

NOTES

Catalytic Oxidation of Carbon Monoxide over Superconducting and Related Cuprates

Cuprates are multimetallic oxides composed of copper and one to five more electropositive metals which are usually alkalis, alkaline earths, and rare earths. Most high-temperature superconductors belong to one of four families based on complex La, Y, Bi, or Tl cuprates (1). The catalytic activity of cuprates was first reported in 1977 (2), but interest increased in 1987 after the discovery of high-temperature superconductors. Cuprates have been found to be active catalysts for several reactions, including reduction and decomposition of N_2O , NO, and NO_2 (3-5), synthesis and dehydrogenation of alcohols (16-21), and oxidation of methane, toluene, alcohols, and CO (2, 16, 20, 22-31).

In spite of the very large number of cuprates, reports of catalytic activity are largely limited to perovskite-like compounds of La and Y. The expression "perovskite-like" is used here for 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 (1, 32, 33). Characteristics associated with the perovskite-like crystal structure, such as variable oxygen content and metallic electrical conductivity, have been suggested to play an important role in catalytic activity (2, 4, 6, 13-15, 18, 19, 22-27, 34). In contrast, some cuprates of the nonperovskite and nonconducting type were found to be more active catalysts than the perovskites (16, 20, 29-31).

The nonperovskite insulator, Y_2BaCuO_5 ,

was reported (31) to be about two orders of magnitude more active for the oxidation of CO than the superconductor $YBa_2Cu_3O_{7-x}$, which has a perovskite-like structure. The perovskite-like La_2CuO_4 was found (29) to be a less active catalyst than the nonperovskites CuO and La_2O_3 . Yet, partial substitution of La for Sr increased the activity of lanthanum cuprates (9, 29) to near the activity level of La_2O_3 . Nevertheless, their activity remained lower than the activity of CuO, which is one of the best oxide catalysts for the oxidation of CO (35, 36). The compound $SrCuO_2$, which is not a perovskite, has an activity between that of $La_{2-x}Sr_xCuO_4$ and La_2CuO_4 (22, 29). In contrast, the activity of another cubic, nonperovskite, alkali earth cuprate, $BaCuO_2$, was found to be higher than that of CuO (30).

Partial surface reduction was found to increase the activity of some insulating cuprates, such as Y_2BaCuO_5 (31) and $BaCuO_2$ (30). In contrast, the activity of compounds of the type $YBa_2Cu_3O_{7-x}$ decreased gradually when x was increased from 0.08 to 1.25 (25). Since the electrical conductivity $YBa_2Cu_3O_{7-x}$ decreases with decreasing oxygen content, it was suggested that conductivity correlates with catalytic activity (25). However, the activity of La_2CuO_4 was found to be independent of its electrical conductivity (22).

Due to the disparate results in the literature, we further investigated the relationship between structure, electrical conductivity, and catalytic activity of cuprates for CO oxidation. Two superconductors, $Bi_2CaSr_2Cu_2O_{10\pm x}$ and $Tl_2CaBa_2Cu_2O_{9\pm x}$, and two insulating compounds, $Y_2Cu_2O_5$ and $Ba_2CuO_{3.5\pm x}$, were studied. The super-

conductors and $\text{Ba}_2\text{CuO}_{3.5\pm x}$ have perovskite-like structures, whereas $\text{Y}_2\text{Cu}_2\text{O}_5$ has an orthorhombic structure (1, 37).

Cuprates were prepared from well ground solid oxides, nitrates, or carbonates, followed by calcination in a procelain crucible in air. The center part of the sample was used to avoid contamination from the crucible. Catalysts (0.44 cm^3) were preheated in a flow of He (40 L/h) at 500°C for 2 h and then cooled to room temperature. $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_{9\pm x}$ was pretreated for only 30 min to avoid possible evaporation of thallium. The reaction gas was 0.97% O_2 and 0.93% CO in a carrier gas of He at a total pressure of 1 atm ($1.0 \times 10^5 \text{ Pa}$) and a space velocity (SV) of $1.04 \times 10^5 \text{ h}^{-1}$. These conditions correspond to the most severe conditions for CO oxidation in a typical catalytic converter for an automobile (36). The activity versus partial pressure dependence was measured in the conventional manner by varying the O_2 partial pressure from 930 to 4400 Pa and keeping a constant CO pressure (916 Pa), and by varying the CO partial pressures from 540 to 4200 Pa and keeping a constant O_2 pressure (4360 Pa). Details of preparation, procedures, equipment, and product analysis have been reported previously (30, 31, 38).

The identity of each catalyst was confirmed by powder X-ray diffraction (XRD). However, it is known that these materials (and most other oxides) have small deviations from the stated stoichiometries (which is not revealed by XRD) and this could possibly affect the results. Since some cuprates are known to form carbonates upon exposure to CO_2 at elevated temperatures, this could also affect the activity (16, 43). As noted in the following discussion, in some cases the surface of a catalyst changes during reaction, so the stated compounds can be regarded as catalyst precursors.

BET surface areas and bulk densities are shown in Table 1. The activities of bismuth and thallium superconductors are shown in Fig. 1. Curve 1 represents the conversions of CO on a fresh $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_{9\pm x}$ catalyst

during the first period of increasing temperature. Cooling the catalyst showed hysteresis with lower activity (curve 2). In contrast, the activity of $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{10\pm x}$ (curve 3) remained stable during a variety of measurements over a period of 50 h. The open and filled circles of curve 3 represent results of heating and cooling cycles at the beginning and at the end of the catalytic experiments, respectively. XRD spectra showed no change in the structures of $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_{9\pm x}$ and $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{10\pm x}$ after reaction. A slight amount of thallium may have evaporated from the thallium-based catalyst at around 450°C . A thin, translucent, light grey layer was observed on the wall of the reactor after the experiments were finished. Since the pure superconducting phase, $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_{9\pm x}$, has been reported to only lose thallium when calcined above 850°C (39–42), the mirror is believed to be from some unreacted thallium oxide impurity. It is possible that the loss of activity of the thallium catalyst is due to the surface being covered by thallium metal.

Curve 1 in Fig. 2 shows the oxidation of CO on fresh $\text{Y}_2\text{Cu}_2\text{O}_5$. The jump in conversion observed near 300°C remained stable during 40 h of reaction. Curve 2 represents the results of two heating and cooling cycles, carried out near the beginning (shortly after the jump in activity) and at the end of the experiments. Since the characteristic green color and the XRD pattern of the catalyst were unchanged after the reaction, the increased activity is due to new surface sites and not a change in the bulk composition. Temperature programmed reduction experiments showed (38) that the bulk reduction of $\text{Y}_2\text{Cu}_2\text{O}_5$ starts near 300°C . Similar increases in the activity of fresh catalysts have also been observed on other nonconducting cuprates, such as Y_2BaCuO_5 (31) and BaCuO_2 (30). Thus, a partial surface reduction with the formation of Cu^+ ions may be responsible for the enhanced activity (30, 31).

Curve 3 in Fig. 2 shows that, in contrast

TABLE I

Kinetic Results for CO Oxidation over Superconducting and Nonconducting Cuprate Catalysts

Number	Catalyst	Reaction order		E (kJ/mol)	Reaction rate (10^{13} molec./cm ² /s)		Surface area (m ² /g)	Bulk density (cm ³ /g)	Reference
		O ₂	CO		200° C	300° C			
1.	Ba ₂ CuO _{3.5±x}	0.0	0.3	136	0.002*	0.7*	0.10	2.97	—
2.	BaCuO ₂	0.0	1.2	63	33	450*	0.25	2.10	(30)
3.	Ba ₂ Cu ₃ O ₅	0.3	0.3	165	28	1100*	0.54	3.07	(30)
4.	Y ₂ Cu ₂ O ₅	—	—	—	—	84	0.29	1.26	—
5.	La ₂ CuO ₄	0.5	0.5	55	0.47*	5.4*	0.66	—	(22, 29)
6.	Y ₂ BaCuO ₅	0.0	1.1	46	35	270*	0.48	1.58	(31)
7.	YBa ₂ Cu ₃ O _{5.85}	—	—	—	—	1.4	0.10	2.68	(25)
8.	YBa ₂ Cu ₃ O _{6.92}	0.0	1.0	115	0.91	150*	0.10	2.68	(25)
9.	Bi ₂ CaSr ₂ Cu ₂ O _{10±x}	0.5	0.3	79	0.38*	12.7	0.73	2.27	—
10.	Tl ₂ CaBa ₂ Cu ₂ O _{9±x}	—	—	—	—	0.9	0.69	3.34	—
11.	CuO	0.0	0.7	92	1.05	38	0.30	1.22	(30, 35)
12.	Co ₃ O ₄	0.5	0.5	55	104	1050*	0.44	—	(35, 36)
13.	Pt (wire)	—	—	—	—	420	—	—	(35, 36)
14.	Pd (wire)	—	—	—	—	2100	—	—	(35, 36)

Note. Data marked by an asterisk are extrapolated using the Arrhenius equation. Samples 8–10 are high T_c superconductors; samples 1, 3, 5, 7–10 have perovskite-like crystal structure.

to Y₂Cu₂O₅, the perovskite-like insulator, Ba₂CuO_{3.5±x}, has low activity. However, unlike Tl₂CaBa₂Cu₂O_{9±x} (Fig. 1), the activity remained stable after cooling the catalyst and during 40 h of reaction. The data

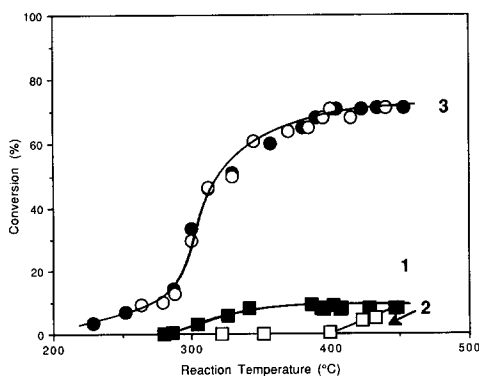


FIG. 1. Activity of Tl₂CaBa₂Cu₂O_{9±x} (curve 1 is for heating, curve 2 for cooling) and Bi₂CaSr₂Cu₂O_{10±x} (curve 3: filled circles are for fresh, open circles for used samples) catalysts for oxidation of carbon monoxide; carrier gas, He; partial pressure of reactants, $P_{O_2} = 970$ Pa, $P_{CO} = 930$ Pa; total pressure = 1.0×10^5 Pa; SV = 1.04×10^5 h⁻¹.

of curve 3 were collected at various times during the reaction. XRD did not show any significant difference between the structure of the fresh and used Ba₂CuO_{3.5±x} catalysts.

Figure 3 compares the reaction rates of

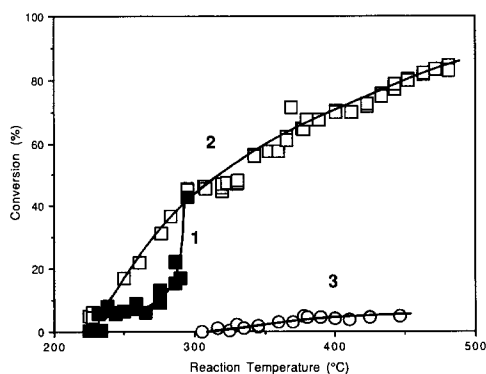


FIG. 2. Activity of Y₂Cu₂O₅ (curve 1 is for fresh and curve 2 for steady-state samples) and Ba₂CuO_{3.5±x} (curve 3 is for fresh and used samples) catalysts for oxidation of carbon monoxide. Reaction conditions are the same as those in Fig. 1.

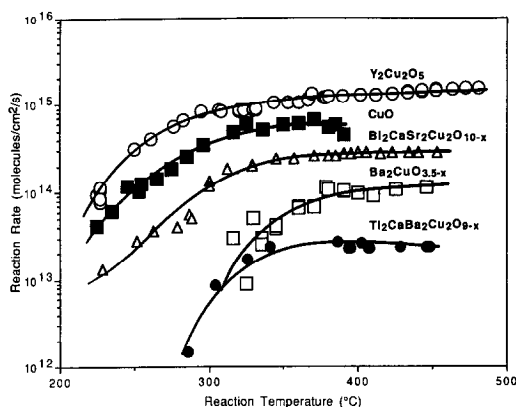


FIG. 3. Comparison of activity of $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{10\pm x}$, $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_{9\pm x}$, $\text{Y}_2\text{Cu}_2\text{O}_5$, $\text{Ba}_2\text{CuO}_{3.5\pm x}$, and CuO . Data for CuO are from Ref. (30). Reaction conditions for other cuprates are the same as those in Fig. 1.

the four cuprates with data reported earlier for CuO (30). Independent of the electrical conductivity, all catalysts having perovskite-like crystal structure are less active than CuO . The bismuth based sample contained about 10% of CuO impurity (38). Due to the higher activity of CuO , the activity of pure $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{10\pm x}$ is presumed to be lower than that shown in Fig. 3. In contrast, the nonperovskite insulator, $\text{Y}_2\text{Cu}_2\text{O}_5$, is more active than CuO . Similar results have been reported for other perovskite-like cuprates (as La_2CuO_4 , $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (22, 25, 29)) and nonperovskite cuprates (as Y_2BaCuO_5 and BaCuO_2 (30, 31)).

Table 1 provides a comparison between the activity of cuprates and the best oxide and metal catalysts. Reaction rates at 200 and 300°C were chosen to minimize extrapolation. Extrapolated values are marked by an asterisk (*). The average error for reaction orders is about ± 0.1 and that for activation energies is about $\pm 10\%$. Although the reaction conditions for some catalysts shown in Table 1 were somewhat different, it can be established that the nonconducting cuprates, $\text{Ba}_2\text{Cu}_3\text{O}_5$, BaCuO_2 , and Y_2BaCuO_5 , are among the most active catalysts for oxidation of CO .

The reaction orders and activation energies are within the ranges observed on other metal oxides (35, 36). A high activation energy and low reaction orders for both oxygen and carbon monoxide were measured on nonconducting perovskite-like $\text{Ba}_2\text{CuO}_{3.5\pm x}$. The values are near those for perovskite-like $\text{Ba}_2\text{Cu}_3\text{O}_5$, but different from those on BaCuO_2 , which is a nonperovskite. The results also indicate that the mechanism of CO oxidation on cuprates of the metallic conductor type is different from the mechanism on metal catalysts, where generally high reaction orders (>1) were found with respect to oxygen and zero or negative orders with respect to CO (35, 36). Kinetic data were not obtained for $\text{Y}_2\text{Cu}_2\text{O}_5$ because the temperature of the catalyst bed increased significantly when the partial pressure of CO increased. A similar but less strong effect was sometimes observed on other cuprates (30) and monometallic oxides (35).

Reaction rates in Fig. 3 and Table 1 also indicate that an oxygen-deficient perovskite-like structure and metallic conductivity are generally detrimental to the activity of cuprate catalysts. The very low catalytic activity of the best superconductor, $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_{9\pm x}$ (38), compared to the activities of $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{10\pm x}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$ indicates an inverse relationship between electrical conductivity and catalytic activity. This conclusion is in contrast to that of Jiang *et al.* (25), who suggested a linear relationship between these factors for compounds of the type $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.

The low catalytic activity of the perovskite-like cuprates in comparison to CuO and other cuprates may be due to the presence of O^- ions. Applying the widely accepted Mars-van Krevelen mechanism (44), the lattice oxygen ions are transferred to CO and are subsequently replaced from the gas phase. O^{2-} ions in CuO and some cuprates are presumed to be highly reactive in CO oxidation. Being doubly negative, these ions should also be more tightly held than the O^- ions present in most perovskite-

like compounds. Thus, it is suggested that the more weakly bonded O^- ions rapidly exchange with CO but are of low reactivity for catalytic oxidation. Hence, perovskite-like cuprates are predicted to be of lower activity for CO oxidation than the nonperovskite cuprates.

The result for $Y_2Cu_2O_5$ indicates that the addition of yttrium can improve the catalytic activity of copper oxide based catalysts for the oxidation of carbon monoxide. Similar conclusions can be drawn for the other non-conducting, nonperovskite yttrium and barium cuprates (Table 1). Noller and Vinek (45) claimed that the activity of oxides for catalytic oxidation increases with their basicity. The enhanced activity caused by yttrium and barium, which are considerably more basic than copper, is in good agreement with this.

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