

Comparison of Oxidation of Carbon Monoxide on Superconducting and Insulating Y–Ba–Cu–O Catalysts

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Investigation of the catalytic activity of Y_2BaCuO_5 has shown high and stable activity for CO oxidation when the catalyst is slightly reduced, comparable with the activity of the best catalysts for CO oxidation. This oxide was found to be about two orders of magnitude more active than the superconducting perovskite $YBa_2Cu_3O_{7-x}$. Furthermore, in contrast to the perovskite catalyst, surface reduction increased the activity of Y_2BaCuO_5 . Zero-order kinetics were observed for O_2 on both the oxidized and reduced forms of the catalyst, but the reaction order for CO was in the range of 1.1 to 1.5. Differences between the oxidized and reduced forms of the catalyst and between the two types of Y–Ba–Cu–O catalysts are discussed. © 1990 Academic Press, Inc.

INTRODUCTION

The discovery of high temperature (T_c) superconductors has created enormous interest in the properties of alkali and rare earth cuprates. At this time there are few catalytic data on this large group of metal oxides (composed of two to five different metals). The first catalytic studies of high T_c compounds were recently published. $YBa_2Cu_3O_{7-x}$, which for $x < 0.5$ has metallic conductivity at room temperature and becomes superconducting near 90 K, was reported as an active catalyst for ammoxidation and the total oxidation of toluene (1), for NO decomposition (2–4), and for NO reduction by CO (5). The high activity of this oxide for the decomposition of NO is the subject of several recent patents (6). This oxide was also reported to be an excellent catalyst for the selective oxidation and dehydrogenation of methanol (7) and for the

oxidation of CO (8). A fluorinated modification was found to be active and selective for the partial oxidation of methane (9).

In the majority of cases, the superconducting phase partially decomposes during reaction (7, 9, 10). Therefore, it is likely that the resulting stable phases, such as Y_2BaCuO_5 and $BaCuO_2$, may influence the catalytic activity. However, little is known about the catalytic behavior of these other cuprates. $BaCuO_2$ and $Ba_2Cu_3O_5$ were reported to be active for the selective oxidation of methanol (11), and $BaCuO_2$ and $Y_2Cu_2O_5$ were mentioned (4) as practically inactive for NO decomposition.

We report the first study of the catalytic activity of Y_2BaCuO_5 , which contains the same elements as the superconducting oxide $YBa_2Cu_3O_{7-x}$. It is a green, orthorhombic, nonconducting compound which is often found as a contaminant of high T_c superconductors which contain yttrium (12).

EXPERIMENTAL

Y_2BaCuO_5 was prepared from reagent grade Y_2O_3 , CuO, and $Ba(NO_3)_2$. Stoichio-

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metric amounts of the oxides were fired in air at 940°C in a porcelain crucible for 10 h. The X-ray powder pattern, measured on a Rigaku Model CN4148H2 diffractometer (with 12 kW rotating anode and computerized data system including JCPDS data base), agreed with the literature spectrum of Y_2BaCuO_5 (12–14). The BET surface area was measured by N_2 adsorption at 77 K using a Sundstrand Model 314D electronic pressure transducer to measure the uptake of gas in a fixed volume.

For carrying out the reactions, a 0.6985g (0.44 ml) sample of the cuprate was placed in a borosilicate reactor. The reactor is of the flow-through type with a 10-mm i.d. sample chamber and the catalyst was supported on a frit of porous glass. The catalyst was pretreated in a flow of He at 500°C for 3 h and then cooled to the reaction temperature. Appropriate amounts of pure reactant gases (O_2 and CO) and sufficient He carrier gas to achieve a total pressure of 1 atm (1×10^5 Pa) were admitted to a gas manifold and the mixture was passed through the reactor. Each gas flow was controlled by a Brooks Model 5850 mass flow controller. The reaction system is constructed of brass with bellows seal valves (overall leak of total system $<6 \times 10^{-7}$ atm · ml/s), has a base pressure of 1×10^{-7} Torr, and is free of grease, mercury, and elastomers. Products were analyzed by gas chromatography on 3 ft \times $\frac{1}{8}$ in. silica gel and 4.5 ft \times $\frac{1}{8}$ in. molecular sieve 5A columns at 90°C. The columns were connected in the series/bypass mode (with a restrictor to balance the flow in the bypass mode) with silica gel as the upstream column. The gas flow was switched using an automated Carle Model 5520 valve. Peak areas were integrated using a Hewlett–Packard Model 3393A digital integrator with appropriate calibration factors for each gas. To minimize the effects of nonzero conversion and temperature gradients in the catalyst bed due to the exothermicity of the reaction, the data used for kinetic calculations was limited to the conversion range of 1 to 10%. By placing a fine gauge thermocou-

ple directly in the catalyst bed and measuring the temperature rise as a function of conversion, it was found that at the common experimental condition of $P_{CO} = 950$ Pa and space velocity $SV = 102,000$ h $^{-1}$, the temperature rise at 10% conversion is about 2 K. The experimental error given with the kinetic results is the standard deviation.

RESULTS AND DISCUSSION

Reaction on oxidized catalysts. Table 1 summarizes the kinetic behavior of the oxidized and reduced forms of the catalyst. In Figs. 1 and 2 the letter sequence of the curves indicates the temporal order of the experiments (some similar intervening measurements are not shown). The stoichiometric ratio of the reactants for the reaction $2CO + O_2 = 2CO_2$ is $O_2/CO = 0.5$. Figure 1 shows results of experiments carried out under oxygen rich conditions ($O_2/CO = 1.05$) at a high space velocity (corresponding to the highest space velocity expected in an automobile exhaust). The fresh catalyst had a surface area of 0.48 m 2 /g. After a few hours of reaction the activity of the fresh catalyst (Fig. 1a) had declined by about 10% and then the activity remained constant as shown by Fig. 1b which was measured after about 50 h of reaction. After an initial rapid increase in conversion, both curves leveled off at about 55% conversion. Figure 1c, measured at a higher partial pressure of $CO + O_2$, shows a somewhat larger suppression of the activity at elevated temperatures. These results suggest that a change in the surface area or composition may be occurring at elevated temperatures.

Figure 2 shows similar data for another sample of the Y_2BaCuO_5 catalyst. The fresh catalyst (Fig. 2a) had a surface area of 0.80 m 2 /g. The surface areas after the kinetic measurements of Figs. 2b and 2d were 0.79 and 0.66 m 2 /g, respectively. This indicates that the attenuation in activity at high temperatures cannot be attributed to a loss in surface area.

Changing the oxygen partial pressure in the range of 620 to 7000 Pa at a constant

TABLE 1

Summary of Kinetic Data for CO Oxidation on Y_2BaCuO_5 Catalysts

Catalyst order in O_2	Order in CO	E_a (kJ/mol)	Rate at 200°C (molecules/cm ² /s)
Oxidized 0 ± 0.1	1.5 ± 0.4	104 ± 13	3.7×10^{12}
Reduced 0 ± 0.1	1.1 ± 0.1	46 ± 7	3.5×10^{14}

CO pressure of 570 Pa did not change the reaction rate, indicating a zero-order reaction with respect to O_2 . The dependence of the reaction rate on the CO pressure at a constant oxygen pressure of 4410 Pa was measured at four different temperatures between 236 and 272°C and at CO pressures between 550 and 4200 Pa. The conventional plots of $\log(\text{rate})$ versus $\log(P_{CO})$ were somewhat more scattered than normal and gave an average order of 1.5 ± 0.4 with respect to CO. Arrhenius plots of $\log(\text{rate constant})$ versus $1/T$ over the temperature range of 236 to 279°C and at four different partial pressures of CO in the range of 550 to 4200 Pa yielded a value of 104 ± 13 kJ/mol.

Reaction on reduced catalysts. When ki-

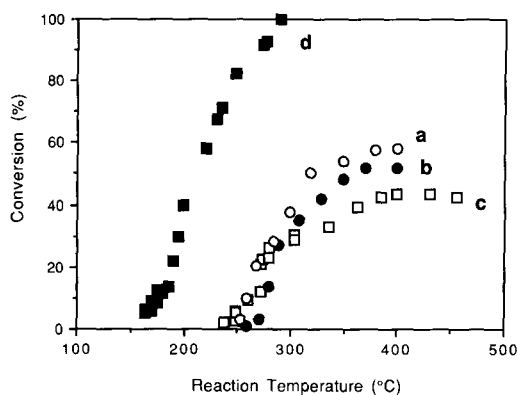


FIG. 1. Activity of Y_2BaCuO_5 catalysts for CO oxidation. Carrier gas is He; $O_2/CO = 1.05$; $SV = 102,000$ h^{-1} ; CO partial pressures are 570, 570, 940, and 940 Pa for curves a, b, c, and d, respectively; total $P = 1 \times 10^5$ Pa. Curves a, b, and c are for oxidized catalysts, and curve d is for a reduced catalyst.

netic measurements were made with a higher partial pressure of CO ($O_2/CO < 0.9$), a remarkably large increase of activity was observed after several minutes of reaction. Although the reaction mixture is still oxygen rich with respect to the stoichiometric ratio, it is possible that some reduction occurred. Consequently, the catalyst of Fig. 1c was partially reduced by exposure to a 40 liter/h flow of 5% CO in He at 350°C for 3 h. As shown on Fig. 1d, this treatment resulted in a very large increase in activity even when running the reaction at $O_2/CO = 1.05$ and 100% conversion was achieved at 250°C. This clearly establishes that, as expected, diffusion was not responsible for the attenu-

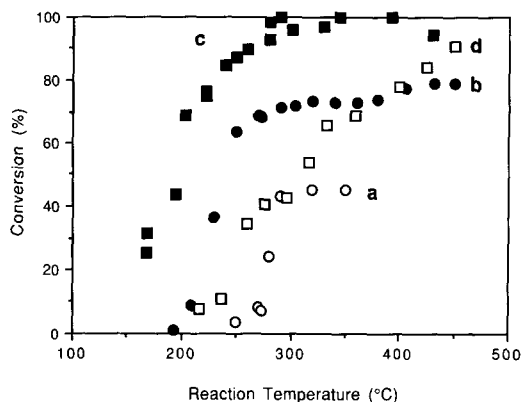


FIG. 2. Activity of Y_2BaCuO_5 catalysts for CO oxidation. Carrier gas is He; $O_2/CO = 1.06$; $SV = 105,000$ h^{-1} ; CO partial pressure is 940 Pa; total $P = 1 \times 10^5$ Pa. Curve a is for the oxidized catalyst. Curve b is for the catalyst after reduction at 350°C for 1 h in 5% CO in He flowing at 47 L/h. Curve c is for the catalyst after an additional 1 h of reduction. Curve d shows the activity during the cooling cycle.

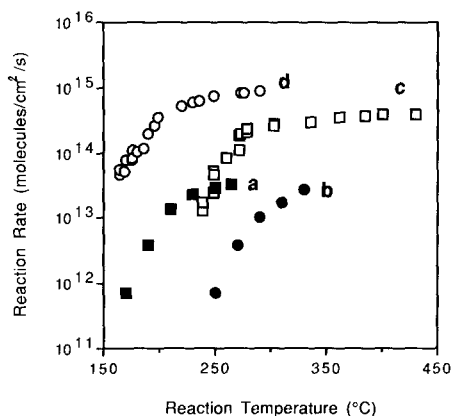


FIG. 3. Comparison of activity of oxidized and reduced Y-Ba-Cu-O catalysts for CO oxidation. Curves a and b are for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (calculated from data of Ref. (8)). $P_{\text{CO}} = 3.2$ kPa; carrier gas is N_2 ; $\text{SV} = 84,000$ h^{-1} ; $\text{O}_2/\text{CO} \cong 6$. Curve a is for the oxidized catalyst and curve b is for the reduced catalyst. Curves c and d are for Y_2BaCuO_5 . $P_{\text{CO}} = 0.93$ kPa; carrier gas is He; $\text{SV} = 103,000$ h^{-1} ; $\text{O}_2/\text{CO} = 1.05$. Curve c is for the oxidized catalyst and curve d is for the reduced catalyst.

ation in activity of the oxidized catalysts at high temperature. The activity remained stable after running the reaction under various conditions for a period of 100 h. Neither the original X-ray powder diffraction pattern nor the characteristic green color of Y_2BaCuO_5 was changed by this pretreatment, suggesting that partial reduction took place only on the surface of the oxide. The original low activity of the catalyst returned after reoxidation in a flow of 5% O_2 in He at 450°C for 2 h. That indicates that the change of the surface is reversible.

Changing the oxygen partial pressure in the range of 900 to 4400 Pa at a constant CO pressure of 900 Pa did not change the reaction rate over the partially reduced catalyst, indicating a zero-order reaction with respect to O_2 . The dependence of the reaction rate on the CO pressure at a constant oxygen pressure of 4420 Pa was measured near 170°C and at CO pressures between 550 and 4200 Pa. Very linear plots of $\log(\text{rate})$ versus $\log(P_{\text{CO}})$ were obtained, with an average order with respect to CO of 1.1 ± 0.1 .

Arrhenius plots of $\log(\text{rate constant})$ versus $1/T$ over the temperature range of 160 to 180°C and at four different partial pressures of CO in the range of 550 to 4370 Pa yielded a value of 46 ± 7 kJ/mol.

In order to better understand the nature of the catalyst activation and deactivation processes, additional experiments were performed on the catalyst of Fig. 2a. Reduction for 1 h at 350°C in a 47 liter/h flow of 5% CO in He substantially increased the activity, as shown in Fig. 2b. An additional hour of reduction further increased the activity as evidenced by Fig. 2c, but more reduction at these conditions had no further effect. The catalyst of Fig. 2c was deliberately heated to the rather high temperature of 450°C . The activity was then monitored as the catalyst was cooled (Fig. 2d). The hysteresis shows a large drop in activity. As previously noted, this cannot be attributed to a drop in surface area. It appears that at temperatures above $\sim 400^\circ\text{C}$ the catalyst is altered, and this presumably is the reason for the attenuation in activity at high temperatures.

Comparison to the activity of superconducting oxides. Figure 3 compares the activity of the oxidized and reduced forms of the Y_2BaCuO_5 catalyst with data for the oxidized and reduced forms of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ as reported by Jiang et al. (8). It should be noted that the latter data were collected at a 3.3-fold higher partial pressure of CO, and correction for this difference would lower the rates about 4-fold. There are several notable differences in the behavior of the two types of catalysts. Reduction of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ causes a gradual decrease in activity. The effect of a mild reduction ($x < 0.9$) causes a modest (< 10 -fold) drop in conductivity which has been explained by gradual removal of the easily exchangeable O_I type lattice oxygen atoms (these are formally electron rich O^- ions in a peroxide type coordination (15)). Stronger reduction ($x > 0.9$) results in up to a 10^5 -fold decrease in conductivity. This has been attributed to the loss of the O_{III} and O_{IV} lattice atoms. Reduction also results in an orthorhombic to te-

tragonal phase transition (16, 17). In contrast, mild reduction of Y_2BaCuO_5 greatly increases the activity.

The oxidized forms of the two types of catalysts have similar activity. Jiang (8) reports an activation energy of 115 kJ/mol (O stoichiometry corresponds to $x = 0.08$; no activation energy was reported for the reduced catalyst), which is the same within experimental error as found for Y_2BaCuO_5 . However, the reduced Y_2BaCuO_5 catalyst is roughly 60-fold more active than these catalysts and about 1000-fold more active than the reduced form of $YBa_2Cu_3O_{7-x}$ (the relative activities of the Y_2BaCuO_5 catalysts are about 4-fold higher if correction is made for the difference in partial pressures of CO). The activation energy of reduced Y_2BaCuO_5 is also lower. The activity of the reduced Y_2BaCuO_5 is similar to the best CO oxidation catalysts such as CuO, Co_3O_4 , and Pt (18, 19). These results suggest, contrary to the interpretation of Jiang, that the metal-like conductivity at room temperature and the superconductivity at 90 K of $YBa_2Cu_3O_{7-x}$ does not result in distinctive catalytic activity for CO oxidation. It is also found that this compound has the expected very low activity for the hydrogenation of ethylene at 273 K and for H_2 - D_2 exchange at both 78 and 273 K (20).

The exact nature of the change in the surface composition which occurs during the activation and deactivation of Y_2BaCuO_5 and $YBa_2Cu_3O_{7-x}$ is not known at this time. In a recent analysis of catalytic oxidation reactions, Noller and Vinek (21) point out the need for both electron pair donor (EPD) and electron pair acceptor (EPA) sites in a catalyst. A metal cation functions as an EPA site. It is further noted that materials with a single oxidation state for the metal, and especially if it is a high oxidation state for the element, have very low or zero catalytic activity. In this respect it is notable that in Y_2BaCuO_5 the copper is only present as Cu^{2+} (22, 23). Thus, it is reasonable that the generation of some Cu^+ may considerably enhance the catalytic activity for oxidation.

Preliminary temperature-programmed reduction experiments (done using a flow of 5% H_2 in Ar) show that reduction of Y_2BaCuO_5 occurs in two distinct steps. The first step starts at 320°C. The second step starts at 430°C and leads to a complete reduction to Cu(O). Thus, we attribute the enhanced activity of the mildly reduced Y_2BaCuO_5 to the removal of some surface oxygen and enhanced access to Cu^+ EPA sites.

In contrast, in $YBa_2Cu_3O_{7-x}$ the copper is generally believed to be present in more than one oxidation state. In addition to the expected Cu^{2+} , numerous papers describe the presence of Cu^+ , Cu^{3+} , and even Cu^{4+} (15, 17, 24). These references also describe the possibility that the oxygen exists partly as peroxide, O_2^- , or superoxide, O_2^- , which further complicates the assignment of oxidation states to the copper. Thus, in relation to the model of Noller and Vinek the multiple oxidation states of copper in unreduced $YBa_2Cu_3O_{7-x}$ suggest that it would have higher catalytic activity for oxidation than would Y_2BaCuO_5 . Also, the effect of partial reduction on activity is less clear for this catalyst.

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