

## Reactivity and catalytic activity of layered $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (123) type defect perovskites<sup>+</sup>

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**Abstract.** The chemical modifications of structure, reactivity and catalytic properties of layered triple perovskite oxides, related to the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (123) system, have been briefly reviewed. These oxides form a versatile family of materials with wide-ranging chemical and physical properties. The multiple sites available for chemical doping, and the ability to reversibly intercalate oxygen at the defect sites have rendered these oxides important model systems in the area of oxide catalysis. An attempt has been made to comprehend the hitherto known catalytic reactions and correlate them to various factors like structure, oxygen diffusional limitations, different geometries adopted by various substituents, oxidative non-stoichiometry and activation energy for oxygen desorption. In particular, results on the enhanced catalytic activity of cobalt-substituted 123 oxide systems towards the selective catalytic oxidation of ammonia to nitric oxide and carbon monoxide to carbon dioxide are presented.

**Keywords.** Layered defect perovskites; reactivity; catalytic activity;  $\text{NH}_3$  oxidation; CO oxidation.

### 1. Introduction

Mixed metal oxides like perovskites ( $\text{ABO}_3$ ), sheelites ( $\text{ABO}_4$ ), pyrochlores ( $\text{A}_2\text{B}_2\text{O}_7$ ), spinels ( $\text{AB}_2\text{O}_4$ ) and layered perovskites of  $\text{K}_2\text{NiF}_4$  structure have attracted the attention of crystal chemists, due to their structure and wide-ranging physical properties. Particularly, the ability to modify composition, structure and oxygen stoichiometry by means of chemical substitution in these systems has made these oxides important model systems in the study of oxide catalysis (William and Halpern 1954). The catalytic properties of perovskites (Tejuca *et al* 1989) and sheelites (Sleight 1977) have been reviewed earlier, and oxides of the  $\text{K}_2\text{NiF}_4$  structure with alternative layers of A–O rocksalt and  $\text{ABO}_3$  perovskites have been extensively investigated for their structure (Rabenau and Eckerlin 1958), transport (Singh *et al* 1984) and catalytic properties (Ramanujachary *et al* 1985; Nitadori *et al* 1986). Though the layered triple perovskite system was known to crystal chemists about a decade ago (Alario-Franco *et al* 1985) the observation of superconductivity at 90 K, in the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (Y123) system brought about a renewed interest in perovskite-related oxides. Since then various cationic substitutions have been made in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  system to understand

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the mechanism and origin of superconductivity. The effect of oxygen content on the structure and physical properties (Jorgenson *et al* 1990) and mechanism of oxygen diffusivity are well understood (La Graf *et al* 1993). However the ability to reversibly intercalate about one mole of oxygen atoms per mole of Y123, has prompted crystal chemists to tap this oxygen in a Mars–van Krevelen pathway (Mars and van Krevelen 1954; Jiang *et al* 1989) for useful catalytic applications. The ability to reversibly intercalate oxygen in Y123 has placed this oxide among those uniform heterogeneous catalysts (Thomas *et al* 1988) like bismuth molybdates (Graselli and Burrington 1981) and calcium manganates (Reller *et al* 1984). The first report, on the use of Y123 as a catalyst, was made by Hansen *et al* (1988) where they employed the oxide system successfully in the ammoxidation of toluene to benzonitrile. Since then, Y123 and related oxides have been used in many catalytic and gas solid reactions. In this article we briefly review the progress made on Y123 and related systems as oxidation catalysts with emphasis on their structure, non-stoichiometry, oxygen reactivity and catalytic activity. Also, we present the results of some of the investigations carried out in our laboratory on the catalytic and stoichiometric oxidation of small molecules like  $\text{NH}_3$  and CO over Y123 and cation-substituted 123 systems.

## 2. Non-stoichiometry and oxygen diffusion

The structural and physical properties of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system are highly influenced by non-stoichiometry (Jorgenson *et al* 1990). For values of  $\delta < 0.5$ , the compound is orthorhombic and superconducting, and for  $\delta > 0.5$ , the compound is tetragonal and non-superconducting. Figure 1 gives the structure of the orthorhombic unit cell of Y123. The structure supports two types of copper ions viz Cu(1), or the

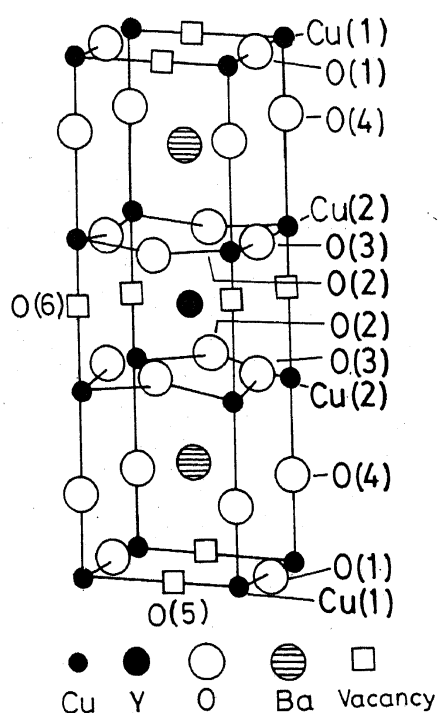


Figure 1. Schematic diagram of the unit cell of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system.

chain copper atoms at (0 0 0) and Cu(2) at (0 0  $z$ ) positions. The Cu(1) is surrounded by oxygen atoms at a distance of 1.942 Å and 1.845 Å in square planar geometry. The second copper atom at Cu(2) adopts square pyramidal geometry, with an apical oxygen at a distance of 2.3 Å along the  $c$  axis. In the tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_6$ , the Cu(1) atoms are two-fold coordinated, and the coordination of five oxygens around Cu(2) remains unchanged. Both in the orthorhombic and tetragonal forms of Y123, the O(6) (0 0 1/2) sites at the rare earth plane and the O(5) (1/2 0 0) sites at the basal plane are totally vacant. The reversible intercalation of oxygen in the O(1) (0 1/2 0) sites, accounts for both its physical and chemical properties. The diffusional limitations encountered by the oxygen in the  $a$ - $b$  basal planes have been recognised as a key factor in controlling the oxygen reactivity of this system. The structural phase transitions and lability of reactive oxygen species are diffusion-controlled and strongly depend on the defect concentration (La Graf *et al* 1993). Tu *et al* (1989), by electrical resistivity measurements on  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  under different ambients, have established that the out-diffusion rate of oxygen was independent of  $\delta$  and estimated a surface energy barrier of 1.7 eV for the out-diffusion of oxygen. La Graf *et al* (1993) carried out an extensive study of the mechanistic aspects of the oxygen diffusion in the  $a$ - $b$  plane and suggested that diffusion of oxygen along the Cu-O chain ( $b$ -axis) was favourable, if the oxygen started at the end of a chain and the adjacent chain site was vacant. Intra-chain diffusion along the  $a$ -axis between the two copper-oxygen chains was found to be slow which is dependent on oxygen concentration and is less favourable. Various factors influencing diffusion, like the correlation effects, thermodynamic constraints, vacancy and interstitials and different types of atomic jumps have been discussed in detail by La Graf *et al* (1993). In the tetragonal as well as orthorhombic forms of Y123 the O(1) and O(5) sites have been recognised as the key sites enhancing the oxygen diffusion either by an interstitial or vacancy mechanism. In the light of this, it is apparent that the defect chemistry and oxygen mobility in the  $a$ - $b$  basal planes, and hence the catalytic activity could be controlled by the substitutions of *iso* and aliovalent transition metal cations in the place of copper.

### 3. Chemical modification of structure and reactivity

A variety of cationic substitutions have been made in the Y123 systems (Kistenmacher *et al* 1988; Tarascon *et al* 1988). The effect of substitution of transition metal ions such as Ni, Zn, Fe, Co and Al for copper in Y123, on the structure and oxygen contents were investigated in detail by Tarascon *et al* (1988). They observed that trivalent ions such as Fe, Co and Al occupied the Cu(1) sites and it induces an orthorhombic to tetragonal structural transition, as well as the oxygen content being increased with increasing amounts of dopant. On the other hand, divalent ions such as Ni and Zn did not alter orthorhombicity, also the oxygen content did not show any variation. The trivalent ions occupy the Cu(1) and hence bring in extra oxygen at O(5) sites to account for the transition from orthorhombic to tetragonal structure and also for the increased oxygen content. One oxygen atom per formula unit can be removed from the undoped phase by heating in vacuum. Hegde (1988) estimated the activation energy for the desorption of chain oxygens from polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  employing temperature programmed desorption (TPD) to be 28 kcal/mol. Tarascon *et al* (1988) proposed that transition metal substitutions made at Cu(2)

sites may not affect the removal of oxygen from the basal plane Cu–O chain. Also they showed by TGA experiments that the amounts of oxygen removed from Fe-, Co- and Al-doped samples decreased with increasing dopant concentration. These observations were followed by a variety of substitutions in Y123 system. Cava *et al* (1988) analysed the  $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7+\delta}$  system for various values of  $x$  and found that the system undergoes an orthorhombic to tetragonal transition at  $x = 0.4$ , and the amount of removable oxygen was found to decrease with increasing  $x$ . Lindemer *et al* (1989) have briefly reviewed the TGA studies on phase transitions, thermodynamics and non-stoichiometry in the 123 based systems.

One way to study the reactivity of cation substituted Y123 is to estimate activation energy of oxygen desorption. We (Ramesh and Hegde 1992) have studied the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Pr123) and  $\text{YBa}_2\text{Cu}_2\text{CoO}_{7+\delta}$  (YCo123) for their oxygen lability. Figure 2 gives the oxygen desorption profiles for these oxides. Activation energies of oxygen desorption for Y123, Pr123, and YCo123 estimated from Polanyi–Vigner plots were 28.2, 26.4 and 22.3 kcal/mol respectively. The onset temperature for oxygen desorption was also found to be the lowest for YCo123 among the three solids. Subsequently the effects of cobalt substitution for copper on the desorption temperature of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  were investigated. The substitution of cobalt in Y123 and Pr123 brought down the activation energy for oxygen desorption. Figures 3a and b show the variation of activation energy for oxygen desorption  $E_a$  as a function of dopant concentration  $x$  in  $\text{YBa}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_{7\pm\delta}$  and  $\text{PrBa}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_{7\pm\delta}$  respectively. The above study led to the formation of a new orthorhombic non-superconducting phase,  $\text{PrBa}_2\text{Cu}_2\text{CoO}_{7+\delta}$  (PrCo123) where significant amount of  $\text{Co}^{3+}$  was suggested to occupy Cu(2) positions with the excess oxygen at O(6) sites (Hegde *et al* 1993). The effect of a larger rare earth ion directing

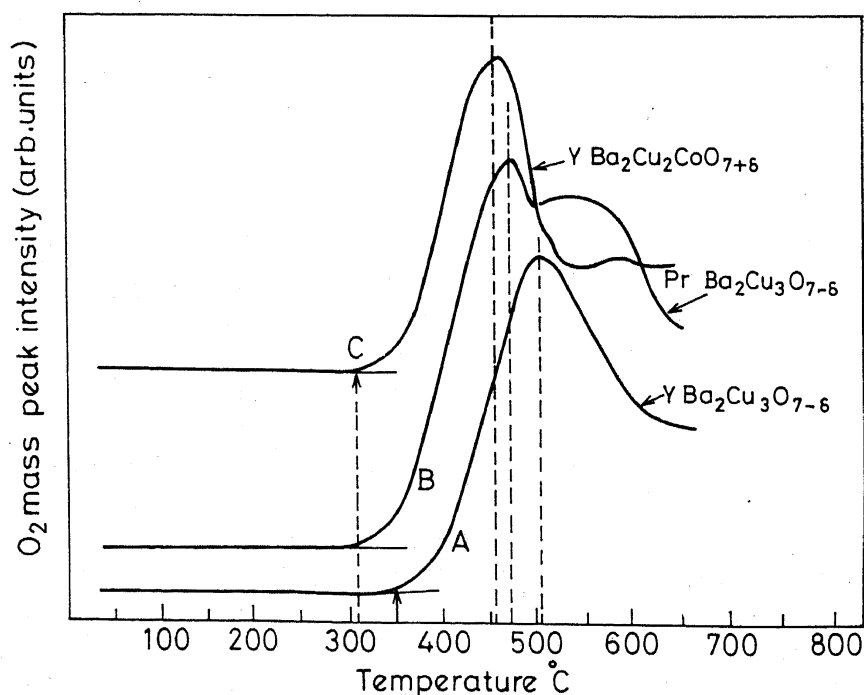


Figure 2. Temperature programmed desorption profiles of oxygen from  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (A),  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (B) and  $\text{YBa}_2\text{Cu}_2\text{CoO}_{7+\delta}$  (C).

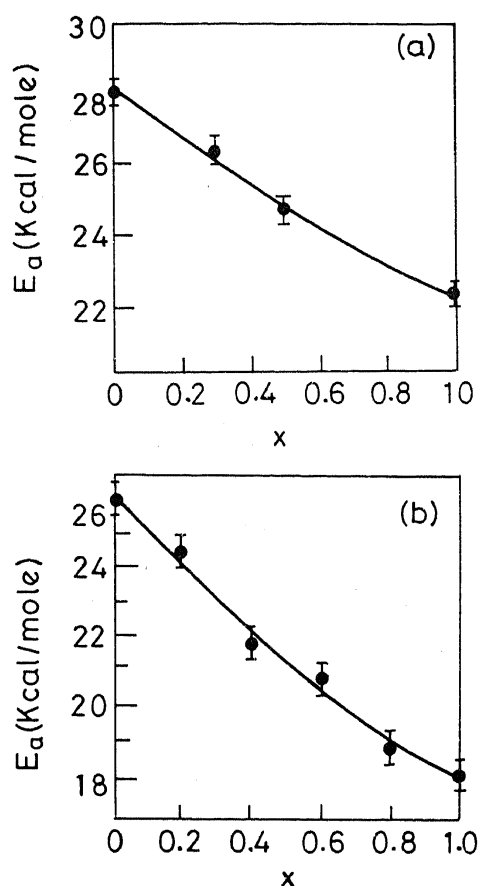


Figure 3. The variation of activation energy for oxygen desorption  $E_a$  as function of cobalt concentration  $x$  in (a)  $\text{YBa}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_{7\pm\delta}$  and (b)  $\text{PrBa}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_{7\pm\delta}$ .

a substituent, preferring the chain site in Y123 to a sheet site was observed by Slater *et al* (1991). In the case of substitution of iron in  $\text{LaBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7-\delta}$ , about 40% of the  $\text{Fe}^{3+}$  ions were found to occupy Cu(2) sites in  $\text{LaBa}_2\text{Cu}_2\text{FeO}_{7\pm\delta}$  against  $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+\delta}$ , where the percentage of Fe at Cu(2) sites is negligible. Also the presence of rare earth plane oxygen in iron-doped  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  was verified by neutron diffraction methods. Activation energy of oxygen desorption also decreased substantially from 28 kcal/mol in Y123 to about 19 kcal/mol in  $\text{LaBa}_2\text{Cu}_2\text{CoO}_{7+y}$ . Recently, the substitution of nickel in  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is shown to alter the oxygen lability in this system (Sundar Manoharan *et al* 1994). The decrease in the oxygen desorption energies of cation-substituted Y123 systems suggests that the catalytic activity of these oxides could be controlled by means of elemental substitutions.

#### 4. Non-catalytic and catalytic reactions over Y123 type systems

The first catalytic reactions with Y123 catalyst was carried out by Hansen *et al* (1988) for the ammoxidation of toluene to benzonitrile. Since then many catalytic reactions have been carried out over Y123-based systems. Table 1 gives the list of such catalytic reactions with Y123 as catalyst. Hansen *et al* (1988) showed that  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  as a catalyst was superior to conventional ammoxidation catalysts such as  $\text{V}_2\text{O}_5$ . They

Table 1. Catalytic reactions with Y123 and cation-substituted Y123 oxides.

Reaction	Catalyst	Reference(s)
$C_6H_5 - CH_3 \rightarrow C_6H_5 - CN$	Y123	Hansen <i>et al</i> (1988, 1990)
$CH_4 \rightarrow CO_2 + H_2O$	Y123 Y123/F <sub>2</sub> doped	Salvador (1989) Lee <i>et al</i> (1989)
$CO \rightarrow CO_2$	Y123	Halasz <i>et al</i> (1990) Pickering and Thomas (1991) Jiang <i>et al</i> (1989) Otamiri and Andersson (1991) Lee and Ng (1989)
$NO + CO \rightarrow 1/2N_2 + CO_2$	Y123	Mizuno <i>et al</i> (1988) Halasz <i>et al</i> (1991)
$CH_3OH \rightarrow H-CHO$	Y123	Halasz (1989)
$CH_3OH \rightarrow CO_2 + H_2O$	Y123	Hegde <i>et al</i> (1992)
$NH_3 \rightarrow NO$	Y123 Pr123 YBa <sub>2</sub> Cu <sub>2</sub> CoO <sub>7</sub>	Ramesh and Hegde (1992)
$C_6H_5 - CH_3 \rightarrow C_6H_5 - CHO$	Y123	Andersson (1992)
NO decomposition	Y123	Tabata <i>et al</i> (1988) Shimada <i>et al</i> (1988)
NO decomposition	Y123	Arakawa and Adachi (1989)
Reaction with H <sub>2</sub> O	Y123	Yan <i>et al</i> (1987) Barns and Laudise (1987)
N <sub>2</sub> , Ar intercalation	Y123	Gabelica <i>et al</i> (1987)
H <sub>2</sub> intercalation	Y123	Yang <i>et al</i> (1987)
Ammoxidation	Y123 Zn/Ni doped	Otamiri and Andersson (1991)
$H_2O_2 \rightarrow H_2 + O_2$	Y123	Rophael <i>et al</i> (1991)
$CH_3CH_2OH \rightarrow CH_3-CHO$	Y123	Sun and Lee (1993)
CH <sub>3</sub> OH oxidation	Y123/Ag composites	Klisurski <i>et al</i> (1990)
Reaction with small molecules		Qiu <i>et al</i> (1988)

found a shift in product selectivity as a function of the oxygen deficiency. For lower oxygen contents, the oxide was selective to the formation of benzonitrile and at higher oxygen content the selectivity was towards carbon dioxide. Mizuno *et al* (1988) reported the rapid absorption of NO and CO in a catalytic reaction at 573 K and found that YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  catalysed the oxidation of CO by nitric oxide. The reactivity of the basal plane oxygen was also utilized in many stoichiometric oxidations. Salvador (1989) reported the stoichiometric combustion of methane over YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  to carbon dioxide. The stoichiometric combustion of methane, utilizing lattice oxygen was followed by an orthorhombic to tetragonal structural transition.

Oxidation of toluene was also carried out over the 123 based systems. Andersson (1992) studied the catalytic oxidation of toluene to benzaldehyde over the oxygenated,

and oxygen deficient forms of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ . By the XPS analysis of the catalysts before and after several redox cycles, Andersson (1992) modelled the Y–Ba–Cu–O system as a highly dispersed copper oxide over a support, with variable oxygen content. He interpreted the selectivity of the catalyst to the presence of nucleophilic oxygen species, and cations acting as milder oxidants. Halasz *et al* (1991) have investigated a variety of perovskite-related layered cuprates for the decomposition of nitric oxide and found that  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is a better catalyst than CuO.

The non-catalytic and catalytic oxidation of carbon monoxide over Y123 systems have revealed many interesting aspects of the reactivity and catalytic activity of the system. Pickering and Thomas (1991) investigated the oxidation of CO over  $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$  by employing *in situ* X-ray diffraction combined with structural characterization of the resulting phases by the Rietveld refinement method. They observed a shallow minimum in the catalytic activity as a function of increasing  $\delta$  and interpreted it in terms of two competing reaction pathways; one dominating at lower values of  $\delta$  and the other at higher  $\delta$  values. For higher values of  $\delta$ , CO oxidation proceeded with the consumption of lattice oxygens at the O(1) site, and for lower values of  $\delta$  the active species was identified as the dissociated gaseous oxygen adsorbed at the two-fold coordinated Cu(1) sites. The exchangeability of the O(1) lattice oxygen in a cyclic process like the Mars–van Krevelen pathway can be suggested to be adopted by the system. The stoichiometric reaction of CO with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  was studied in detail by Lin *et al* (1993) employing TGA, DTA, FTIR and XPS. They estimated the heat of formation of  $\text{CO}_2$  as 60 kcal/mol and the activation energy for CO oxidation was estimated as 16 kcal/mol. Lin *et al* (1993) in line with

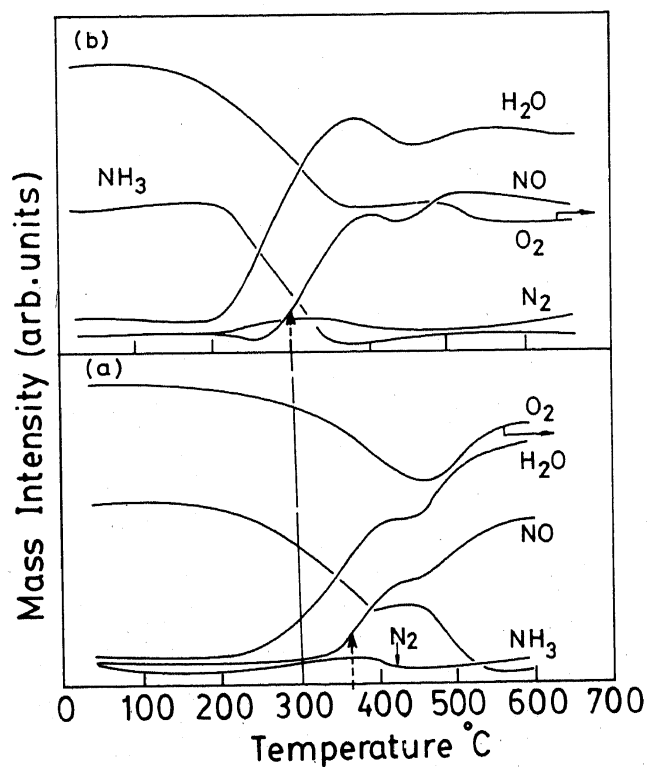
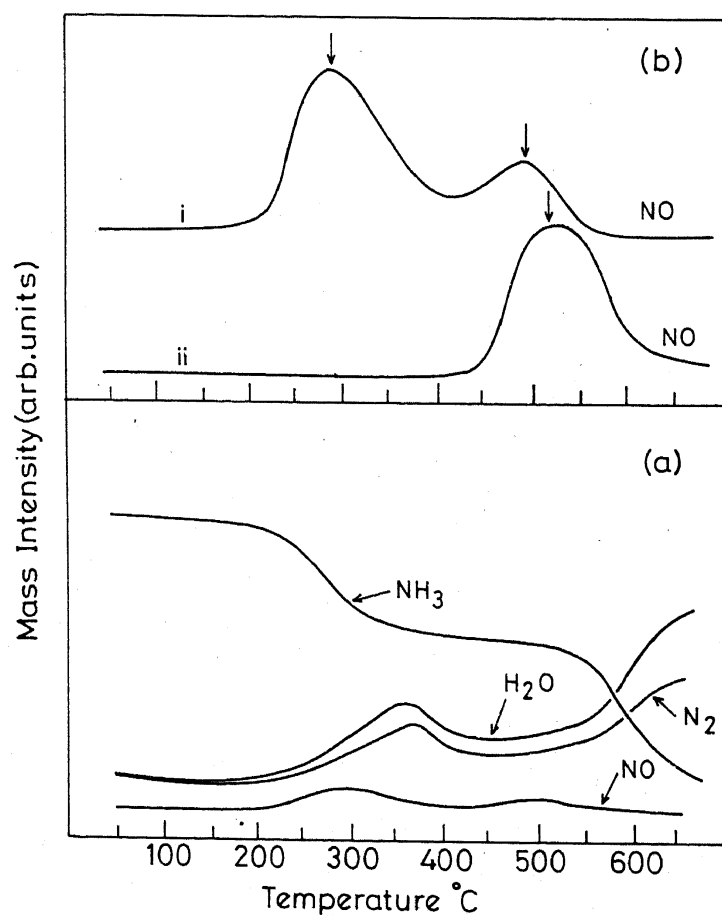


Figure 4. Temperature programmed reaction (TPR) profiles of the catalytic oxidation of ammonia over (a)  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and (b)  $\text{YBa}_2\text{Cu}_2\text{CoO}_{7\pm\delta}$ .

the mechanism of oxidation of CO over  $\text{MnO}_2$ , CuO and NiO (Stone 1962) proposed an intermediate carbonate-formation mechanism, where the adsorbed state of CO on an oxide is a surface carbonate, which decomposes in a subsequent step to give carbon dioxide. They substantiated this mechanism by the formation of barium carbonate, as confirmed by FTIR investigation.

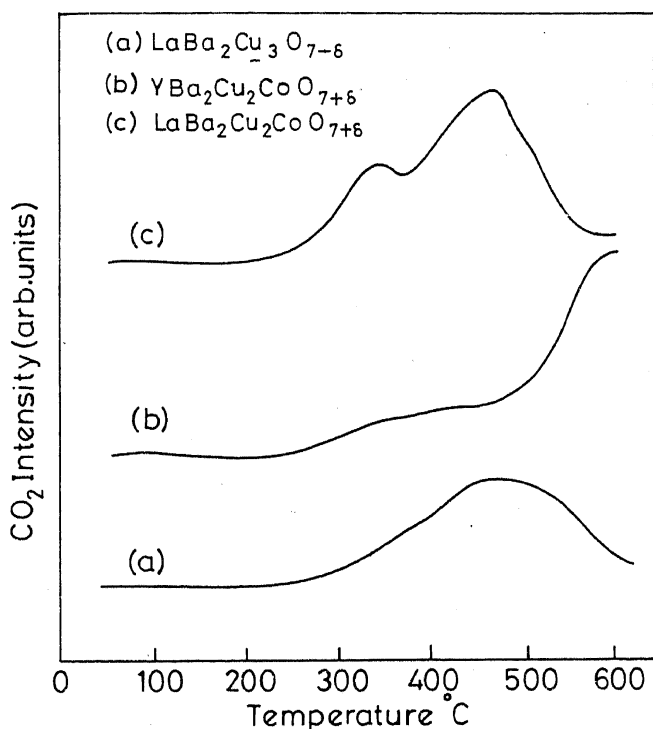
### 5. Catalytic oxidation of small molecules like CO and $\text{NH}_3$

Noble metals are employed to catalyse  $\text{NH}_3$  specifically to nitric oxide. The lower oxygen desorption energy of Y123 and its reactivity with ammonia in a stoichiometric reaction prompted us to test the catalytic activity of Y123 and related substituted systems towards selective catalytic oxidation of ammonia (Ramesh and Hegde 1992). Figures 4a and b give the temperature-programmed reaction profiles of the catalytic oxidation of ammonia over  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{YBa}_2\text{Cu}_2\text{CoO}_{7+\delta}$  (YCo123) systems respectively. The selectivity could be inferred to be near-total over both the oxides and the onset temperature for NO formation to be lower for YCo123. Structural studies revealed that the oxygens at the O(1) sites were utilised and the enhanced



**Figure 5.** (a) Temperature programmed reaction profiles of the stoichiometric oxidation of ammonia over  $\text{PrBa}_2\text{Cu}_2\text{CoO}_{7\pm\delta}$ . (b) Comparison of the NO profile of (i)  $\text{PrBa}_2\text{Cu}_2\text{CoO}_{7\pm\delta}$  with the NO formation over (ii)  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .





**Figure 6.** Temperature programmed reaction profiles of  $\text{CO}_2$  formation in the non-catalytic oxidation of carbon monoxide over (a)  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , (b)  $\text{YBa}_2\text{Cu}_2\text{CoO}_{7+\delta}$  and (c)  $\text{LaBa}_2\text{Cu}_2\text{CoO}_{7+\delta}$ .

reactivity of the cobalt-doped samples was attributed to the presence of holes in the form of  $\text{Co}^{4+} \text{O}^{2-} \rightleftharpoons \text{Co}^{3+} \text{O}^{-1}$ . The cobalt-substituted  $\text{PrBa}_2\text{Cu}_2\text{CoO}_{7+\delta}$  (PrCo123) was also tested for its reactivity towards the stoichiometric oxidation of ammonia. Figure 5a gives the TPR profiles of the anaerobic oxidation of  $\text{NH}_3$  over PrCo123. Two NO peaks are observed in the NO profile indicating the presence of two types of labile oxygen in the system. In the orthorhombic  $\text{PrBa}_2\text{Cu}_2\text{CoO}_{7+\delta}$  these two labile oxygens were suggested to be occupying the O(1) and O(6) positions. Since significant cobalt ions in  $\text{PrBa}_2\text{Cu}_2\text{CoO}_{7+\delta}$  were believed to occupy the Cu(2) position, the NO peak at lower temperature was assigned to the abstraction of oxygens at O(6) and the other NO peak to the O(1) associated with chain Cu(1). Figure 5b gives the comparison of the NO profile over PrCo123 with  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Carbon monoxide oxidation was also carried out over  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (La123), YCo123 and  $\text{LaBa}_2\text{Cu}_2\text{CoO}_{7+\delta}$  (LaCo123). Figure 6 gives the TPR profiles of the anaerobic oxidation of CO over the above three oxide systems. The LaCo123 system which is structurally similar to PrCo123 also supports two kinds of labile oxygens and the onset temperature for  $\text{CO}_2$  formation was found to be the lowest among the three oxides and further structural and spectroscopic investigations are underway.

## 6. Conclusions

The layered triple perovskite oxides of the Y123 type have been critically reviewed as potential model systems in the understanding of oxide catalysts. Elemental

substitution in these oxide systems is presented as a chemical means to modify the reactivity and catalytic activity. The chemical behaviour of the oxides has been interpreted in terms of factors like non-stoichiometry, metal-ion environment, and oxygen diffusion exemplified by the results on the stoichiometric and catalytic oxidation of small molecules like ammonia and carbon monoxide.

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