temp. range 250-550^{0}C	Cat (b) showed better activity in temp region (250–350^0 C), optimum NO conversion, 82.89% is attained at reaction temp=415.38^{0}C
22	$Ce_{17}Cu_{36}$HM, NH_4^+ form of mordenite by ion exch-ange method, cal 500^{0}C	500ppm NO, 500ppm NH_3, 5%O2, 5%H_2O,SV=150000h^{-1}, deactivation 20000ppm HCl, 150-450^{0}C	CeCuHM is HCl-tolerable SCR catalyst
Three way catalyst			
23	$Cu_{4.7\%}Rh_{(0\text{-}2000ppm)}$ on Al_2O_3, CeO_2- Al_2O_3, CeO_2- ZrO_2, Copption-impregnation, Caln=650^{0}C	TWC activity was measured in simultaneous conversion of CO, NO_x and C_3H_6, cat 30-50mg, SV=25000h^{-1}, Cat testing under cycling condn	Reaction order: CO oxidn>C_3H_6 oxidn>NO reduction. Cu is active though less than Rh. Support OSC favour the oxidn reactions & NO conversion
Diesel soot oxidation			
Ref.	Catalyst Pepn. Method	Exptal Operating parameter	Remark
24	Cu–Ce/Zr = 5/4 & Cu/(Cu + Ce + Zr) = 1/10. Citric acid sol–gel using nitrate salts.	TPO, soot/cat = 1/10, tight & loose contacts, 110 mg, heated at 20 ^{0}C/ min. 1000ppm NO + 9.5% O_2 in N_2 flow 500ml/min.	Cu-Ce best catalyst for tight contact. NO facilitates oxidn. Ti =300,T_{max}= 312,T_f =350^0 C
25	Cu–Ce/Zr = 5/4 & Cu/(Cu + Ce + Zr) = 1/10. Citric acid sol–gel using nitrate salts.	TPO, soot/cat = 1/10, tight & loose contacts, 110 mg, heated at 10^{0}C/ min. 9.5% O_2 in N_2 flow 500 ml/min.	CuO–CeO_2–ZrO_2 cats were less active but more thermally stable, tight contact, Ti =300, T_{max}= 324, T_f =360^0 C.
26	Cu/CeO_2, K/CeO_2, Cu,K/ CeO_2, pption & co-impre-gnation	TPO soot/cat = 1/10, tight & loose contacts. 110 mg. heated at 10^{0}C/min. 1000 ppm NO + 10% O_2 in N_2 flow 500 ml/m.	Cu,K/CeO_2 catalysts show excellent activity, Ti =300, T_{max}= 312, T_f =350^0 C.
27	Cu-Ce & Cu-Ce-Al, citric acid sol gel, Cu:Ce = 1:9 molar, (Cu+Ce):Al = 2:1 Caln 500 & 800^{0}C	TPO soot/cat = 1/10, tight & loose contacts. 110 mg. heated at 10^{0}C/min. 1150 ppm NO + 9.6% O_2 in N_2 flow 500 ml/m.	Al_2O_3 increases stability and dispersion of CuO & CeO_2, lowers soot oxidn temp & increases NO reduction
28	CuO–CoO/CeO_2–ZrO_2, CuO–NiO/ CeO_2–ZrO_2, Wet Impregnation using nitrate salts.	TGA, Soot/cat = ¼, tight contact, 100 mg , Heated at 10 ^{0}C/min in air	CuO–CoO (5wt% each)/ CeO_2–ZrO_2 an excellent cat Ti =227, $T_{50\%}$= 363^{0}C

Table 1.A. (cont.)

SO_2 reduction		
5%CuCe(50%Zr)O_2, 5%CuCe (4.5%La)O_2, urea gelation/ copption method, caln 650^{0}C	SO_2 redn by CO:whsv=0.09 g.s/ml, 1%SO_2-2%CO-He. SO_2 redn by CH_4:1%SO_2-0.5%CH_4-He, whsv= 0.36g s/ml	La-doped cat is a highly active for SO_2 redn by CO & CH_4, Cu increases the selectivity to S^0 by catalyzing the total oxidn of CH_4
5%Cu-Ce(10%La)O_x, 15%Cu-Ce(10%La)O_x urea gelation/ co-pption, Caln 650^{0}C for SO_2-CO & 720^{0}C for SO_2-CH_4	1%SO_2–2%CO–10.7%H_2O-He, 0.09 g s/ml, 1% SO_2–2%CH_4-He, 0.18 g s/ ml, 250-700^{0}C, 1 atm press.	Cu- modified catalysts are active & selective for SO_2 redn by CO, NO in feed enha-nces both the SO_2 conversion & S^0 yield.
CuO–CeO_2sorbent-catalyst, hexa-decylamine surfactant/ impregn method	TGA reactor, SO_2/ N_2 gas mix-ture (3600 ppm), 90 ml/min, heated at 20^{0}C/min, RT-760^{0}C, adsorpn gain of wt. was noted	de-Sox performance of prepd cat was higher than conventi-onnal ones. The improved adsorption capacity is due to interaction between Cu-ceria
Cu/Ce-mesoporous silica, Si/(Cu + Ce) = 8.7(10.3 mol% Cu+Ce), caln 600^{0}C	200mg cat, SO_2/CO reaction: total feed 160 ml/min & GHSV 25600h^{-1}, for SO2/NO/CO reaction: total feed 200ml/ min & GHSV= 32000 h^{-1}	Highly active and stable redox catalyst able to completely reduce NO and SO_2 simulta-neously by CO at a high GHSV= 32000 h^{-1} to N_2 and elemental sulfur
Decomposition of ammonia		
CuO:CeO_2=6:4, copption caln 500^{0}C.	fixed-bed reactor, 220–260 ^{0}C, 1 atm, feed 1000ppm NH_3, 4% O_2-He, GHSV 92000ml/h.g, 150-400^{0}C.	98% NH_3 removal and high selectivity toward N_2 achieved at 400^{0}C.
Nanoscale catalysts Cu:Ce = 6:4, copption, caln 500^{0}C	fixed-bed reactor, temp 150-400^{0}C, 1g cat, 1000ppm NH_3-4%O_2, ghsv=92000ml/ (gh)	L–H kinetic model with first order reaction represent the NH_3 oxidation, apparent E = 27.8 kJ/mol
Oxidation of phenol		
5wt%Cu–1wt%Ce/AC, impregn. method, caln 250^{0}C	Batch ads expt for isotherm at 30^{0}C, phenol oxdn in TG/MS, fixed bed reactor for ads-oxdn cycles	Cu–Ce/AC good catalyst–sor- bent for phenol ads & cat dry oxdn, adsorptn. capacity =209 mg/g in fresh & stabilizes to 78mg/g after 9 consecutive ads–oxdn cycles .
CuO*x*/$Ce_{0.65}Zr_{0.35}^{o}_2$ Impregnation method, caln 500^{0}C	Autoclave, 0.75g cat, 250ml of 1000mg/l phenol, 5.05 Mpa air at 150^{0}C, pH=7.0	CuO*x*/$Ce_{0.65}Zr_{0.35}O_2$ most effective in view of catalytic activity and CO_2 selectivity

Table 1. Recent literature review at a glance on CuO/CeO_2 catalyst development for various reactions:
(B) Reactions of commercial importance

Steam reforming of methalol (SRM) and Oxidative reforming of methanol (OSRM)			
37	Cu/CeO_2, copption , caln 450^0C, reduction 350^0C with $10\%H_2$	fixed-bed reactor, 220–260 ^0C, 1 atm, 0.3 g cat <70 mesh,	26.9 wt.% Cu-loading optimum for SRM, carbonaceous deposit deactivate cat.
38	$Cu/CeO_2/Al_2O_3$,co-ption,Caln 500^0C, redn 300^0C with 5% H_2	fixed-bed microreactor, 180–280^0C, 1 atm, 500 mg, 0.45-0.55mm size	activity increased for SRM up to $20wt\%CeO_2$, CeO_2 enhance dispersion & prevent sintering.
39	$CuO–CeO_2$, urea combustion SRM, CSRM	fixed-bed microreactor, 0.3g cat, totalflow=70ml/min,W/F=0.257 gs/ml, 5%MeOH, $H_2O/ CH_3OH = 0.1$	optimum behavior obtained with 75% excess of urea and Cu/(Cu+ Ce) ratio equal to 0.15
41	$Ce_{0.9}$ $Cu_{0.1}Oy$, deposition–pption; copption; complexa-tion–combustion , OSRM	300 mg cat, 240-360^0C, 20% MeOH, 26% H_2O, 6% O_2-He, total flow = 100ml/min	Complexation–combustion is the best method, high activity is related to the formation of solid solution and the improved redox properties.
40	$Cu/CeO_2/\gamma$- Al_2O_3 impregnat-ion, washcoated platelets, Caln 600^0C, reduced in H_2 at 250^0C	10-channel microreactor, MeOH/ H_2O ratio=1/1.1, 1 bar press	SRM reaction mechanism, oxygen reverse spillover from ceria to copper is involved in the catalysis cycle
42	CuO/CeO_2 & $Cu/CeO_2/ZrO_2$, coprecipitation method, SRM	0.1g cat, 4.5%MeOH, 6.8% H_2O, 7%/N_2-He, flow rate = 16380 ml/g/h	80 wt.%.CuO in CuO/CeO_2 optm. ZrO_2 promoting effect; optm ratio $CuO/CeO_2/ ZrO_2$ = 8/1/1.
44	Impregnation method, Cu/CeO_2 prereduced cat, OSRM	0.1mg cat, 200-260^0C, pp of $MeOH/H_2O/O_2$=30/4.6/25.2 torr, O_2/MeOH=0.83, $H_2O/$ MeOH=0.15	highest H_2 selectivity was observed on the $2Cu/CeO_2$ catalyst in the range of 210-230^0C
43	$Cu/CeO_2/Al_2O_3$, copption	OSRM, O_2/MeOH = 0-0.5, W/F=3-15kg.s/mol, steam/MeOH=1.5, 200-300^0C, 1 atm.	Cu/Ce/Al: 30/20/50 was found to be highly active & selective, opti-mum temp=280^0C
45	$Cu/CeO_2/ZnO/Al_2O_3$ = 30/10/ 20/40% by wt., copption	OSRM, pre-reduced cat, W/F= 3-15kg.s/mol, S/M/O=1.5/1/ 0.1 -0.2 molar, 200-300^0C	three intrinsic L–H kinetic mod- els were developed based on the 2 proposed reaction mechanisms
46	CuO/CeO_2, co-pption. 100Cu/ (Cu + Ce) =30–80 at.%, pre-reduced: 10% H_2-He, 100 ml/min at 300^0 C, OSRM	0.5g cat, 150-210µm, Temp 160-300^0C, 1 atm, $H_2O/$ MeOH = 1.5– He for SRM; 5% O_2, 10% CH_3OH, 15% H_2O – He	Optimum: 70 at.% $CuO–CeO_2$ highest & stable activities at 300^0C for both SRM & OSRM. Cu^0 is active catalyst species formed < 180^0C
Water gas shift reaction (WGSR)			
47	CeO_2 by urea gelation (ug) & template-assisted (ta) method, Cu-Pd-CeO_2 by wet impregn (wi) & deposition pption (dp)	0.5ml cat, 210^0C, GHSV 17760 h^{-1}, feed for wgs 0.2%CO, 10% CO_2, 40% H_2O-Ar, for O_2 assisted wgs $1\%O_2$(air) added	Activity order: Cu-Pd on CeO_2 (ug)> CeO_2(ta), wi >dp, Cata (ug) shows 100% CO conve-rsion in O_2 assited wgs with extremely high H_2 concn.
48	$5\%CuO_x$-CeO_2 nanopar-ticles by reversed microe-mulsion & impregnation, caln 500^0C	5mg cat, sv=1.5 x 10^5 /h, temp 200-500^0C, H_2O/CO = 0.6	Cu facilitates the formation of O vacancies in ceria, both Cu^0 & O vacancies in ceria involved in generation of the active sites
49	$CuPd/CeO_2$ (20–30 wt%Cu & 0.5–1 wt% Pd) in the OWGS reaction	feed for O_2 assisted wgs: (4%CO, $10\%CO_2$, 2% air, 26%Ar-H_2) + steam, CO/H_2O=1/10, 180-240^0C	Catalyst containing 20–30 wt% Cu was found to be more active compared to that containing lower Cu loading of about 1 wt%
50	CuO_x-CeO_2 (20-90at% Cu), Co-pption, nitrate precursors, 1mol/l NaOH precipitant, caln 500^0C	1g cat, 1atm, 150-360^0C, Cat redn 30% CO-He, 25ml/min, 300^0C, Feed 5%CO, $10\%CO_2$, $15\%H_2O$-He, 50ml/min	Activity of cat increased with Cu loading & synergy of Cu & ceria was confirmed. Opti-mum Cu loading 80 at%, cat showed stability at 360^0C

Table 1.B. (Cont.)

Preferential oxidation of CO			
53	CuO-CeO_2, Urea nitrate combustion, Caln 500^{0}C	50-120mg cat, temp 40-280^{0}C, feed 50-100ml/min,W/F=0.03-0.144gs/ml, 1% CO, 1.25% O_2, 50% H_2-He	Simple one pot method, nano-crystalline CuO-CeO_2, optim-um ratio Cu/(Cu + Ce) = 0.15. $T_{100\%}$= 120^{0}C.
54	CuO-CeO_2, pption, caln 500^{0}C, size: 0.15-0.18mm	166–176^{0}C for a feed of 1% CO, 1% O_2, 50% H_2, 20% H_2O, 13.5% CO_2-He, SV = 42 g h/m^3	CO content reduced < 10 ppm, catalyst showed a slow, reversible deactivation, but the activity restored on heating at 300^0 C under an inert flow.
82	$Cu_{.1}Ce_{.9}O_{2-y}$ sol-gel method	Cat 37-251 mg, temp 45-155^{0}C, feed 100 mL/min	100% selective in the temp range from 45 to 90 ◦C
55	CuO-CeO_2, CuO–CeO_2–ZrO_2, & CuO–ZrO_2, CuO (1–10 wt%), pption	Feed:74.17% H_2, 0.49%CO, 23.26%CO_2, 2.08% CH_4, 2.5–10 liters/h; GHSV = 5000–20,000h^{-1}	Activities order: CuO–ZrO_2≤ CuO–CeO_2–ZrO_2<CuO–CeO_2 optimim CuO=5 wt% , deactivation of H_2O diminished >150^{0}C
56	CuO-CeO_2: a)copp, caln 650^{0}C, b)Urea-nitrate combn caln 550^{0}C, c) citrate-hydrothermal, caln 300-500^{0}C, d) impregn, caln 400^{0}C	Cat 50-120 mg, temp 50-225^{0}C, feed 50-100 ml/min, W/F= 0.03-0.144 gs/ml, 1% CO, 1.25% O2, 50% H_2-He	Activity order: b> c > a > d, method b) gives easily reducible well dispersed CuO species strongly interacting with ceria.
86	Cu-Ce: Citrate method Caln. 450-550^{0}C	Cat 15 mg, temp 50-200^{0}C,feed 300 ml/min, 300 ppm CO & 300 ppm O_2 – He, SV=83000h^{-1}	CO conversion and selectivity value over 90% at temp. around 165^{0}C.
57	Au/CeO_2 and CuO/CeO_2, depositn–pption (DP) & modified deposition–pption (MDP)	Temp: 50–250^{0}C, Cat: 0.05–0.12 g, feed:50–100 ml/min, 1% CO, 1.25% O_2, 50% H_2, 0–15% CO_2, 0–10% H_2O-He	Au/ceria showed higher acti-vity than CuO/CeO_2 at temp <120^{0}C, while CuO/CeO_2 were able to operate at higher temps, with better selectivity.
58	7%CuO/$Ce_{0.9}Zr_{0.1}O_2$-Al_2O_3 (20%), suspension/ copption/ impregn	Cat: 180mg, feed: H2/CO/ O_2/He (50/1/1/48), 30ml/ min, F/W=10000ml/g.h, temp: RT-150^{0}C	Doping Zr into CeO_2 increased the mobility of lattice oxygen & activity comparable with, & its selectivity was much larger than, that of the noble catalyst 5%Pt/Al_2O_3.
61	5%CuO-CeO_2, chelating method/ coprecipitation, caln: 500^{0}C, 60-80 mesh	50-200mg cat, feed:0−50% H_2,0.5% -2.0% O_2,0.5%− 2.0% CO-Ar, SV=120000 ml/gh, temp=80-160^{0}C	chelating method is superior than coprecipitation method, CO conversions at 120^{0}C are 99.6% and 88.6%, resp.
59	CuO/CeO_2 (1 wt% Cu & 5 wt% Cu), impregn & copption, caln 500^{0}C	Temp: 25–250^{0}C, feed: 1.5 g h/mol at 102^{0}C, 1% CO, 1.25% O_2, 50% H_2-Ar	Activity depends on the prepn method & Cu loading, 1 wt% Cu gives 100% CO conversion at 100^{0}C
60	0.05%(Pt, Pd and Ru)-doped (5%CuO-CeO_2), copption & impregn methods, caln 700^{0}C	250mg cat, feed: 156ml/min 0.8%CO, 23.5% CO_2, 3.8% air-H_2,	doping did not change crystal structure of the catalyst, Pt-doped cat has highest activity.
62	0.5-8%CuO/CeO_2, impregn method, caln. 450^{0}C,	Feed: 0.5%CO, 0.5%O_2 50% H_2-N_2, W/F= 0.02 to 0.085 g s/ml, temp:70-210^{0}C	4wt %CuO optimum, light off temp. 70^{0}C, highly activity and selective cat towards CO oxdn.
85	CuO-CeO_2: Urea thermal decompn method, Cu at ratio- 0-60, caln. 450^{0}C	Cat. 30mg, temp.100-300^{0}C, redn: 2% H_2-N_2, feed 60ml/ min, 2.8%CO, 3.5%O_2 – N_2	More active and selective than a commercial Pt/Al_2O_3. Activity increases as the Cu content increases
64	5CuO-CeO_2(M) (M=La, Pr, Nd, Y), co-pption method	50mg cat, feed: 50% H_2, 1% O_2, 1% CO, 10% CO2, 20% H_2O-Ar	Pr doping enhanced activity, the CO-PROX conversion > 99% at 120^{0}C
65	CuO-CeO_{2v}coppn, Cu content 20 at% (=Cu/(Cu + Ce) × 100) Caln. 500^{0}C	Cat.-50 mg, 100 mg flow rate 100 ml (STP)/min feed gas 1% CO, 1% O_2, 50% H_2,	CO oxidn orders: 0.91, 0.37 & 0.62 w.r.t. partial press of CO, CO_2 and H_2O, resp, E for CO & H_2 oxidn:94.4 and 142 kJ/mol, resp
66	CuO-CeO_2, wet impregn (WI) & deposition pption (DP) methods, cal 500^{0}C.	0.1g cat, feed: 1%CO, 0.5–1% O_2, 0–60%H_2-He, 200ml/min, temp: RT-200^{0}C	Optimum CuO=7wt%, WI method is better than DP, resulting higher activity
67	CuO-CeO_2(20at%Cu), copption	200-300mg cat, feed: 2000-6000ml/min, 500-3000ppp CO, 500-4500ppm O_2, 2O_2/CO = 0.33-3, 0-70%H_2, 0-15%CO_2, 0-2%CH_4, 0-15% H_2O, temp: 90-300^{0}C.	H_2 in feed had little influence on the CO conversion, CO_2 and H_2O decreased the acti-vity, power-law expression gave a good fit in limited concn ranges, reaction orders depend on the reactant molar fractions.

Table 1. Recent literature review at a glance on CuO/CeO_2 catalyst development for various reactions: *(C) Reactions of other importance*

69	$Cu_{0.7}Fe_{2.3}O_4/Ce–ZrO_2$, co-pption method, caln 900^{0}C, CH_4 reforming	1g cat, feed:15% CH_4, 30ml /min, Ar 30ml/min with H_2O pp=31.1kPa, temp:900 &700^{0}C	Ce/Zr=3/1 molar shows highest activity for syn gas prodn, ten repeated cycles, the cat showed the greatest durability
71	Ni-free 20wt%Cu-10wt% CeO_2-YZ anode for direct oxdn of hydrocarbon fuels, impre-gn method, caln 950^{0}C	direct oxdn of n-butane at 700^{0}C in SOFC	Wet impregn: An alternative method for fabrication of high performance and nanostructu-red electrodes of SOFC has been critically reviwed
72	Cu–CeO_2–ScZ & Cu–CeO_2–yZ fuel cell anodes by coimprgn method, caln: 450^{0}C, 20wt.%Cu–10wt.%CeO_2,18wt.%Cu–12wt%CeO_2, 15wt.% Cu–15 wt.%CeO_2,	H_2 redn of electrodes at 800^0 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	maximum power density of single cell reached 604 mW cm^{-2} and 408 mW cm^{-2} at 800^{0}C in H_2 and ethanol steam resp., and cell obtained stable output in ethanol steam over an operation period of 50 h.
73	Cu or Cu–Ni with CeO_2, $Ce_{0.9}Gd_{0.1}O_{2-x}$ were prepd by copption, caln: 950^{0}C, 40% metals loading, Cu/Ni = 1:1	CH_4 oxidn : TPO, temp: RT-900^{0}C, direct oxidation of CH_4 in solid oxide fuel cell	Potential application of cats examined as anodes of SOFC for direct oxidation of hydro-carbons, CH_4 oxidn order: CuNi–CG > CuNi–CT > CuNi–C
74	Pure and Li_2O-doped CuO/CeO_2, impregn method, caln 500^{0}C	Activity tests for H_2O_2 decomposition at 30^{0}C, 50mg cat, 0.5ml H_2O_2 in 10ml H_2O.	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
97	10-40 wt% Cu/CeO_2, copptn, pre-reduced cat, methanol synthesis	Fixedbed reactor, 0.5g cat, 33% CO, 67%H_2, (3.6 l/h, 2MPa), 195^{0}C	Activity at 195^{0}C is comparable with commercial Cu-Zn catalyst at 230-250^{0}C
75	3 wt% $Cu/Ce_{0.5}Zr_{0.5}O_2$, deposition pption, caln 600^{0}C, methanol synthesis	Cat: 0.15g, feed: H_2 & CO, H_2/CO=3, 60ml/min, temp: 200-250^{0}C, press: 3Mpa	3 wt% $Cu/Ce_{0.5}Zr_{0.5}O_2$ is four fold active than that of 3 wt% Cu/ZrO_2 in methanol synthesis

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/CeO_2 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-CeO_2 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-CeO_2 catalysts exhibit versatile applications owing to the large interest in all the low temperature redox reactions. The high activity of CuO-CeO_2 is attributed to the quick reversible Cu^{2+}/Cu^{+} redox couples assisted by Ce^{4+}/Ce^{3+} cycles. The CuO-CeO_2 catalysts show excellent activities in comparision to traditional copper-based systems because of the following properties: (i) outstanding oxygen storage capacity (OSC), (ii) high mobility of oxygen in the crystal structure, release of nascent oxygen with high reactivity, (iii) the strong metal–support interactions (SMSI), i.e., Cu species–CeO_2 support, and (iv) the synergistic redox effect of Cu on CeO_2 and vice versa. There is a significant increase in the thermal stability of the material by doping ceria with zirconium oxide, because of the formation of a solid solution inhibiting the sintering at high temperature. The introduction of zirconium ions also enhances the formation of structural defects, which supports an increase in the oxygen storage capacity.

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References

[1] Liu, W., and Flytzani-Stephanopoulos, M. 1995. Total Oxidation of Carbon Monoxide and Methane over Transition Metal-fluorite Oxide Composite Catalysts I. Catalyst Composition and Activity. *J. Catal.* 153: 304-316.

[2] Luo, M. F.; Zhong, Y. J.; Yuan, X. X.; and Zheng, X. M. 1997. TPR and TPD Studies of CuO/CeO_2 Catalysts for Low Temperature CO Oxidation. *Appl. Catal. A.* 162: 121-131.

[3] Harrison, P. G.; Ball, I. K.; Azelee, W.; Daniell, W.; and Goldfarb, D. 2000. Nature and Surface Redox Properties of Copper(II)-Promoted Cerium(IV) Oxide CO-Oxidation Catalysts. *Chem. Mater.* 12: 3715-3725.

[4] Zhang, S-M.; Huang, W-P.; Qiu, X-H.; Li, B-Q.; Zheng, X-C; and Wu, S-H. 2002. Comparative Study On Catalytic Properties of Low-Temperature CO Oxidation of Cu/CeO_2 and CuO/CeO_2 Prepared via Solvated Metal Atom Impregnation and Conventional Impregnation. *Catal. Letters* 80: 41-46.

[5] Zhou, K.; Xu, R.; Sun, X.; Chen, H.; Tian, Q.; Shen, D.; and Lia, Y. 2005. Favorable Synergetic Effects Between CuO and the Reactive Planes of Ceria Nanorods. *Catal Letters* 101: 169-173.

[6] Sundar, R. S.; and Deevi, S. 2006. CO Oxidation Activity of Cu–CeO_2 Nano-Composite Catalysts Prepared by Laser Vaporization and Controlled Condensation. *J of Nanoparticle Research* 8: 497–509.

[7] Zheng, X.; Zhang, X.; Wang, S.; Wang, X.; and Wu, S. 2007. Effect of Addition of Base on Ceria and Reactivity of CuO/CeO_2 Catalysts for Low-Temperature CO Oxidation. *Journal of Natural Gas Chemistry* 16: 179–185.

[8] Cao, J-L.; Wang, Y.; Zhang, T-Y.; Wu, S-H.; Yuan, Z-Y. 2008. Preparation Characterization and Catalytic Behaviour of Nanostructured Mesoporous $CuO/Ce_{0.8}Zr_{0.2}O_2$ Catalyst for Low Temperature CO Oxidation. *Appl. Catal. B* 78: 120-128.

[9] Aguila, G.; Gracia, F.; and Araya, P. 2008. CuO and CeO_2 Catalysts Supported on Al_2O_3, ZrO_2, and SiO_2 in the Oxidation of CO at Low Temperature. *Appl. Catal. A: Gen* 343: 16–24.

[10] Zou, Z-Q.; Meng, M.; Guo, Li-H.; and Zha, Yu-Q. 2009. Synthesis and Characterization of CuO/Ce_{1-x} Ti_xO_2 Catalysts used for Low-

Temperature CO Oxidation. *J of Hazardous Materials* 163: 835–842.

[11] Terribile, D.; Trovarelli, A.; de Leitenburg, C.; Primavera, A; and Dolcetti, G. 1999. Catalytic Combustion of Hydrocarbons with Mn and Cu-Doped Ceria-Zirconia Solid Solutions, *Catal Today* 47: 133-140.

[12] Wang, C.-H.; Lin, S.-S.; Chen, C.-L.; and Weng, H-S. 2006. Performance of the Supported Copper Oxide Catalysts for the Catalytic Incineration of Aromatic Hydrocarbons. *Chemosphere* 64: 503–509.

[13] Tang, X.; Xu, Y.; Shen, W. 2008. Promoting Effect of Copper on the Catalytic Activity of MnOx–CeO_2 Mixed Oxide for Complete Oxidation of Benzene. *Chem Eng J*. 144: 175–180.

[14] Luo, J.-Y.; Meng, M.; Yao, J.-S.; Li, X.-G.; Zha, Y.-Q.; Wang, X.; and Zhang, T.-Y.. 2009. One-Step Synthesis of Nanostructured Pd-Doped Mixed Oxides MOx-CeO_2 (M = Mn, Fe, Co, Ni, Cu) for Efficient CO and C_3H_8 Total Oxidation. *Appl Catal B: Env*. 87: 92-103.

[15] Larsson, P-O.; and Andersson, A. 2000. Oxides of Copper, Ceria Promoted Copper, Manganese and Copper Manganese on Al_2O_3 for the Combustion of CO, Ethyl Acetate and Ethanol. *Appl Catal B: Env* 24: 175–192.

[16] Hu, C.; Zhu, Q.; Jiang, Z.; Zhang, Y.; and Wang, Y. 2008. Preparation and Formation Mechanism of Mesoporous CuO–CeO_2 Mixed Oxides with Excellent Catalytic Performance for Removal of VOCs. *Microporous and Mesoporous Materials* 113: 427-434.

[17] Delimaris, D.; and Ioannides, T. 2009. VOC Oxidation over CuO–CeO_2 Catalysts Prepared by a Combustion Method. *Appl Catal B: Env* 89: 295–302.

[18] Bera, P.; Aruna, S.T.; Patil, K.C.; and Hegde, M.S. 1999. Studies on Cu/CeO_2: A New NO Reduction Catalyst. *Journal of Catalysis* 186: 36–44.

[19] Xiaoyuan, J.; Liping, L.; Guanghui, D.; Yingxu, C.; and Xiaoming, Z. 2004. The Active Species and Catalytic Properties of CuO/CeO_2-TiO_2 Catalysts for NO+CO Reaction. *J of Mater Science* 39: 4663-4667.

[20] Amin, N. A. S.; Tan, E. F.; and Manan, Z. A. 2003. Selective Reduction of NO_x with C_3H_6 over Cu and Cr Promoted CeO_2 Catalysts. *Appl Catal B: Env* 43: 57-69.

[21] Amin, N. A. S.; and Chong, C. M. 2005. SCR of NO with C_3H_6 in the Presence of Excess O_2 over Cu/Ag/CeO_2-ZrO_2 Catalyst, *Chem. Eng. J.* 113: 13–25.

[22] Choung, J. W.; and Nam, I.-S. 2006. Role of Cerium in Promoting the Stability of CuHM Catalyst Against HCl to Reduce NO with NH3. *Appl Catal A: Gen* 312: 165–174.

[23] Courtois, X.; and Perrichon, V. 2005. Distinct Roles of Copper in Bimetallic Copper–Rhodium Three-Way Catalysts Deposited on Redox Supports *Appl Catal B: Env* 57: 63–72.

[24] Wu, X.; Liu, D.; Li, K.; Li, J.; and Weng, D. 2007. Role of CeO_2–ZrO_2 in Diesel Soot Oxidation and Thermal Stability of Potassium Catalyst, *Catalysis Communications* 8: 1274–1278.

[25] Liang, Q.; Wu, X.; Weng, D.; and Lu, Z. 2008. Selective Oxidation of Soot over Cu Doped Ceria/Ceria–Zirconia Catalysts. *Catalysis Communications* 9: 202–206.

[26] Weng, D.; Li, J.; Wu, X.; and Lin, F. 2008. Promotional Effect of Potassium on Soot Oxidation Activity and SO_2-Poisoning Resistance of Cu/CeO_2 Catalyst. *Catalysis Communications* 9: 1898–1901.

[27] Wu, X.; Lin, F.; Weng, D.; and Li, J. 2008. Simultaneous Removal of Soot and NO over Thermal Stable Cu–Ce–Al Mixed Oxides. *Catalysis Communications* 9: 2428–2432.

[28] Reddy, B. M.; and Rao, K. N. 2009. Copper Promoted Ceria–Zirconia Based Bimetallic Catalysts for Low Temperature Soot Oxidation. *Catalysis Communications* 10: 1350–1353.

[29] Zhu, T.; Kundakovic, L.; Dreher, A.; and Flytzani-Stephanopoulos, M. 1999. Redox Chemistry over CeO_2-Based Catalysts: SO_2 Reduction by CO or CH_4. *Catalysis Today* 50: 381-397.

[30] Flytzani-Stephanopoulos, M.; Zhu, T.; and Li, Y. 2000. Ceria-Based Catalysts for the Recovery of Elemental Sulfur from SO_2-Laden Gas Streams. *Catalysis Today* 62: 145–158.

[31] Rodas-Grapaý´n, A.; Arenas-Alatorre, J.; Go´mez-Corte´s, A.; and Dý´az, G. 2005. Catalytic Properties of a CuO–CeO_2 Sorbent-Catalyst for de-SO_x Reaction. *Catal Today* 107–108: 168–174.

[32] Pantazis, C. C.; Petrakis, D. E.; and Pomonis, P. J. 2007. Simultaneous and/or Separate SO_2/NO Reduction by CO over High Surface Area Cu/Ce Containing Mesoporous Silica, *Appl Catal B: Env* 77: 66–72.

[33] Hung, C.-M. 2008. Catalytic Decomposition of Ammonia over Bimetallic CuO/CeO_2 Nanoparticle Catalyst. *Aerosol and Air Quality Research* 8: 447-458.

[34] Hung, C.-M. 2008. Decomposition Kinetics of Ammonia in Gaseous Stream by a Nanoscale Copper-Cerium Bimetallic Catalyst. *Journal of Hazardous Materials* 150: 53–61.

[35] Lei, Z.; and Liu, Z. 2007. Behavior of Cu–Ce/AC Catalyst–Sorbent in Dry Oxidation of Phenol. *Fuel Processing Technology* 88: 607–615.

[36] Kim, K.-H.; Kim, J.-R.; and Ihm, S.-K. 2009. Wet Oxidation of Phenol over Transition Metal Oxide

Catalysts Supported on $Ce_{0.65}Zr_{0.35}O_2$ Prepared by Continuous Hydrothermal Synthesis in Supercritical Water. *J of Hazardous Materials* 167: 1158–1162.

[37] Liu, Y.; Hayakawa, T.; Suzuki, K.; Hamakawa, S.; Tsunoda, T.; Ishii, T.; and Kumagai, M. 2002. Highly Active Copper/Ceria Catalysts for Steam Reforming of Methanol. *Appl Catal A: Gen.* 223: 137–145.

[38] Zhang, X.; and Shi, P. 2003. Production of Hydrogen by Steam Reforming of Methanol on CeO_2 Promoted Cu/Al_2O_3 Catalysts. *J of Mole Catal A: Chem*. 194: 99-105.

[39] Papavasiliou, J.; Avgouropoulos, G.; and Ioannides, T. 2004. Production of Hydrogen via Combined Steam Reforming of Methanol over $CuO–CeO_2$ Catalysts. *Catalysis Communications* 5: 231–235.

[40] Men, Y.; Gnaser, H.; Zapf, R.; Hessel, V.; and Ziegler, C. 2004. Parallel Screening of $Cu/CeO_2/c$-Al_2O_3 Catalysts for Steam Reforming of Methanol in a 10-Channel Micro-Structured Reactor. *Catalysis Communications* 5: 671–675.

[41] Shan, W.; Feng, Z.; Li, Z.; Zhang, J.; Shen, W.; and Li, C. 2004. Oxidative Steam Reforming of Methanol on $Ce_{0.9}Cu_{0.1}O_Y$ Catalysts prepared by Deposition–Precipitation, Coprecipitation, and Complexation–Combustion methods. *J of Catalysis* 228: 206–217.

[42] Oguchi, H.; Nishiguchi, T.; Matsumoto, T.; Kanai, H.; Utani, K.; Matsumura, Y.; and Imamura, S. 2005. Steam Reforming of Methanol over $Cu/CeO_2/ZrO_2$ Catalysts. *Applied Catalysis A: General* 281: 69–73.

[43] Patel, S.; and Pant, K. K. 2007. Hydrogen Production by Oxidative Steam Reforming of Methanol Using Ceria Promoted Copper–Alumina Catalysts. *Fuel Processing Technology* 88: 825–832.

[44] Pérez-Hernández, R.; Gutiérrez-Martínez, A.; and Gutiérrez-Wing, C. E. 2007. Effect of Cu Loading on CeO_2 for Hydrogen Production by Oxidative Steam Reforming of Methanol. *Int J of Hydrogen Energy* 32: 2888 – 2894.

[45] Patel, S.; and Pant, K. K. 2009. Kinetic Modeling of Oxidative Steam Reforming of Methanol over $Cu/ZnO/CeO_2/ Al_2O_3$ Catalyst. *Appl Catal A: Gen 356 189–200.*

[46] Udani, P. P. C.; Gunawardana, P. V. D. S.; Lee, H. C.; and Kim, D. H. 2009. Steam Reforming and Oxidative Steam Reforming of Methanol over $CuO–CeO_2$ Catalysts. *Int J of Hydrogen Energy* 1–8, Available online at www.sciencedirect.com.

[47] Bickford, E. S.; Velu, S.; and Song, C. 2005. Nano-Structured CeO_2 Supported Cu-Pd Bimetallic Catalysts for the Oxygen-Assisted Water–Gas-Shift Reaction. *Catalysis Today* 99: 347–357.

[48] Wang, X.; Rodriguez, J. A.; Hanson, J. C.; Gamarra, D.; Martý´nez-Arias, A. and Ferna´ndez-Garcý´a, M. 2006. In Situ Studies of the Active Sites for the Water Gas Shift Reaction over $Cu-CeO_2$ Catalysts: Complex Interaction Between Metallic Copper and Oxygen Vacancies of Ceria. *J. Phys. Chem. B* 110: 428-434.

[49] Fox, E. B.; Velu, S.; Engelhard, M. H.; Chin, Ya-Huei; Miller, J. T.; Kropf, J.; and Song, C. 2008. Characterization of CeO_2-Supported Cu–Pd Bimetallic Catalyst for the Oxygen-Assisted Water–Gas Shift Reaction. *Journal of Catalysis* 260: 358–370.

[50] Gunawardana, P. V. D. S.; Lee, H. C.; and Kim, D. H. 2009. Performance of Copper–Ceria Catalysts for Water Gas Shift Reaction in Medium Temperature Range. *Int. J of Hydrogen Energy* 34: 1336–1341.

[51] Yusheng, S.; Lei, L.; Yingying, Z.; Xingyi, L.; Qi, Z.; and Kemei, W. 2009. Effect of Yttrium Addition on Water-Gas Shift Reaction over CuO/CeO_2 Catalysts. *Journal of Rare Earths* 27: 411-417.

[52] Maluf, S. S.; and Assaf, E. M. 2009. $La_{2-x}Ce_x Cu_{1-y}Zn_yO_4$ Perovskites for High Temperature Water-Gas Shift Reaction. *Journal of Natural Gas Chemistry* 18 – Available online at www.sciencedirect.com.

[53] Avgouropoulos, G,; and Ioannides, T. 2003. Selective CO Oxidation over $CuO-CeO_2$ Catalysts Prepared via the Urea–Nitrate Combustion Method. *Applied Catalysis A: General* 244: 155–167.

[54] Kim, D. H.; and Cha, J. E. 2003. A $CuO–CeO_2$ mixed-oxide catalyst for CO clean-up by selective oxidation in hydrogen-rich mixtures. *Catal Letters* 86: 107-112.

[55] Ratnasamy, P.; Srinivas, D.;. Satyanarayana, C. V. V; Manikandan, P.; Kumaran, R S. S.; Sachin, M.; and Shetti, V. N. 2004. Influence of the Support on the Preferential Oxidation of CO in Hydrogen-Rich Steam Reformates over the $CuO–CeO_2–ZrO_2$ System. *Journal of Catalysis* 221: 455–465.

[56] Avgouropoulos, G.; Ioannides, T.; and Matralis, H. 2005. Influence of the preparation method on the performance of $CuO–CeO_2$ catalysts for the selective oxidation of CO. *Appl Catal B: Env.* 56: 87–93.

[57] Avgouropoulos, G.; Papavasiliou, J.; Tabakova, T.; Idakiev, V.; and Ioannides, T. 2006. A Comparative Study of Ceria-Supported Gold and Copper Oxide Catalysts for Preferential CO Oxidation Reaction. *Chemical Engineering Journal* 124: 41–45.

[58] Chena, Y.-Z.; Liaw, B.-J.; Chang, W.-C.; and Huang, C.-T. 2007. Selective Oxidation of CO in Excess Hydrogen over $CuO/Ce_xZr_{1-x}O_2.Al_2O3$

Catalysts. *International J of Hydrogen Energy* 32: 4550 – 4558.

[59] Gamarra, D.; Horn´es, A.; Kopp´any, Zs.; Schay, Z.; Munuera, G.; Soria J.; and Mart´ınez-Arias, A. 2007. Catalytic Processes During Preferential Oxidation of CO in H_2-Rich Streams over Catalysts Based on Copper–Ceria. *J of Power Sources* 169: 110–116.

[60] Jung, C. R.; Kundu, A.; Nam, S. W.; and Lee, H.-I. 2007. Doping Effect of Precious Metal on the Activity of CuO-CeO_2 Catalyst for Selective Oxidation of CO. *Applied Catalysis A: General* 331: 112–120.

[61] Liu, Z.; Zhou, R.; and Zheng, X. 2007. Preferential Oxidation of CO in Excess Hydrogen over CuO-CeO_2 Catalyst Prepared by Chelating Method. *Journal of Natural Gas Chemistry* 16167–172.

[62] Caputo, T.; Lisi, L.; Pirone, R.; and Russo, G. 2008. On the Role of Redox Properties of CuO/CeO_2 Catalysts in the Preferential Oxidation of CO in H2-Rich Gases. *Applied Catalysis A: General* 348: 42–53.

[63] Go´mez-Corte´s, A.; Ma´rquez, Y.; Arenas-Alatorre, J.; and Dı´az, G. 2008. Selective CO Oxidation in Excess of H_2 over High-Surface Area CuO/CeO_2 Catalysts. *Catalysis Today* 133–135: 743–749.

[64] Liu, Z.; Zhou, R.; and Zheng, X. 2008. Influence of Rare-Earth Metal Doping on the Catalytic Performance of CuO-CeO_2 for the Preferential Oxidation of CO in Excess Hydrogen. *J of Natural Gas Chem.* 17: 283-287.

[65] Lee, H. C.; and Kim, D. H. 2008. Kinetics of CO and H_2 oxidation over CuO-CeO_2 catalyst in H2 mixtures with CO_2 and H_2O. *Catalysis Today* 132: 109–116.

[66] Gurbani, A.; Ayastuy, J. L.; Gonza´lez-Marcos, M. P.; Herrero, J. E.; Guil, J. M.; and Gutie´rrez-Ortiz, M. A. 2009. Comparative Study of CuO–CeO_2 Catalysts Prepared by Wet Impregnation and Deposition–Precipitation. *Int J of Hydrogen Energy* 34: 547–553.

[67] Scho¨nbrod, B.; Marin˜o, F.; Baronetti, G.; and Laborde, M. 2009. Catalytic Performance of a Copper–Promoted CeO_2 Catalyst in the CO Oxidation: Influence of the Operating Variables and Kinetic Study. *Int J of Hydrogen Energy* 34: 4021–4028.

[68] Hung, C.-M. 2006. Selective Catalytic Oxidation of Ammonia to Nitrogen on CuO-CeO_2 Bimetallic Oxide Catalysts. *Aerosol Air Qual. Res.* 6: 150-169.

[69] Cha, K.-S.; Kim, H.-S.; Yoo, B.-K.; Lee, Y.-S.; Kang, K.-S.; Park, C.-S.; and Kim, Y.-H. 2009. Reaction Characteristics of Two-Step Methane Reforming over a Cu-Ferrite/Ce–ZrO_2 Medium, *Int J of Hydrogen Energy* 34: 1801–1808.

[70] He, H.; Vohs, J. M.; and Gorte, R. J. 2003. Effect of Synthesis Conditions on the Performance of Cu-CeO_2-YSZ Anodes in SOFCs, *J. Electrochem. Soc.* 150: A1470–A1475.

[71] Jiang, S. P. 2006. A review of wet impregnation—An Alternative Method for the Fabrication of High Performance and Nano-Structured Electrodes of Solid Oxide Fuel Cells, *Mater Sci and Eng A* 418: 199–210.

[72] Ye, X.-F.; Wang, S.R.; Hu, Q.; Chen, J.Y.; Wen, T.L.; and Wen, Z.Y. 2009. Improvement of Cu–CeO_2 anodes for SOFCs running on Ethanol Fuels, *Solid State Ionics* 180: 276–281.

[73] Hornés, A.; Gamarra, D.; Munuera, G.; Fuerte, A.; Valenzuela, R. X.; Escudero, M. J.; Daza, L.; Conesa, J. C.; Bera, P.; and Martínez-Arias A. 2009. Structural, Catalytic/ redox and Electrical Character- ization of Systems Combining Cu–Ni with CeO_2 or $Ce_{1-x}M_xO_{2-\delta}$ (M=Gd or Tb) for Direct Methane Oxidation. *J of Power Sources* 192: 70–77.

[74] Deraz, N.M. 2009. Characterization and Catalytic Performance of Pure and Li_2O-doped CuO/CeO_2 Catalysts. *Applied Surface Science* 255: 3884–3890.

[75] Konstantin A.; Pokrovski, and Bell, Alexis T. 2006. An Investigation of the Factors Influencing the Activity of $Cu/Ce_xZr_{1-x}O_2$ for Methanol Synthesis via CO Hydrogenation. *Journal of Catalysis* 241: 276–286.

[76] Kundakovic Lj.; and Stephanopoulos, M. F. 1998. Cu- and Ag- Modified Cerium Oxide Catalysts for Methane Oxidation. *J. Catal.* 179: 203-221.

[77] Bjo¨rn, S.; Didier, G.; Robert, E. B.; Andreas, H.; Arne, A.; and Wallenberg, L.R. 2002. Carbon Monoxide Oxidation on Nanostructured CuO_x/CeO_2 Composite Particles Characterized by HREM, XPS, XAS, and High-Energy Diffraction. *J. Catal.* 211: 119-133.

[78] Arias, A.; Martý´nez, A. B.; Hungrý´a, Fernan´dez-Garcý´a, M.; Conesa, J. C.; and Munuera, G. 2004. Interfacial Redox Processes under CO/O_2 in a Nanoceria-Supported Copper Oxide Catalyst. *J. Phys. Chem. B* 108: 17983-17991.

[79] Zheng, X.; Wang, S.; Wang, S.; Zhang, S.; Huang, W.; and Wu, S. 2004. Copper Oxide Catalysts Supported on Ceria for Low-Temperature CO Oxidation. *Catalysis Communications* 5: 729–732.

[80] Zheng, X.; Zhang, X.; Wang, X.; Wang, S.; and Wu, S. 2005. Preparation and Characterization of CuO/CeO_2 Catalysts and their Application in Low-Temperature CO Oxidation. *Appied Catal A. General* 295: 142-149.

[81] Liu, W.; Sarofim, A. F.; and Stephanopoulos, M. F. 1994. Reduction of Sulfur Dioxide by Carbon Monoxide to Elemental Sulfur over Composite Oxide Catalysts. *Appl Catal B. Environmental* 4:

167-186.

[82] Sedmark, G.; and Hocevar, S. 2003. Kinetics of selective CO Oxidation in Excess of H_2 Over the Nanostructured $Cu_{0.1}Ce_{0.9}O_{2-y}$ catalyst. *J. Catal.* 213: 135-150.

[83] Sedmark, G.; Hocevar, S.; and Levec, J. 2004. Transient Kinetic Model of CO Oxidation Over a Nanostructured $Cu_{0.1}Ce_{0.9}O_{2-y}$ Catalyst. *J. Catal.* 222: 87-99.

[84] Liu, Y.; Fu, Q.; and Stephanopoulos, M. F. 2004. Preferential Oxidation of CO in H_2 over CuO-CeO_2 Catalysts. *Catal. To*day 93–95: 241-246.

[85] Marin˜ o, F.; Descormr, C.; and Duprez, D. 2005. Supported base Metal Catalysts for the Preferential Oxidation of Carbon Monoxide in the Presence of Excess Hydrogen (PROX). *Appl. Catal. B* 58: 175.

[86] Marban, G.; and Fuertes, A.B. 2005. Highly Active and Selective CuO_x/CeO_2 Catalyst Prepared by A Single-Step Citrate Method for Preferential Oxidation of Carbon Monoxide. *Appl. Catal. B* 57: 43-53.

[87] Park, J.; Jeong, J.; Yoon, W.; Jung, H.; Lee, H.; Lee, D.; Park, Y.; and Rhee, Y. 2004. Activity and Characterization of the Co-Promoted CuO–CeO_2/γ-Al_2O_3 Catalyst for the Selective Oxidation of CO in excess Hydrogen. *Appl. Catal. A.* 274: 25-32.

[88] Cheektamarla, P.; Epling, W.; and Lane, A. 2005. Selective Low-Temperature Removal of Carbon Monoxide from Hydrogen-Rich Fuels over Cu–Ce–Al Catalysts. *J. Power Sources* 147: 178-183.

[89] Park, J. W.; Jeong, J. H.; Yoon, W. L.; Kim, C. S.; Lee, D. K.; Park, Y. K.; Rhee, Y. W. 2005. Selective Oxidation of CO in Hydrogen-Rich Stream Over Cu–Ce Catalyst Promoted with Transition Metals. *Int. J. Hydr. Energy* 30: 209-220.

[90] Shiau, C.; Ma, M.; and Chuang, C. 2006. CO Oxidation over CeO_2-Promoted Cu/γ-Al_2O_3 Catalyst: Effect of Preparation Method. *Appl. Catal. A* 301: 89-95.

[91] Manzoli, M.; Di Monte, R.; Boccuzzi, F.; and Coluccia. S. 2005. CO oxidation over CuO_x-CeO_2-ZrO_2 Catalysts: Transient behaviour and Role of Copper Clusters in Contact with Ceria. *Appl. Catal. B* 61: 192-205.

[92] Schwarz, J. A.; Contescu C.; and Contescu, A. 1995. Methods for Preparation of Catalytic Materials. *Chem. Rev.* 95: 477-510.

[93] Hu, Yuhai; Dong, L.; Wang, J.; Ding, W.; and Chen, Y. 2000. Activities of supported copper oxide Catalysts in the NO+CO Reaction at Low Temperatures. *Journal of Molecular Catalysis A. Chemical* 162: 307–316.

[94] Xiaoyuan, J.; Liping, L.; Yingxu, C.; and Xiaoming, Z. 2003. Effects of CuO/CeO_2 and CuO/γ-Al_2O_3 Catalysts on NO + CO reaction. *Journal of Molecular Catalysis A. Chemical* 197: 193–205.

[95] Hermans, L. A. M.; and Geus, J. W. 1979. *Preparation of Catalysts II*, Elsevier, Amsterdam, p. 113.

[96] Zimmer, P.; Tscho¨ pe, A.; and Birringer, R. 2002. Temperature-Programmed Reaction Spectroscopy of Ceria- and Cu/Ceria-Supported Oxide Catalyst. *Journal of Catalysis* 205: 339–345.

[97] Shen, W. J.; Ichihashi, Y.; and Matsumura, Y. 2002. Methanol Synthesis from Carbon Monoxide and Hydrogen over Ceria Supported Copper Catalyst Prepared by Co-Precipitation Method. *Catal. Lett*. 83: 33-35.

[98] Ho˘cevar, S.; Batista, J.; and Levec, J. 1999. Wet Oxidation of Phenol on $Ce_{1-x}Cu_xO_{2-\delta}$ Catalyst. *Journal of Catalysis* 184: 39–48.

[99] Djinovic´, P.; Batista, J.; and Pintar, A. 2008. Calcination Temperature and CuO loading dependence on CuO-CeO_2 Catalyst Activity for water-gas shift reaction. *Applied Catalysis A. General* 347: 23–33.

[100] Soler Illia, G. J. A. A.; Jobba´gy, M.; Candal, R. J.; Regazzoni, A. E.; Blesa, M. A. 1998. Synthesis of Metal Oxide Particles from Aqueous Media: The Homogeneous Alkalinization Method, *J. Dispersion Sci. Technol.* 19: 207.

[101] Jobba´gy, M.; Marin˜o, F.; Scho¨nbrod, B.; Baronetti, G.; and Laborde, M. 2006. Synthesis of Copper-promoted CeO_2 Catalysts, *Chem. Mater.* 18: 1945-1950

[102] Tao, H.; Jian, Y.; Jun, Z.; Danjun, W.; Huanling, S. and Lingjun, C. 2007. Preparation of a Cu–Ce–O Catalyst by Urea Combustion for Removing CO from Hydrogen, *Chinese Journal of Catalysis* 28: 844-846.

[103] Purohit R. D.; Sharma, B. P.; Pillai, K.T.; and Tyagi, A.K. 2001. Ultrafine Ceria Powders via Glycine-nitrate Combustion. *Mater. Res. Bull.* 36(15): 2711–2721.

[104] Zhu, J.; Gao, Q.; and Chen, Zhi. 2008. Preparation of Mesoporous Copper Cerium Bimetal Oxides with high performance for Catalytic Oxidation of Carbon Monoxide, *Appl Catal B. Environmental* 81: 236–243.

[105] Skårman, B.; Nakayama, T.; Grandjean, D.; Benfield, R. E.; Olsson, E.; Niihara, K.; and Wallenberg, L. R. 2002. Morphology and Structure of CuO_x/CeO_2 Nanocomposite Catalysts Produced by Inert Gas Condensation: An HREM, EFTEM, XPS, and High-Energy Diffraction Study. *Chem. Mater*. 24: 3686-3699.

[106] Guillou, N.; Nistor L. C.; Fuess, H.; and Hahn, H. 1997. Microstructural Studies of Nanocrystalline CeO_2 Produced By Gas Condensation. *Nanostruct. Mater.* 8: 545-557.

[107] Birringer, R.; Gleiter, H.; Klein, H. P.; and Marquardt, P. 1984. Nanocrystalline Materials an approach to a Novel Solid Structure with gas-like Disorder, *Phys. Lett. A* 102: 365-369.

[108] Siegel, R. W. 1991. Cluster-assembled Nano Materials. *Annu. Rev. Mater. Sci*. 21, 559.

[109] Moser, W. R. 1996. *Advanced Catalysts and Nanostructured Materials*. Academic Press: San Diego, CA.

[110] Hagemeyer, A.; Jandeleit, B.; Liu, Y.; Poojary, D. M.; Turner, H. W.; Volpe Jr., A. F.; Weinberg, W. H. 2001. Applications of Combinatorial Methods in Catalysis. *Appl. Catal. A. Gen.* 221: 23-43.

[111] Reddington, E.; Sapienza, A.; Gurau, B.; Viswanathan, R.; Sarangapani, S.; Smotkin, E. S.; and Mallouk, T. E. 1998. Combinatorial Electrochemistry: A Highly Parallel, Optical Screening Method for Discovery of Better Electro catalysts. *Science* 280: 1735-1737.

[112] Wilhelm F. M.; and Saalfrank, J. 2004. Discovery, Combinatorial Chemistry and a Newselective CO-oxidation Catalyst, *Chemical Engineering Science* 59: 4673-4678

[113] Heidi M. R.; An, H.; McGinn, P. J. 2003. Combinatorial Synthesis and Characterization of Mixed Metal Oxides for Soot Combustion. *Applied Catalysis B. Environmental* 44: 347–354.

[114] Pillai, U. R.; and Deevi, S. 2006. Room Temperature Oxidation of Carbon Monoxide Over Copper Oxide Catalyst. *Appl Catal B. Environmental* 64: 146-151.

[115] Spivey, J. J. 1987. Complete Catalytic Oxidation of Volatile Organics. *Ind. Eng. Chem. Res.* 26: 2165-2180.

[116] Maitra, A. M. 1993. Critical Performance Evaluation of Catalysts and Mechanistic Implications for Oxidative Coupling of Methane, *Appl. Catal. A* 104: 11-59.

[117] Tang, X.; Zhang, B.; Li, Y.; Xu, Y.; Xin, Q.; and Shen, W. 2004. Carbon Monoxide Oxidation over CuO/CeO_2 Catalysts. *Catal. Today* 93–95: 191-198.

[118] Thomas, J.; and Thomas, W. 1997. *Heterogeneous Catalysis*, VCH, Weinheim, Germany 577.

[119] Dow, W. P.; Wang, Y. P.; and Huang, T. J. 2000. TPR and XRD Studies of Yttria-doped Ceria/γ-Alumina-Supported Copper Oxide Catalyst. *Appl. Catal. A* 190: 25-34.

[120] Kaspar, J.; and Fornasiero, P. in Trovarelli, A. (Editor). 2002. *Catalysis by Ceria and Related Materials,* Imperial College Press, London.

[121] Kaspar, J.; Fornasiero, P.; and Hickey, N. 2003. Automotive Catalytic Converters: Current Status and Some Perspectives. *Catalysis Today* 77: 419-449.

[122] Shelef, M.; Graham, G. W.; and McCabe, R. W. 2002. in Trovarelli A. (Editor), *Catalysis by Ceria and Related Materials,* Imperial College Press; London.

[123] Sugiura, M., Ozawa, M.; Suda, A.; Suzuki, T.; and Kanazawa, T. 2005. Development of Innovative Three-Way Catalysts Containing Ceria–Zirconia Solid Solutions with High Oxygen Storage/Release Capacity. *Bulletin of the Chemical Society of Japan* 78: 752-767.

[124] Kim, T.; Vohs, J.M.; and Gorte, R. J. 2006. Thermodynamic Investigation of the Redox Properties of Ceria-Zirconia Solid Solutions. *Industrial & Engineering Chemistry Research* 45: 5561-5565.

[125] Zhou, G.; Shah, P. R.; Kim, T.; Fornasiero, P.; and Gorte, R. J. 2007. Oxidation Entropies and Enthalpies of Ceria–Zirconia Solid Solutions. *Catalysis Today* 123: 86-93.

[126] Trovarelli, A.; Zamar F.; Llorca J.; de Lietenburg, Dolcetti G.; and Kisss J. T. 1997. Nanophase Fluorite-Structured CeO_2-ZrO_2 Catalyst Prepared by High-Energy Mechanical Milling. *J of Catal.* 169: 490-502.

[127] Hori, C. E.; Permana H.; Ng K. Y. S.; Brenner A.; More K.; Rahmoeller K. M.; and Belton D. 1998. Thermal Stability of Oxygen Storage Properties in a Mixed CeO_2-ZrO_2 system. *Applied Catalysis. Environmental* 16: 105-117.

[128] Boaro, M.; Vicario M.; de Leitenburg C.; Dolcetti G.; and Trovarelli A. 2000. The Dynamics of Oxygen Storage in Ceria-Zirconia Model Catalysts Measured by CO Oxidation under Stationary and Cycling Feed Stream Compositions. *J of Catalysis* 193: 338-347.

[129] Boaro, M.; Trovarelli A.; Hwang J. H.; and Mason T. O. 2002. Electrical and Oxygen Storage/Release Properties of Nanocrystalline Ceria-Zirconia Solid Solutions. *Solid State Ionics* 147: 85-95.

[130] Ma, L.; Luo, M.F.; and Chen, S. 2003. Redox Behaviour and Catalytic Properties of $CuO/Ce_{0.8}Zr_{0.2}$ Catalysts. 242: 151-159.

[131] Kozlov, A.; Kim D. H.; Yezerets A.; Andersen P.; Kung H.; and Kung M. 2002. Effect of Preparation Method and Redox Treatment on the Reducibility and Structure of Supported Ceria-Zirconia Mixed Oxide. *Journal of Catalysis* 209: 417-426.

[132] Imanura, S.; Sawada, H.; Uemura, K.; and Ishida, S. 1988. Oxidation of Carbon Monoxide Catalyzed by Manganese Silver Composite Oxides. *J. Catal.* 109: 198–205.

[133] Bera, P.; Priolkar, K. R.; Sarode, P. R.; Hegde, M. S.; Emura, S.; Kumashiro R.; and Lalla, N. P. 2002. Structural Investigation of Combustion Synthesized Cu/CeO_2 Catalysts by EXAFS and other Physical Techniques: Formation of a $Ce_{1-x}Cu_xO_{2-d}$ Solid Solution. *Chem. Mater*. 14: 3591.

[134] Nico J. J.; Dekker, Johan A. A.; Hoorn, Sander Stegenga, Freek Kapteijn; and Moulijn, J.A. 1992. Kinetics of the CO oxidation by O_2 and N_2O over $Cu\text{-}Cr/Al_2O_3$. *AIChE Journal* 38: 385-396.

[135] Rattan, G.; and Prasada, R. 2009. Effect of Preparation Method and Calcinations Temperature on Low Temperature CO Oxidation over $CuO–CeO_2$ Catalysts, Paper presented in International Conference, *Chemcon-2009*, Dec. 27-30, Andhra University, Visakhapatnam, India

[136] Dockery, D. W.; Pope, C. A.; Xu, X; Spengler, J. D.; Ware, J. H.; Fay, M. E.; Ferris, B. G; and Speizer, F. E. 1993. An Association between Air Pollution and Mortality in Six U.S. cities. *New Engl J Med* 329: 1753–9.

[137] Siegmann, K.; and Siegmann, H. C.1998. Molecular Precursor of Soot and Quantification of the Associated Health Risk. In: Mora´n-Lo´pez, editor. *Current Problems in Condensed Matter*. New York; Plenum Press, p. 143–60.

[138] Setiabudi, A.; Makkee, M.; and Moulijn, J. A. 2003. An optimal NO_x Assisted Abatement of Diesel Soot in an Advanced Catalytic Filter Design. *Applied Catalysis B. Environmental* 42: 35–45.

[139] Farrauto, R. J.; and Voss, K. E. 1996. Monolithic Diesel Oxidation Catalysts. *Applied Catalysis B. Environmental* 10: 29-51.

[140] Hongmei, An; Paul J.; and McGinn, 2006. Catalytic Behavior of Potassium Containing Compounds for Diesel Soot Combustion. *Applied Catalysis B. Environmenta*l 62: 46–56.

[141] Larsson, P. O.; and Andersson, A. 1998. Complete Oxidation of CO, Ethanol, and Ethyl Acetate over Copper Oxide Supported on Titania and Ceria Modified Titania. *J. Catal.* 179: 72-89.

[142] Flytzani-Stephanopoulos, M.; and Liu, W. 2002. "Catalytic Reduction of Sulfur Dioxide into Elemental Sulfur" Chapter in *Encyclopedia of Catalysis* Eds. by Horvath et al., John Wiley & Sons, Inc.

[143] Geng, Q.; Guo, Q.; Cao, C.; Zhang, Y.; and Wang, L. 2008. Investigation into Photocatalytic Degradation of Gaseous Ammonia in CPCR. *Ind. Eng. Chem. Res.* 47: 4363-4368.

[144] Lin, C. H.; Wu, Y. L.; Lai, C. H.; Watson, J. G.; and Chow, J. C. 2008. Air Quality Measurements from the Southern Particulate Matter Supersite in Taiwan. *Aerosol Air Qual. Res*. 8: 233-264.

[145] Dravell, L. I.; Heiskanen, K.; Jones, J. M.; Ross, A. B.; Simell, P.; and Williams, A. 2003. An Investigation of Alumina-Supported Catalysts for the Selective Catalytic Oxidation of Ammonia in Biomass Gasification. *Catal. Today* 81: 681-692.

[146] Liu, W.; and Flytzani-Stephanopoulos, M. 1996. Transition Metal-Promoted Oxidation Catalysis by fluorite Oxides: A Study of CO Oxidation over $Cu\text{-}CeO_2$. *The Chemical Engineering Journal* 64: 283-294.

[147] Avgouropoulos G.; Ioannides T.; Matralis H.; Batista J.; and Hocevar S. 2001. $CuO\text{-}CeO_2$ Mixed Oxide Catalysts for the Selective Oxidation of Carbon Monoxide in Excess Hydrogen. *Catalysis Letters* 73: 33-40.

[148] Wang, J. B.; Lin, S. C.; and Huang, T. J. 2002. Selective CO Oxidation in Rich Hydrogen Over CuO/Samaria-Doped Ceria. *Applied Catalysis A. General*. 232: 107-120.