



# Liquid phase selective oxidation of benzene over nanostructured $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ ( $0.03 \leq x \leq 0.15$ )



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## ABSTRACT

Liquid phase direct oxidation of benzene to phenol was carried out over copper loaded on oxides such as ceria, alumina, magnesia, ferric oxide, zinc oxide with 30%  $\text{H}_2\text{O}_2$  as oxidant under atmospheric pressure. Of all the catalytic formulations prepared via a novel solution combustion synthesis, the ceria based catalysts showed highest activity. Particularly, over the  $\text{Cu}_{0.10}\text{Ce}_{0.90}\text{O}_{2-\delta}$  catalyst, 43% conversion of benzene with 100% selectivity was observed at 70 °C and atmospheric pressure. The activity of this combustion synthesized catalyst is also higher than the corresponding catalyst prepared by incipient wetness impregnation and coprecipitation methods. Powder XRD, TEM and XPS studies show ionically substituted copper over ceria as the predominant phase in the combustion derived catalyst whereas on the impregnated and coprecipitated catalysts copper is present in the dispersed copper oxide form. Influences of temperature and time,  $\text{H}_2\text{O}_2$  concentration and solvent have also been investigated. Enhanced activity over the combustion synthesized catalyst wherein  $\text{Cu}^{2+}$  ion is present as substitutional ion in ceria has been attributed to Cu–O–Ce ionic interaction. Ionic substitution also brings stability to the active copper ion component in the combustion synthesized catalyst with lower risk of Cu-leaching as compared to the corresponding impregnated and coprecipitated catalysts as evidenced from the recycling experiments.

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## 1. Introduction

Direct oxidation of benzene to phenol finds huge potential in the field of organic synthesis from an economical and environmental point of view [1–20]. In addition, phenol is one of the most important chemicals in the fields of agrochemicals, petrochemicals, plastics and pharmaceuticals. The phenol production shows an upward trend; its current worldwide production is nearly seven million tons per year [4]. Phenol has been mainly manufactured using the cumene method [4] because of high selectivity for the formation of phenol. However, this cumene process consists of three steps and produces acetone as a byproduct, which results in many problems due to economical and environmental concerns. The one-step production of phenol by direct insertion of oxygen into the benzene ring is an attractive and challenging method, not

only from a practical point of view but also from a purely scientific point of view. Although a direct oxidation process of benzene to phenol would be the most economical route, until now only the indirect manufacturing process has been operative. The reason is that the activation of the C–H bonds in benzene is difficult due to the resonance stability.

Various new catalytic systems have been developed for the oxidation of benzene to phenol both in gas-phase and in liquid-phase using  $\text{N}_2\text{O}$ ,  $\text{O}_2$  or  $\text{H}_2\text{O}_2$  as the oxidant [5–8]. Different types of copper catalysts such as Cu/HMCM-41 [1], Cu-ZSM-5 [9] Cu/ $\text{Al}_2\text{O}_3$  [10], Cu/APO-11 [11] and RHA-10Cu20Ce [12] have been reported to be efficient systems for phenol production from benzene. However, these catalysts are prone to copper leaching during oxidation, which can be controlled by adopting specific preparation procedure and by incorporation with other metals [3]. Association of two or more active metals can perform well in a reaction system with enhanced degree of interaction of the components over a support with new redox and acid properties [21]. Ceria is well known for its oxygen storage/release capacity due to the oxygen vacancies and changes in the redox state of cerium (4+/3+).

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This property makes ceria a better catalyst for the reduction of  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{NO}_x$  emissions and in catalytic oxidation [22]. Djinovic et al. reported that  $\text{CuO-CeO}_2$  catalyst under proper temperature treatment, showed better water gas shift activity due to increased acidity/basicity which enhanced the adsorption of  $\text{CO}$  on the catalyst surface [23]. The enhanced activity of these classes of catalysts is generally related to the strong interactions between  $\text{Cu}$  species and surface oxygen vacancies of  $\text{Ce}$  with facile electron interplay of  $\text{Cu}^{2+}/\text{Cu}^+$  and  $\text{Ce}^{4+}/\text{Ce}^{3+}$  redox couples [24].

Here we show that combustion synthesized ionically dispersed copper on ceria,  $\text{Cu}_{0.10}\text{Ce}_{0.90}\text{O}_{2-\delta}$ , has a higher selective hydroxylation activity towards benzene to phenol than other copper loaded oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{ZnO}$ ) in acetonitrile solvent at  $70^\circ\text{C}$  and atmospheric pressure. The effect of temperature,  $\text{H}_2\text{O}_2$  concentration and solvent on this reaction has also been investigated. Combustion synthesized  $\text{Cu}_{0.10}\text{Ce}_{0.90}\text{O}_{2-\delta}$  has also been shown to be more active than the corresponding impregnated and coprecipitated catalysts.

## 2. Experimental

### 2.1. Preparation of catalysts

We have synthesized the catalysts by single step solution combustion method in an open muffle furnace kept in a fume hood with exhaust by the combustion of the corresponding metal nitrate salts with oxalyl dihydrazide [ $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$  (ODH)] as the fuel. Oxalyl dihydrazide was prepared by the dropwise addition of diethyl oxalate ( $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$ , Sisco Research Laboratories Pvt. Ltd., 99%) to ice-cooled aqueous solution of hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$ , Qualizens Fine Chemicals, 99%) as reported in [25]. Specifically, solution combustion synthesis (SCS) for the preparation of  $\text{Cu}_{0.10}\text{Ce}_{0.90}\text{O}_{2-\delta}$  involves combustion of the metal salts  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  with ODH, taken in a molar ratio 0.90:0.10:2.26, at the temperature of ignition of the redox mixture ( $\sim 350^\circ\text{C}$ ). In a typical preparation, 5 g of  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  (Loba Chemie, 99%), 2.450 mL 10%  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Merck India, 99%) solution and 2.7075 g of ODH are dissolved in 30 mL of double distilled water in a borosilicate dish. The solution is then transferred to the preheated muffle furnace maintained at  $\sim 350^\circ\text{C}$ . Initially the solution boils with frothing and foaming followed by complete dehydration when the surface gets ignited and burns with a flame yielding a voluminous solid product within a minute. This catalyst will be represented as  $\text{CuCe10SCS}$ . We have also prepared  $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$  ( $x = 0.03, 0.07$  and  $0.15$ ) catalysts in a similar manner.

Combustion synthesis of 5 at.% copper over other oxides that include  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$  and  $\text{MgO}$  was carried out similarly by the combustion of stoichiometric redox mixture of the corresponding metal nitrate salts,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck India, 99%) or  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck India, 99%) or  $\text{Zn}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$  (Merck India, 99%) or  $\text{Mg}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$  (Merck India, 99%) and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  with ODH at  $350^\circ\text{C}$ .

For comparison, we have also prepared  $\text{Cu}_{0.10}\text{Ce}_{0.90}\text{O}_{2-\delta}$  by the incipient wetness impregnation (IWI) and coprecipitation (COP) methods. For the preparation of the impregnated catalyst, the support (solution combustion synthesized  $\text{CeO}_2$ ) was first dried and then impregnated with an appropriate volume of the aqueous solution of copper nitrate, corresponding to the support pore volume. The sample was then dried overnight at  $100^\circ\text{C}$ , crushed and calcined at  $500^\circ\text{C}$  for 3 h in air to get the catalyst ( $\text{CuCe10IWI}$ ).

In the coprecipitation method, 5 g  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and 0.1464 g  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  were dissolved in 50 mL of double distilled water in a 250 mL beaker and then a saturated solution of sodium carbonate was added drop wise to it with vigorous stirring. A white precipitate thus obtained was filtered, washed 4–5 times with hot water and

then dried at  $110^\circ\text{C}$  for  $\sim 12$  h. The dried precipitate was crushed and then calcined at  $650^\circ\text{C}$  for 4 h to get the coprecipitated catalyst,  $\text{CuCe10COP}$  [26]. Table 1 lists all the catalysts investigated here with their nominal composition and nomenclature.

### 2.2. Characterization of catalysts

The synthesized materials have been characterized by XRD, BET, HRTEM and XPS. X-ray powder diffraction patterns were collected in a Rigaku diffractometer fitted with a horizontal goniometer mounted on a rotating anode. These data were recorded at 4 kW (40 kV, 100 mA) at  $1^\circ \text{min}^{-1}$  with a step size of  $0.02^\circ$  in the range  $20$ – $80^\circ$ . The rotating anode has  $\text{Cu}$  anode with effective wavelength of  $1.5418 \text{ \AA}$ . There is a diffracted beam monochromator (Graphite crystal) which takes care of  $K_\beta$  lines and fluorescence.

The BET surface areas of some samples were measured in a TriStar3000 surface area analyzer (Micromeritics). Before each measurement, the samples were degassed at  $150^\circ\text{C}$  in vacuum for 60 min.

Microstructural characterization by High Resolution Transmission Electron Microscopy (HRTEM) was performed at an accelerating voltage of 200 kV in a JEOL 2010F instrument equipped with a field emission source. The point-to-point resolution was 0.19 nm, and the resolution between lines was 0.14 nm. The magnification was calibrated against a Si standard. No induced damage of the samples was observed under prolonged electron beam exposure. Samples were dispersed in alcohol in an ultrasonic bath, and a drop of supernatant suspension was poured onto a holey carbon-coated grid. Images were not filtered or treated by means of digital processing, and they correspond to raw data.

Surface characterization was done with X-ray photoelectron spectroscopy (XPS) on a SPECS system equipped with an Al anode XR50 source operating at 150 mW and a Phoibos 150 MCD-9 detector. The pressure in the analysis chamber was always below  $10^{-7}$  Pa. The area analyzed was about  $2 \text{ mm} \times 2 \text{ mm}$ . The pass energy of the hemispherical analyzer was set at 25 eV and the energy step was set at 0.1 eV. Charge stabilization was achieved by using a SPECS Flood Gun FG 15/40. The sample powders were pressed to self-consistent disks. The following sequence of spectra was recorded: survey spectrum, C 1s, Ce 3d, Cu 2p and C 1s again to check for charge stability as a function of time and the absence of degradation of the sample during the analyses. Data processing was performed with the CasaXPS program (Casa Software Ltd., UK). The binding energy (BE) values were referred to the C 1s peak at 284.8 eV. Atomic fractions (%) were calculated using peak areas normalized on the basis of acquisition parameters after background subtraction, experimental sensitivity factors and transmission factors provided by the manufacturer.

### 2.3. Catalytic test

The oxidation of benzene by  $\text{H}_2\text{O}_2$  was carried out in the temperature range  $\text{RT} - 80^\circ\text{C}$  at atmospheric pressure. In a typical experiment, 0.15 g of catalyst was added to a liquid mixture containing 20 mL of acetonitrile, 10 mL of 30 wt.%  $\text{H}_2\text{O}_2$  (97.9 mmol) and 5 mL of benzene (56.3 mmol) in a 250 mL two-necked round bottomed flask. For uniform mixing, the contents were stirred continuously ( $\text{rpm} = 850$ ) during the course of reaction by a magnetic stirrer. The reaction system consisted of two liquid phases – an organic phase containing benzene and acetonitrile, and an aqueous phase containing acetonitrile and 30%  $\text{H}_2\text{O}_2$ .

The reaction compositions were analyzed using a gas chromatograph (Nucon 5765, New Delhi) using a fused silica capillary column (EC5) of  $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$  film thickness from Alltech and equipped with a FID detector. The injector and detector temperatures were  $220^\circ\text{C}$  and  $240^\circ\text{C}$ . The initial and final column temperatures were  $110^\circ\text{C}$  and  $150^\circ\text{C}$ , respectively with a

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