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# $YBa_2Cu_3O_x$ as an electroconductive catalyst for combustion of carbon monoxide

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## Abstract

$YBa_2Cu_3O_x$, known as a high-Tc superconductor, was used as an electroconductive catalyst and its characteristics in CO oxidation were investigated. Charging 3 V, direct current, heated $YBa_2Cu_3O_x$ up to about 500°C, at which it could catalyze CO oxidation. Thus, this oxide has proper features required for electrically temperature-controlled combustion catalysts: one is self-heating property caused by electric current (Joule's heat) and the other is catalytic activity for combustion. The catalytic activity of $YBa_2Cu_3O_x$ was greatly affected by the oxygen deficiency in the solid which was directly related to the partial pressure of oxygen in the reaction system.

*Keywords:* CO combustion; $YBa_2Cu_3O_x$ catalysts

## 1. Introduction

Catalysts are recently gaining important roles in a wide range of fields in which chemical reactions are involved, typically in environmental technologies. Consequently, requirements for catalyst performance are getting more and more exacting. An example is the removal of hydrocarbons emitted from automobile in the period of cold start. Conventional tail-gas cleaning catalysts do not operate at such low temperatures. If a solid would have a proper electric conductivity to heat itself quickly to a temperature at which catalytic activity becomes practical, a new catalytic system would be realized, referred as electroconductive catalyst. The electroconductive catalyst, which is both catalytic and electrically conductive, is superior to the electrically heated catalyst (EHC), in which a catalytically active substance is coated on an electrically conductive material (such as metal honeycomb), because of simplification of the catalyst assembly. Such an electroconductive catalyst will be employed as a catalyst for the removal of pollutants in the cold-start-exhausts from automobiles.

The purpose of this study is to investigate the self-heating property of $YBa_2Cu_3O_x$ induced by charging DC voltage and its catalytic activity for CO combustion. In addition, several other electroconductive oxides having a high-Tc superconducting property were also tested as potential electroconductive catalysts.

## 2. Experimental

### 2.1. Preparation of catalysts

$YBa_2Cu_3O_x$ was prepared by a conventional solid state reaction in a similar manner as de-

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scribed in a previous paper [1]. Conditions for the preparation of other superconducting oxides are shown in Table 1. All of these catalysts were prepared by the solid state reaction. X-Ray diffraction analysis using a Cu K$\alpha$ radiation, with RAD I-C, Rigaku Co., Ltd., evidenced that all catalysts used in this work consisted of a single phase crystalline structure. The method to attach silver electrodes to catalyst pellets for charging direct current was same as described previously [1].

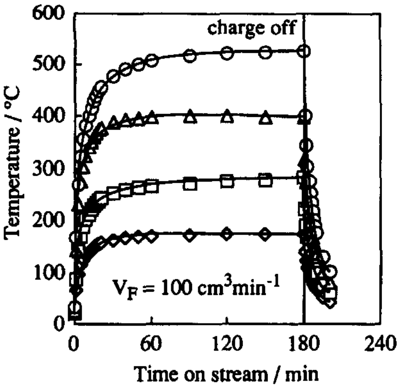

Fig. 1. Increase in the temperature of $YBa_2Cu_3O_x$ pellet in CO combustion (CO, 2%; $O_2$, 1%) as a function of time on charging diferent DC currents: ○, 3.0 V; △, 2.5 V; □, 2.0 V; ■, 1.5 V.

## 2.2. Measurements of catalytic activity

Catalytic activity for CO combustion was measured in a continuous flow reactor operated under atmospheric pressure. The structure of the reactor is the same as that described in the preceding paper [1]. The composition of reactant gas was 2% CO, 0%–10% $O_2$ and He balance. The total gas flow rate (VF) was 50–100 cm$^3$ min$^{-1}$, corresponding to SV = 3000–6000 h$^{-1}$. Prior to reaction, the catalyst was heated in a stream of $O_2$ at 400°C for 1 h.

Combustion of CO was carried out either by heating a catalyst pellet with a constant voltage using a DC power source (electroconductive mode), or by heating the catalyst pellet in an electric furnace (isothermal mode). Exit gas from the reactor was analyzed by use of an on-line gas chromatography (GC-8AIT, Shimadzu Corp.). Chromatographic separation was achieved by using an active carbon column (80–100 mesh, 2 m, G.L. Science, Inc.).

# 3. Results and discussion

## 3.1. Characteristic features of $YBa_2Cu_3O_x$ catalyst for CO combustion

Fig. 1 shows the self-heating property of $YBa_2Cu_3O_x$ expressed by the temperature as a function of time on charging DC current in the range from 1.5 to 3.0 V. The electric current increased almost proportionally with the voltage up to 3.0 V. When charged by a small voltage, the temperature rapidly increased and reached a steady state. The catalyst temperature observed in the reactant gas flow reached 50–80 K higher

Table 1
Preparation method of various superconducting oxide catalysts

| Catalyst | Raw materials | Surface area (m$^2$ g$^{-1}$) | Calcination | |
|---|---|---|---|---|
| | | | $T$ (°C) | Time (h) |
| $YBa_2Cu_3O_x$ | $Y_2O_3$, $BaCO_3$, CuO | 0.8 | 940 | 6 |
| $Bi_2Sr_2CuO_x$ | $Bi_2O_3$, $SrCO_3$, CuO | 0.7 | 880 | 25 |
| $Bi_2Sr_2CaCu_2O_x$ | $Bi_2O_3$, $CaSr_2Cu_2O_x$ [a] | 0.1 | 852 | 2 |
| $Nd_{1.9}Ce_{0.1}CuO_x$ | $Nd_2O_3$, $CeO_2$, CuO | 0.2 | 1000 | 1 |
| $BaPbO_x$ | $BaCO_3$, PbO | 0.2 | 900 | 25 |
| $BaPb_{0.8}Bi_{0.2}O_x$ | $BaCO_3$, PbO, $Bi_2O_3$ | 0.1 | 900 | 25 |

[a] $CaSr_2Cu_2O_x$ is a matrix material synthesized from CaO, $SrCO_3$ and CuO at 960°C for 48 h.

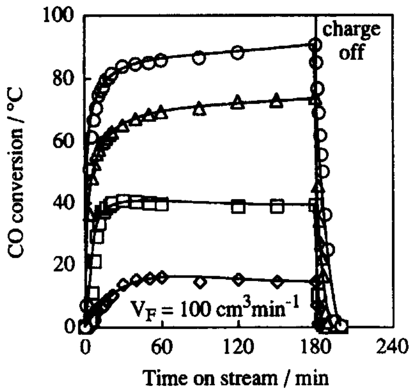

Fig. 2. Time on stream variation in CO conversion in CO combustion on $YBa_2Cu_3O_x$ catalyst under various charging voltages. Same reaction conditions as in Fig. 1.

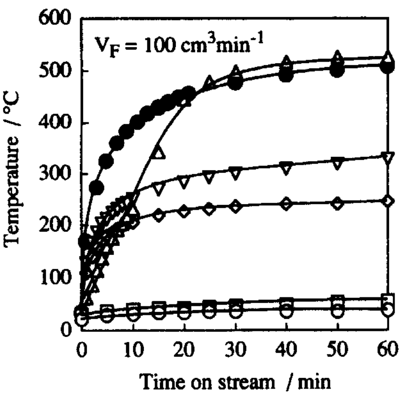

Fig. 4. Time on stream variation in temperature of various superconductors in CO combustion (CO, 2%; $O_2$, 1%) under 3 V charge. ●, $YBa_2Cu_3O_x$; ○, $Bi_2Sr_2CuO_x$; △, $Bi_2Sr_2CaCu_2O_x$; □, $Nd_{1.9}Ce_{0.1}CuO_x$; ◇, $BaPbO_x$; ▽, $BaPb_{0.8}Bi_{0.2}O_x$.

than that in He flow due to the reaction heat of CO oxidation as described in the previous paper [1]. Fig. 2 shows the catalytic activity for CO combustion simultaneously observed, being expressed by CO conversion as a function of time on stream. The catalytic activity also quickly increased when charged and reached a steady state. These results show that $YBa_2Cu_3O_x$ satisfies the requirements for the electroconductive catalyst; electric conductivity to heat up the catalyst body and the intrinsic catalytic activity.

The catalytic activity of $YBa_2Cu_3O_x$ was measured in both electroconductive and isothermal modes as a function of reaction temperature. As shown in Fig. 3, there was no appreciable difference in the level of CO conversion for either modes of reaction and at any DC voltages. This indicates that the catalytic activity depends only on the catalyst temperature and there is no effect caused by electric current upon the catalysis of $YBa_2Cu_3O_x$.

Consequently, it is deduced that the two important features required for the electroconductive catalyst, namely electric conductivity for Joule's heat and catalytic activity, can be discussed independently.

### *3.2. Properties of some superconducting oxides*

Using some typical superconducting oxides, the self-heating property and the catalytic activity of the pellet were measured in electrocon-

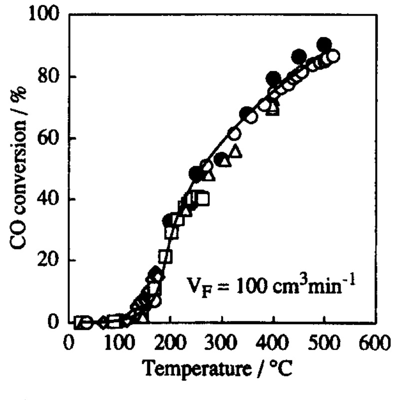

Fig. 3. Catalytic activities of $YBa_2Cu_3O_x$ for CO combustion (CO, 2%; $O_2$, 1%). ○, 3.0 V; △, 2.5 V; □, 2.0 V; ◇, 1.5 V; ●, 0 V (under isothermal condition).

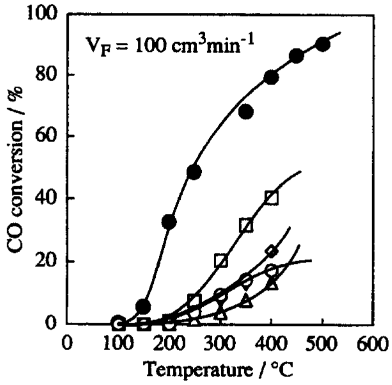

Fig. 5. Catalytic activities of various superconductors for CO combustion (CO, 2%; $O_2$, 1%). Symbols are same as in Fig. 4.

ductive and isothermal modes, respectively. Fig. 4 shows the increase of catalyst temperature as a function of time on stream when a constant 3 V DC was charged, while the catalytic activities were compared in Fig. 5 as a function of reaction temperature.

$Bi_2Sr_2CaCu_2O_x$ showed a good heating property and it was heated to relatively high temperature when electric current passed, although the CO combustion activity was low. In contrast, $Nd_{1.9}Ce_{0.1}CuO_x$ showed relatively high activity, while its heating property was poor. Consequently, these two catalysts could not work as effective electroconductive catalysts. Considering both characteristics for the electroconductive catalyst, $YBa_2Cu_3O_x$ is superior to the other oxides tested.

### 3.3. *Oxidative and reductive properties of* $YBa_2Cu_3O_x$

It is known that the value of $x$ in $YBa_2Cu_3O_x$ varies with temperature or partial pressure of oxygen [2]. As CO oxidation over $YBa_2Cu_3O_x$ catalyst has been suggested to proceed through the reaction between CO and lattice oxygen or adsorbed oxygen species [3], it is reasonably considered that the activity of $YBa_2Cu_3O_x$ catalyst would be influenced by the reaction conditions and the atmosphere of reaction mixture.

The influence of oxygen partial pressure on the activity of $YBa_2Cu_3O_x$ in electroconductive mode is shown in Fig. 6, where CO conversions under various oxygen partial pressures are given as a function of time on stream. In the case of oxidative ($O_2$ concentration, 10%) or stoichiometric ($O_2$ concentration, 1%) reactant gas composition, CO conversion quickly increased and reached a steady state. In contrast, under reductive gas composition ($O_2$ concentration, 0.5% and 0%), the CO conversion exceeded the level corresponding to complete consumption of reactant oxygen molecules and then monotonously decreased with time on stream. It is thus obvious that lattice oxygen in the catalyst reacts with CO. The amounts of lattice oxygen consumed during CO oxidation under reductive conditions (2% CO, 0.5% $O_2$) can be calculated and the results are shown in Fig. 7. The difference in oxygen consumption between $CO_2$ formation and oxygen balance corresponds to the amount of lattice oxygen used for combustion. The detailed TG analysis of lattice oxygen consumption measured in isothermal mode showed a decrease of $x$ in $YBa_2Cu_3O_x$ from 7.1 to 6.2. This suggests that efficient reoxidation of the active sites by mobile lattice oxygen species is occurring during reaction under these conditions. This oxidation process in which the catalyst acts as a reactant by supplying its lattice oxygen has been termed intrafacial

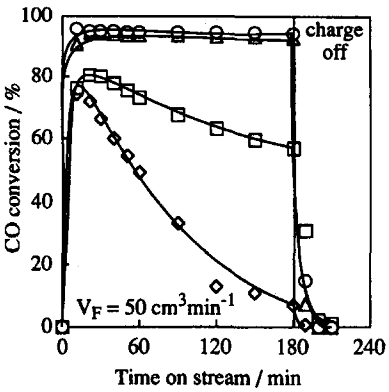

Fig. 6. Effect of $O_2$ concentration on the catalytic activity of $YBa_2Cu_3O_x$ for CO combustion under 3 V charge. CO, 2%; $O_2$: ○, 10%; △, 1%; □, 0.5%; ◇, 0%.

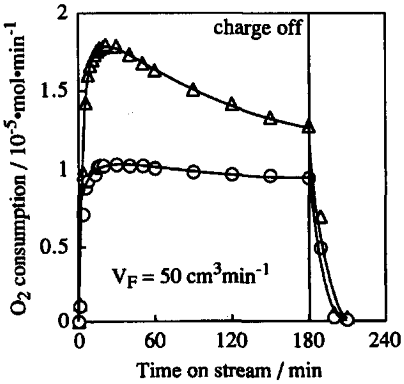

Fig. 7. $O_2$ consumption during CO combustion (CO, 2.0%; $O_2$, 0.5%) on $YBa_2Cu_3O_x$ catalyst under 3 V charge. ○, calculated from oxygen material balance; △, calculated from the amount of $CO_2$ formed.

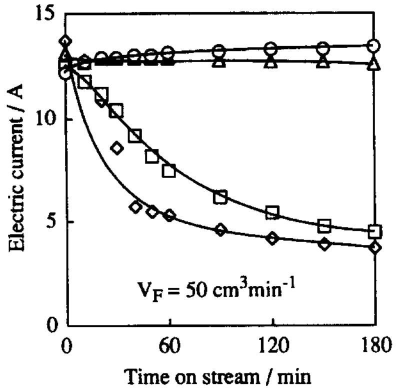

Fig. 8. Effect of $O_2$ concentration on current passing through $YBa_2Cu_3O_x$ in the combustion of CO under 3 V charge. CO, 2%; $O_2$: ○, 10%; △, 1%; □, 0.5%; ◇, 0%.

catalysis which is one of the catalysis by perovskite-type oxides [4].

The electric current and catalyst temperature observed in electroconductive mode under various oxygen partial pressures are shown in Figs. 8 and 9, respectively, as a function of time on stream. The current increased with increasing concentration of oxygen. Under oxidative atmospheres, the current passing through the catalyst was almost unchanged, while it gradually decreased in the case of reductive gas compositions. Concurrently, the catalyst was quickly heated up to a steady state temperature in oxidative gas compositions, while in reductive atmospheres the catalyst temperature increased to a maximum soon after charged and then gradually decreased.

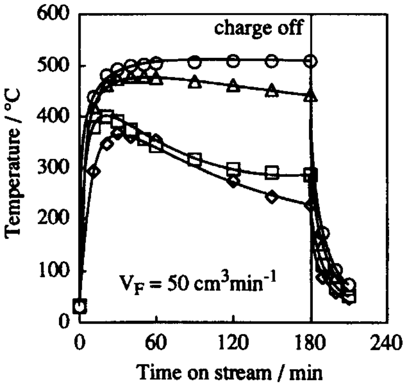

Fig. 9. Effect of $O_2$ concentration on the temperature of $YBa_2Cu_3O_x$ in the combustion of CO under 3 V charge. CO and $O_2$ concentrations are same as in Fig. 8.

It has been reported [5–8] that a high oxygen content or a large number of $x$ in a $YBa_2Cu_3O_x$ causes high electric conductivity which decreases with decreasing $x$. Furthermore, the electric resistivity of $YBa_2Cu_3O_x$ having a constant $x$-value increases with temperature [5,6]. These findings are in accordance with our results that larger electric current in more oxidative conditions is due to more enhanced uptake of oxygen into the catalyst (increase of $x$) in spite of higher temperature and the gradual fall of electric current in reductive conditions is attributed to the consumption of lattice oxygen from the catalyst.

## 4. Conclusion

$YBa_2Cu_3O_x$ satisfies two characteristic features required for electroconductive combustion catalyst. One is the electric conductivity to heat up the catalyst to a temperature high enough for the catalysis and the other is intrinsic catalytic activity. The current passing through the catalyst solid gives no effects of electric fields upon the catalysis by $YBa_2Cu_3O_x$ but merely gives the effect of Joule's heat.

The catalytic properties of $YBa_2Cu_3O_x$ electroconductive catalyst depend on the oxygen partial pressure in the reaction system or the oxygen content in catalyst. It is noted that $YBa_2Cu_3O_x$ catalyst absorbs and desorbs oxygen during oxidation of CO. Oxidative conditions lead to stable catalytic activity, while reductive conditions cause the decrease in lattice oxygen concentration in catalyst and consequently the decrease in catalytic activity as well as decreasing electric conductivity and electric current.

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