Reactivity and catalytic activity of layered YBa$_2$Cu$_3$O$_{7-\delta}$ (123) type defect perovskites

M S HEGDE* and S RAMESH
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

Abstract. The chemical modifications of structure, reactivity and catalytic properties of layered triple perovskite oxides, related to the YBa$_2$Cu$_3$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; NH$_3$ oxidation; CO oxidation.

1. Introduction

Mixed metal oxides like perovskites (ABO$_3$), sheelites (ABO$_4$), pyrochlores (A$_2$B$_2$O$_7$), spinels (AB$_2$O$_4$) and layered perovskites of K$_2$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 K$_2$NiF$_4$ structure with alternative layers of A-O rocksalt and 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 YBa$_2$Cu$_3$O$_{7}$ (Y123) system brought about a renewed interest in perovskite-related oxides. Since then various cationic substitutions have been made in YBa$_2$Cu$_3$O$_{7}$ system to understand

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*For correspondence

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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 NH₃ and CO over Y123 and cation-substituted 123 systems.

2. Non-stoichiometry and oxygen diffusion

The structural and physical properties of the YBa₂Cu₃O₇₋δ system are highly influenced by non-stoichiometry (Jorgenson et al 1990). For values of δ<0.5, the compound is orthorhombic and superconducting, and for δ>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 YBa₂Cu₃O₇₋δ system.
Catalytic activity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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 ambient, 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 YBa$_{2-x}$La$_x$Cu$_3$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 YBa$_2$Cu$_3$O$_{7-\delta}$, PrBa$_2$Cu$_3$O$_{7-\delta}$ (Pr123) and YBa$_2$Cu$_2$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–Vignier 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 YBa$_2$Cu$_3$O$_7$ and PrBa$_2$Cu$_3$O$_{7-\delta}$ were investigated. The substitution of cobalt in Y123 and Pr123 brought down the activation energies 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 YBa$_2$Cu$_3-x$Co$_x$O$_{7+\delta}$ and PrBa$_2$Cu$_{3-x}$Co$_x$O$_{7+\delta}$ respectively. The above study led to the formation of a new orthorhombic non-superconducting phase, PrBa$_2$Cu$_2$CoO$_{7+\delta}$ (PrCo123) where significant amount of 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 YBa$_2$Cu$_3$O$_{7-\delta}$ (A), PrBa$_2$Cu$_3$O$_{7-\delta}$ (B) and YBa$_2$Cu$_2$CoO$_{7+\delta}$ (C).](image-url)
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 LaBa$_2$Cu$_{3-x}$Fe$_x$O$_{7-\delta}$, about 40% of the Fe$^{3+}$ ions were found to occupy Cu(2) sites in LaBa$_2$Cu$_{2}$FeO$_{7+\delta}$ against YBa$_2$Cu$_{3-x}$Fe$_x$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 LaBa$_2$Cu$_{3}$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 LaBa$_2$Cu$_{2}$CoO$_{7+\gamma}$. Recently, the substitution of nickel in LaBa$_2$Cu$_{3}$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 YBa$_2$Cu$_3$O$_{7-\delta}$ as a catalyst was superior to conventional ammoxidation catalysts such as V$_2$O$_5$. They
Table 1. Catalytic reactions with Y123 and cation-substituted Y123 oxides.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
<th>Reference(s)</th>
</tr>
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<tbody>
<tr>
<td>C₆H₅ − CH₃ → C₆H₅ − CN</td>
<td>Y123</td>
<td>Hansen et al (1988, 1990)</td>
</tr>
<tr>
<td>CH₄ → CO₂ + H₂O</td>
<td>Y123</td>
<td>Salvador (1989)</td>
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<tr>
<td></td>
<td>Y123/F₂ doped</td>
<td>Lee et al (1989)</td>
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<tr>
<td>CO → CO₂</td>
<td>Y123</td>
<td>Halasz et al (1990)</td>
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<td></td>
<td></td>
<td>Pickering and Thomas (1991)</td>
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<td></td>
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<td>Otamiri and Andersson (1991)</td>
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<td></td>
<td></td>
<td>Lee and Ng (1989)</td>
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<tr>
<td>NO + CO → 1/2N₂ + CO₂</td>
<td>Y123</td>
<td>Mizuno et al (1988)</td>
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<td></td>
<td></td>
<td>Halasz et al (1991)</td>
</tr>
<tr>
<td>CH₃OH → H − CHO</td>
<td>Y123</td>
<td>Halasz (1989)</td>
</tr>
<tr>
<td>CH₃OH → CO₂ + H₂O</td>
<td>Y123</td>
<td>Hegde et al (1992)</td>
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<tr>
<td>NH₃ → NO</td>
<td>Y123</td>
<td>Ramesh and Hegde (1992)</td>
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<tr>
<td></td>
<td>Pr123</td>
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<td></td>
<td>YBa₂Cu₂CoO₇</td>
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<tr>
<td>C₆H₅ − CH₃ →</td>
<td>Y123</td>
<td>Andersson (1992)</td>
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<tr>
<td>C₆H₅ − CHO</td>
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<tr>
<td>NO decomposition</td>
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<td>Tabata et al (1988)</td>
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<td>Y123</td>
<td>Arakawa and Adachi (1989)</td>
</tr>
<tr>
<td>Reaction with H₂O</td>
<td>Y123</td>
<td>Yan et al (1987)</td>
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<td></td>
<td></td>
<td>Barns and Laudise (1987)</td>
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<tr>
<td>N₂, Ar intercalation</td>
<td>Y123</td>
<td>Gabelica et al (1987)</td>
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<td>H₂ intercalation</td>
<td>Y123</td>
<td>Yang et al (1987)</td>
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<td>Ammonoxidation</td>
<td>Y123</td>
<td>Otamiri and Andersson (1991)</td>
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<td></td>
<td>Zn/Ni doped</td>
<td></td>
</tr>
<tr>
<td>H₂O₂ → H₂ + O₂</td>
<td>Y123</td>
<td>Rophael et al (1991)</td>
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<td>CH₃CHO → CH₃−CHO</td>
<td>Y123</td>
<td>Sun and Lee (1993)</td>
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<td>CH₃OH oxidation</td>
<td>Y123/Ag composites</td>
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<td>Reaction with small molecules</td>
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<td>Qiu et al (1988)</td>
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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 YBa₂Cu₃O₇−δ 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 YBa₂Cu₃O₇−δ 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 YBa$_2$Cu$_3$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 YBa$_2$Cu$_3$O$_{7-δ}$ 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 YBa$_2$Cu$_3$O$_{6+δ}$ 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 δ and interpreted it in terms of two competing reaction pathways; one dominating at lower values of δ and the other at higher δ values. For higher values of δ, CO oxidation proceeded with the consumption of lattice oxygens at the O(1) site, and for lower values of δ 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 YBa$_2$Cu$_3$O$_{7-δ}$ was studied in detail by Lin et al (1993) employing TGA, DTA, FTIR and XPS. They estimated the heat of formation of 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 cover (a) YBa$_2$Cu$_3$O$_{7-δ}$ and (b) YBa$_2$Cu$_2$CoO$_{7-δ}$.](image-url)
the mechanism of oxidation of CO over MnO₂, 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 NH₃

Noble metals are employed to catalyse NH₃ 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 YBa₂Cu₃O⁷₋ₓ and YBa₂Cu₂CoO₇₋ₓ (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](image-url)

**Figure 5.** (a) Temperature programmed reaction profiles of the stoichiometric oxidation of ammonia over PrBa₂Cu₃CoO₇₋ₓ. (b) Comparison of the NO profile of (i) PrBa₂Cu₂CoO₇₋ₓ with the NO formation over (ii) PrBa₂Cu₃O₇₋ₓ.
Catalytic activity of $YBa_2Cu_3O_{7-\delta}$

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

Reactivity of the cobalt-doped samples was attributed to the presence of holes in the form of Co$^{4+}$O$^-$ $\rightleftharpoons$ Co$^{3+}$O$^{-1}$. The cobalt-substituted PrBa$_2$Cu$_2$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 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 PrBa$_2$Cu$_2$CoO$_{7+\delta}$, these two labile oxygens were suggested to be occupying the O(1) and O(6) positions. Since significant cobalt ions in PrBa$_2$Cu$_2$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 PrBa$_2$Cu$_3$O$_{7-\delta}$. Carbon monoxide oxidation was also carried out over LaBa$_2$Cu$_3$O$_{7-\delta}$ (La123), YCo123 and LaBa$_2$Cu$_2$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 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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