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# Decomposition of nitric oxide and its reduction by CO over superconducting and related cuprate catalysts

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Catalytic activities of five non-conducting and three superconducting cuprates were measured for the decomposition of NO and the reduction of NO by CO. The concentration of the reactants and the space velocities approximate the conditions of automotive catalysts. In contrast to earlier results, obtained at 20 to 30 times higher partial pressures of NO and 20 to 100 times lower space velocities, none of the catalysts, including five perovskite-like cuprates, showed significant activity for the decomposition of NO at reaction temperatures up to 700°C. All catalysts were fairly active for the reduction of NO. At temperatures above about 400°C on the perovskite-like cuprates $YBa_2Cu_3O_{7-x}$ and $Ba_2CuO_{3.5-x}$, the rates for NO reduction were higher than on CuO. All catalysts lost activity for NO reduction in the presence of oxygen (oxidizing conditions).

**Keywords:** NO reduction; NO decomposition; reduction of NO by CO; cuprate catalysts; superconducting catalysts

## 1. Introduction

$NO_x$ removal is an important process in catalytic automotive exhaust pollution control [1,2]. Decomposition of NO to $N_2$ and $O_2$ and the reduction of NO to $N_2$ and $CO_2$ have been considered for this purpose [1–4]. Studies of decomposition over noncuprates indicated that the decomposition rates are extremely slow [5]. Derivatives of $La_2CuO_{4-x}$ and $YBa_2Cu_3O_{7-x}$, which have perovskite-like crystal lattices and are the parent structures of two families of high temperature superconductors, have been reported to be active catalysts for both reactions of NO [6–12]. The expression "perovskite-like" is used here for

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compounds containing unit cells which can be viewed as being constructed of subcells, many of which have the perovskite structure. Many cuprates, the superconductors in particular, can be derived by stacking different amounts and sequences of rock salt and perovskite-like layers of metals and oxygen [13–15]. Some decomposition of NO was also observed on the non perovskite, non-conducting cuprates, $Y_2Cu_2O_5$ and $BaCuO_2$ [6]. The reaction conditions applied in these studies (the concentration of NO was 1 to 3% in $N_2$ or He and the space velocity ($SV$) was 500 to 1000 $h^{-1}$) were very different from those prevailing in automotive catalytic converters (NO $\cong$ 0.01–0.2%; $SV \cong$ 20,000–100,000 $h^{-1}$) [1–4] and therefore are not suitable for evaluating the efficacy of cuprates as automotive catalysts.

We report here the catalytic activity for decomposition of NO and reduction of NO by CO of a series of cuprates using more realistic reaction conditions (NO $\cong$ 0.1%; $SV \cong$ 60,000 $h^{-1}$) for comparison with automotive catalysts. Among the catalysts investigated $YBa_2Cu_3O_{7-x}$, $Bi_2CaSr_2Cu_2O_{10-x}$, $Tl_2CaBa_2Cu_2O_{9-x}$, $Ba_2CuO_{3.5-x}$, and $Ba_2Cu_3O_5$ have perovskite-like crystal structures [13, 16,17]. The first three cuprates are superconductors with critical transition temperatures ($T_c$) of 90, 86, and 112 K, respectively, [18] and represent three of the four main families of high temperature superconductors. The catalytic activities of CuO and of the non-conducting, non-perovskite cuprates, $Y_2Cu_2O_5$, $BaCuO_2$, and $Y_2BaCuO_5$, are also reported.

## 2. Experimental

Cuprates were prepared from well ground solid oxides, nitrates or carbonates, followed by calcination in a porcelain crucible in air. Specific surface areas and bulk densities ranged from 0.1 to 1 $m^2/g$ and from 1.2 to 3.4 $cm^3/g$, respectively. Details of preparation procedures as well as the physical properties of the catalysts have been reported previously [18,19]. The compositions of the samples were investigated using a Rigaku CN4148H2 diffractometer equipped with a 12 kW rotating anode. The X-ray powder patterns were analyzed using the JCPDF computerized data base and published data [16,17,20–23].

Catalytic experiments were done with equal contact times for the catalysts using 0.42 $cm^3$ of samples. The samples were contained in a fused quartz reactor (10 mm i.d.) of the flow through type. The sample was supported on a porous quartz frit and covered with quartz wool. Catalysts were preheated in a flow of He (27 L/h) at the starting reaction temperature (300 or 500°C) for 1 h. For catalytic measurements, a flow of 27 mL/h NO, or a flow of 27 mL/h NO and 430 mL/h CO, were mixed with He to achieve a total pressure of 1 atm ($1 \times 10^5$ Pa). For checking the effect of oxygen, 450 mL/h of $O_2$ was also added to the gas stream. Each gas flow was controlled by a Brooks mass flow controller. The reactor system is constructed of stainless steel with bellows seal valves. Products were continuously analyzed using a Thermo Electron Model 10A chemiluminescent NO-$NO_x$ gas analyzer.

## 3. Results and discussion

### DECOMPOSITION OF NITRIC OXIDE

The catalytic activity for decomposition of NO was investigated in the temperature range from 300 to 700°C. Under the reaction conditions applied, none of the nine catalysts showed significant activity. An automobile exhaust has additional components which may affect the results. Earlier reports suggested that the presence of oxygen vacancies [12] and reduced copper ions for assuring a $Cu^+ \rightleftharpoons Cu^{2+}$ [5,6] or $Cu^{2+} \rightleftharpoons Cu^{3+}$ [11] redox cycle is important to get high (up to 73%) NO conversion on cuprates. To assure the presence of reduced copper ions, the catalysts were also tested after pretreatment in a flow of 1.6% CO/He (27 L/h) at 500°C for 5 to 30 minutes. Although at least a partial surface reduction occurred at this temperature [18,24,25], no change in catalytic activity for decomposition of NO was observed. These results indicate that the activity of cuprates observed previously [6–12] was mainly due to the 20 to 30 times higher partial pressure of NO and 20 to 100 times lower space velocities than used here.

A typical experiment is shown in fig. 1. $Y_2BaCuO_5$ was the most active catalyst studied. The sample was pretreated in a flow of He at 300°C. Soon after adding 1000 ppm NO to the carrier gas and passing this mixture through the catalyst bed at 300°C, the NO content decreased significantly. However, the original NO concentration recovered within about 1 h. NO concentrations exceeding 1000 ppm indicate desorption of NO when the temperature was raised to 500 and 600°C. Since these peaks overlapped the adsorption peaks of NO, analysis of the amount of adsorbed NO could not be done at these temperatures. Similar behavior was observed for $Bi_2CaSr_2Cu_2O_{10-x}$, $Y_2BaCuO_5$, $Ba_2Cu_3O_5$, $YBa_2Cu_3O_{7-x}$, and $Ba_2CuO_{3.5-x}$ for which the uptake of NO (below 500°C) was about 0.1, 0.2, 0.5, 1.1 and 1.3 mol NO/mol catalyst, respectively. Other catalysts were investigated only above 500°C and neither significant adsorption nor desorption of NO was observed. Data for NO uptake in Y-Ba-Cu-O compounds agree well with earlier reports [8,26,27]. It is interesting to note that $BaCuO_2$ has been reported to adsorb a similar amount of NO as $YBa_2Cu_3O_{7-x}$ [27]. It appears that the capacity of cuprates to adsorb NO increases if Ba is present.

### REDUCTION OF NITRIC OXIDE BY CO

Activity measurements for the reduction of NO were made subsequent to the decomposition measurements. The catalysts were cooled to 300°C in a flow of

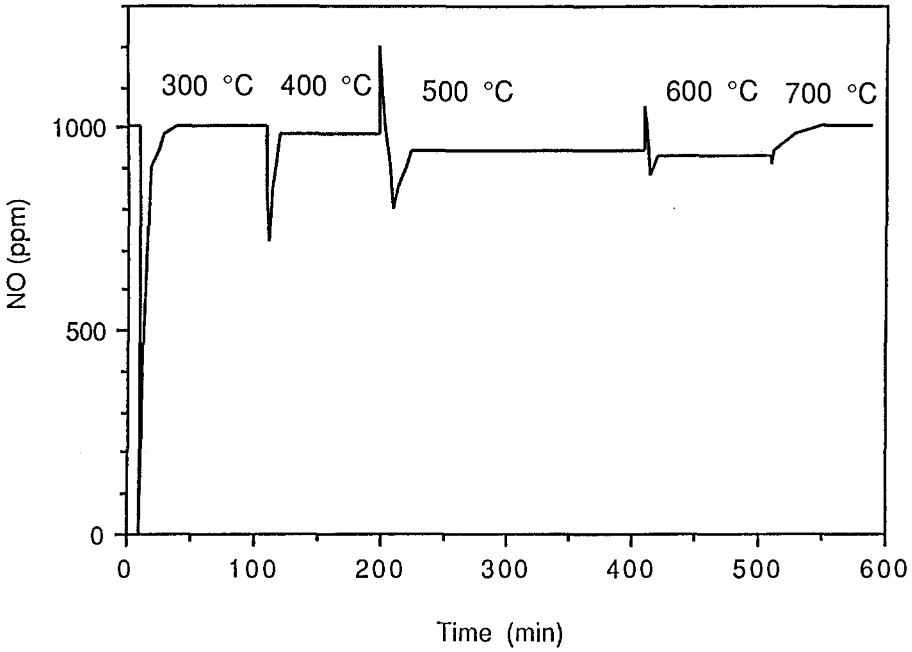

Fig. 1. Variations in concentration of nitric oxide at the outlet of the reactor by increasing the reaction temperature stepwise; catalyst: $Y_2BaCuO_5$; composition of reactant mixture: 0.1% NO and 1.6% CO in He; total pressure $= 1 \times 10^5$ Pa; $SV = 64{,}000\ h^{-1}$.

He/NO and then CO was added to the gas mixture. When measurable conversion of nitric oxide was observed for at least about two hours, the temperature was decreased in steps of 50°C until zero conversion was observed. Thereafter, the temperature was gradually raised until 100% conversion of NO was achieved. Conversions were monitored for at least one hour after each step, to assure steady state conditions. In general, the conversion remained unchanged after about five minutes at a new temperature.

Except for $Bi_2CaSr_2Cu_2O_{10-x}$ and $Tl_2CaBa_2Cu_2O_{9-x}$, the catalysts started to be active between 100 and 250°C and 100% NO conversion was achieved below 500°C (fig. 2). It should be noted that due to the rates in figure 2 being expressed on a per surface area basis, that 100% conversion gives different values of the limiting rates. Only $Tl_2CaBa_2Cu_2O_{9-x}$ failed to achieve 100% conversion, giving a maximum conversion of 40% at 400°C and a conversion of 10% at 550°C. Lowering the temperature resulted in a total disappearance of activity of this catalyst. This is probably due to decomposition. A hard, yellowish-green ball which also contained the quartz wool was found after reaction. The activity versus temperature curves of all the other catalysts remained practically unchanged during heating and cooling cycles.

CuO is one of the most active base metal oxides for the reduction of nitric oxide [4,28,30]. The activity curve of the non-perovskite cuprate, $Y_2Cu_2O_5$,

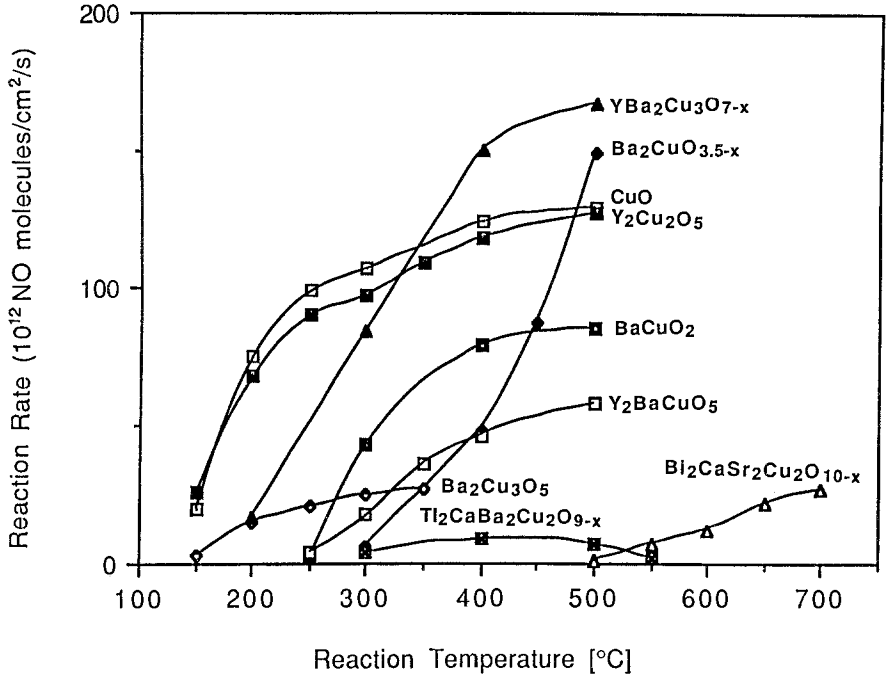

Fig. 2. Comparison of activity for reduction of NO by CO of CuO and cuprate catalysts; reaction conditions are the same as in fig. 1.

resembles that of CuO (fig. 2). The reaction rates on $YBa_2Cu_3O_{7-x}$, which is a perovskite-like metallic conductor, and on $Ba_2CuO_{3.5-x}$, which is a perovskite-like insulator, exceeded the reaction rates on CuO at high reaction temperatures. This result suggests that the electrical conductivity is unimportant in catalytic activity for reduction of NO.

The NO + CO reaction was investigated on Cu-ZSM5 catalysts by Iwamoto et al. [31]. Assuming an area of 500 m²/g for the zeolite, its activity was $1.7 \times 10^{17}$ molecules/m²/s at 400°C. This is 9-fold less than reported here for $YBa_2Cu_3O_7$. However, Cu-ZSM5 is active for the decomposition of NO [32].

The activities at 500°C indicate that the capacity of cuprates to adsorb NO may be important. For example, the uptake of NO on the most active catalyst, $YBa_2Cu_3O_{7-x}$, is 1.1 mol NO/mol catalyst while on the least active catalyst, $Bi_2CaSr_2Cu_2O_{10-x}$, it is 0.1 mol NO/mol catalyst. Since the rate of the NO + CO reaction is much higher than the rate of NO decomposition, NO decomposition can not be an important step in the former reaction.

All catalysts lost activity for NO reduction when similar amounts of $O_2$ and CO were present (oxidizing condition exist when the concentration of $O_2$ exceeds half the concentration of CO). The high selectivity for oxidation of CO by $O_2$ rather than the oxidation of CO by NO is typical [4,29]. In contrast to the activity sequence in fig. 2, the activities for the oxidation of carbon monoxide

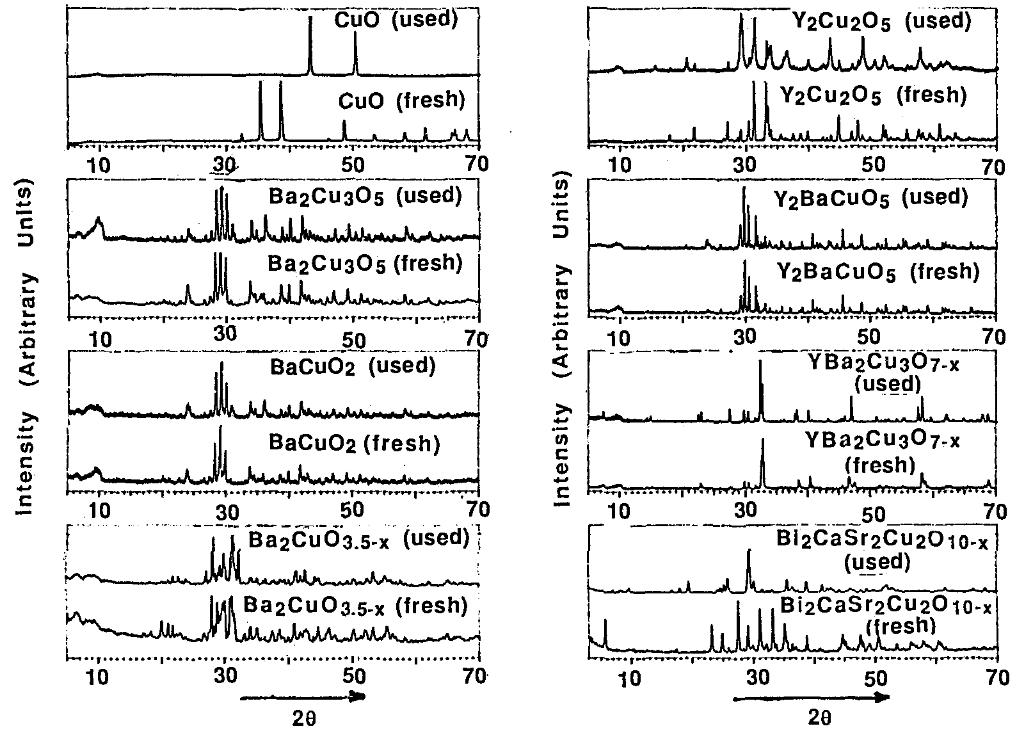

Fig. 3. X-ray powder diffraction patterns of the fresh and used catalysts.

over CuO, $YBa_2Cu_3O_{7-x}$, and $Ba_2CuO_{3.5-x}$, were found [19,24,25] to be lower than those of $Y_2BaCuO_5$, $Ba_2Cu_3O_5$, and $BaCuO_2$. It appears, therefore, that the oxidation of CO is also not rate determining in the NO + CO reaction.

Fig. 3 compares the X-ray powder diffraction patterns of the fresh catalysts and of the samples removed from the reactor after reaction. CuO was reduced to pure metallic copper and roughly 65% of $Y_2Cu_2O_5$ decomposed to $Y_2O_3$ and metallic copper. Probably this is the reason for the similar temperature dependences for the reduction of NO. The structure of $Bi_2CaSr_2Cu_2O_{10-x}$ was also altered during the reaction condition, but the products have not been identified. Fig. 3 also indicates that, apart from characteristic small distortions caused by loss of some oxygen [16,33–36], the basic crystal framework of the other cuprates remained unchanged. The good stability against reduction compared to CuO is in agreement with a temperature programmed reduction study of the cuprates [18].

## 4. Conclusions

1. None of the catalysts investigated has significant activity for the decomposition of NO under reaction conditions approximated by automotive catalytic converters.

2. The amount of NO adsorbed on cuprates increases if barium is present.

3. At temperatures above about 400°C, $YBa_2Cu_3O_{7-x}$ and $Ba_2CuO_{3.5-x}$ are more active for the reduction of NO by CO than is CuO, but all catalysts lost activity in the presence of excess oxygen. Probably neither the oxidation of CO nor the decomposition of NO is rate determining, but the capacity to adsorb NO may be important.

4. During reaction, $Ba_2Cu_3O_5$, $BaCuO_2$, $Ba_2CuO_{3.5-x}$, $Y_2BaCuO_5$, and $YBa_2Cu_3O_{7-x}$ kept their original bulk structures. However, CuO was reduced to metallic Cu and the structures of $Y_2Cu_2O_5$, $Tl_2CaBa_2Cu_2O_{9-x}$, and $Bi_2CaSr_2Cu_2O_{10-x}$ were significantly changed.

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