

## Neutron scattering study of combustion-synthesized $\text{Ce}_{1-x}\text{Cu}_x\text{O}_{2-x}$

KEKA R CHAKRABORTY<sup>1</sup>, P S R KRISHNA<sup>1</sup> and M S HEGDE<sup>2</sup>

<sup>1</sup>Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

<sup>2</sup>Solid State and Structural Chemistry Unit, Indian Institute of Science,  
Bangalore 560 012, India

E-mail: kekar@magnum.barc.ernet.in

**Abstract.** Powder neutron diffraction and Hi- $Q$  neutron diffraction data have been recorded and analysed in order to obtain the local and long range order of Cu in Cu-doped  $\text{CeO}_2$  with three doping levels of Cu. Rietveld method and MCGR techniques of data analysis for the two types of data reveal that the Cu ion is in the 2+ oxidation state and has a vacancy in its first coordination shell. These deductions from the data analysis fit well with the mechanism of catalysis we propose.

**Keywords.** Combustion synthesis; neutron diffraction.

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### 1. Introduction

NO is one of the main constituent of  $\text{NO}_x$  which exists in exhaust gas from motor vehicles and other combustion processes. It is a pollutant and hence needs to be reduced in emissions thus providing thrust for research. Fine particle Ceria has widespread use in automotive three-way catalytic converters to remove toxic gases from engine exhaust. The converters have conflicting tasks to perform like reducing  $\text{NO}_x$  while at the same time oxidizing CO and hydrocarbons. These tasks were found to be performed simultaneously on the surface of small particles of noble metal catalysts such as Pd, but only in a narrow range of oxygen partial pressure, where Ceria played the role of maintaining the local oxygen pressure. However, it has been observed that Ceria has an irreversible deterioration of its oxygen storage properties during operation.

Cu-based catalysts have gained importance [1] due to their good catalytic properties. These catalysts have been found to be superior to conventional catalysts in the sense that they operate at a much lower temperature (at as low as 150°C).

There are conflicting reports in the literature regarding the mechanism of catalysis in Cu/ $\text{CeO}_2$ . The study of the nature of Cu and its role in catalysis needs attention in spite of the extensive work done previously [1]. It is generally believed [2,3] that the highly dispersed CuO phase in  $\text{CeO}_2$  is the active phase for catalytic

activity. In order to gain an insight into the high catalytic activities of Cu/CeO<sub>2</sub> it is essential to find the long range and local structure of each of the atoms in the catalyst.

We present a brief report of neutron diffraction studies on Cu-doped Ceria for three doping levels of Cu. Neutron scattering being more sensitive than X-rays to oxygen atoms, has been used to get a clear picture of long range and local order of all the atoms.

## **2. Experimental**

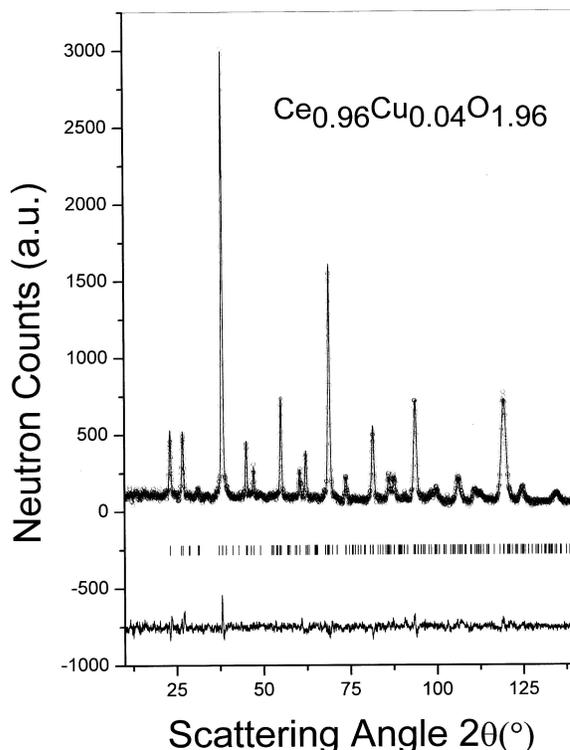
The actual synthesis has been described elsewhere [1] but is briefly given below. A borosilicate dish of 300 cc capacity, containing an aqueous redox mixture of stoichiometric amounts of (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>), Cu(CO<sub>3</sub>)<sub>2</sub>, Cu(OH)<sub>2</sub> and C<sub>2</sub>N<sub>2</sub>O<sub>4</sub>H<sub>6</sub> in 300 cc of water was introduced in a muffle furnace with temperature maintained at 350°C. At the point of complete dehydration, the solution boiled with foaming and frothing and ignited into a flame producing the oxide. This technique called combustion technique produces fine crystallites with sizes in the range of 25–35 nm.

Neutron diffraction data were recorded for all samples on the powder diffractometer [4] at beam port T1013 of the Dhruva reactor. The samples were packed in a vanadium can of 60 mm height and 6 mm diameter. The wavelength used was 1.249 Å. The angular range covered was 10°–130°. The data were analysed using the WINPLOTR suite of programs.

Hi-*Q* neutron diffraction data were also recorded on the Hi-*Q* neutron diffractometer [5] at the Dhruva reactor covering a *Q* range 1 Å<sup>-1</sup>–13.5 Å<sup>-1</sup> using a wavelength of 0.783 Å. The data obtained were subjected to data reduction and correction programs available. These programs ensure that we get the structure factor *S*(*Q*) in absolute units.

## **3. Results and discussion**

In our earlier work [6] on 5% Cu-doped catalyst, neutron diffraction patterns recorded were analysed using the Rietveld method. Figure 1 shows the refined, observed and difference neutron diffraction patterns. The parameters varied were scale factor, cell constants, zero angle of the detector, half-width parameters, isotropic Debye–Waller factors and the occupancies of Ce, Cu and O atoms using constraints. The cell constant obtained was close to the XRD values. The O occupancies when varied with constraints produced a loss of 3.1% O atoms from their regular sites. So the coordinates of the O atoms were varied assuming that the O atoms moved to the interstitials in order to explain the loss of O from lattice sites retaining the same space group as obtained from [7]. We tried employing two different models, as discussed in ref. [5]. In the first model O was assumed to lie anywhere in the  $\langle 110 \rangle$  direction, i.e., with coordinates (*x*, *x*, 0.5), This model gave unrealistic values of fractional coordinate *x*. So it was discarded. The second model assumes that the O atoms are permitted to move to two types of interstitials with coordinates

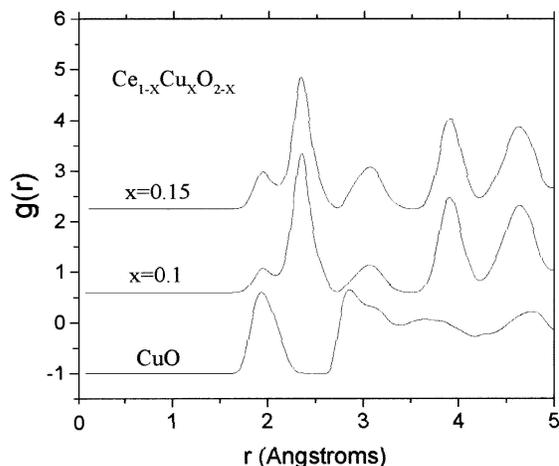


**Figure 1.** Rietveld refined neutron diffraction pattern for 5% Cu-doped CeO<sub>2</sub>.

$(x, x, 0.5)$  and  $(x', x', x')$ . Our data fitted best to this model with  $x = -0.68(3)$  and  $x' = 0.68(1)$ .

In order to get a clearer picture of the presence of the O vacancies, we synthesized 10 and 15% Cu-doped catalysts. On closer inspection the major phase in the neutron diffraction patterns were indexed using a face centered cubic lattice for the 5, 10, 15% Cu-doped and the parent compounds. There were traces of CuO in all the samples (except the parent). The structure of the major phase in each sample conforms to the space group Fm3m. CuO was incorporated as a second phase in the refinement. In the analysis, the various parameters varied were cell constants, zero angle of the detector, the Debye–Waller factors of all the atoms in the unit cell and the O occupancies. There was a decrease in O occupancy with increasing Cu content, when the occupancies were varied using constraints. The formulae for all three compositions are shown in table 1.

The local structures of all these compounds have been obtained from the Hi- $Q$  diffraction data using MCGR (Monte Carlo radial distribution function  $g(r)$ ) analysis. Strictly speaking, MCGR analysis is valid for single phase systems only. So we subtracted the contribution of CuO phase from the powder patterns to get the experimental pattern for major phases and then converted that into the structure factor before using MCGR technique to obtain respective  $g(r)$ 's.



**Figure 2.**  $g(r)$  vs.  $r$  for  $x = 0.1, 0.15$  and CuO.

**Table 1.** Occupancies of Cu, Ce and O from neutron diffraction data.

Sample name		Major phase	CuO phase
Cu 5%	$Ce_{0.96}Cu_{0.04}O_{1.96}$	97.3%	2.7%
Cu 10%	$Ce_{0.94}Cu_{0.06}O_{1.94}$	97.5%	2.5%
Cu 15%	$Ce_{0.91}Cu_{0.09}O_{1.91}$	83.5%	16.5%

Earlier work [1] on these samples using EXAFS was carried out in the Cu-K edge only and hence throws light only on the Cu-A (A any other atom) correlations. EXAFS Spectra of CuO and the catalyst showed similarities in the first coordination shell indicating that Cu environment in both of them was identical. Further analysis which consisted of comparing bond lengths of Cu with other atoms obtained from  $g(r)$  using the MCGR technique with those from EXAFS (only for the 5% Cu-doped catalyst) showed good agreement. In addition it was found that Cu ion in the catalyst had a first coordination number of 3 (with respect to O) indicating the presence of a vacancy around it.

The plot of  $g(r)$  vs.  $r$  thus obtained for  $x = 0.1$  and  $0.15$  doping levels and that of CuO only are shown in figure 2. We found that the local structure of the CuO sample was markedly different from that of the catalysts indicating that there are no CuO phase inclusions, which again means  $Cu^{2+}$  is replacing  $Ce^{4+}$  ion.

In CuO the first coordination shell contained four O atoms and the second, two O atoms. Consolidating our observations on the catalysts we find that the environment of Ce with respect to O is the same for the three catalysts and in the parent compound, namely each Ce atom is surrounded by  $\sim 3.8$  O atoms. Also each Cu atom is surrounded by  $\sim 3$  O atoms in the first coordination shell indicating an O vacancy as obtained from our earlier analysis. While the number of Cu ions surrounding each Cu increases from  $\sim 2$  to 6 with increasing Cu content the corresponding number of Ce ions decreases from  $\sim 7$  to 3. This is not true for pure

CuO. Hence the second phase in the compound, namely CuO is not participating in catalysis, which means in other words that Cu embedded in the  $CeO_2$  matrix is responsible for catalysis.

The MCGR results provide direct evidence for the formation of  $Ce_{1-x}Cu_xO_{2-x}$  type solid solution phase having  $-\square-Cu^{2+}-O-Ce^{4+}$  kind of linkages where  $-\square-$  is a vacancy. The mechanism of catalysis we propose involves,  $Cu^{2+}$  being neutralized, to Cu (with  $2O^{2-}$  and  $2H_2$  as by-products) along with  $2Ce^{4+}$  being transformed to  $2Ce^{3+}$  and  $2H_2O$ . Further, neutral Cu combines with  $2Ce^{3+}$  and  $O_2$  to produce  $Cu^{2+}$ ,  $2Ce^{4+}$  and  $2O^{2-}$ . By doping with Cu which is in the 2+ oxidation state the above-mentioned catalytic reaction can take place. Finally more  $Cu^{2+}$  is produced from neutral Cu in the second stage of the reaction and hence there is a higher rate of catalysis.

#### 4. Conclusion

In conclusion we say that the Cu-doped Ceria is a better catalyst. The use of neutron diffraction and Hi-Q neutron diffraction to determine the average and local structure of these catalysts agrees well with earlier EXAFS data and the mechanism of catalysis as proposed by us is reasonable.

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