Catalysis Letters 3 (1989) 235–246

THE CATALYTIC OXIDATION OF CO ON SUPERCONDUCTOR $Ba_2YCu_3O_{7-\delta}$

JIANG AnRen, PENG Ying, ZHOU QinWei, GAO PeiYing,
YUAN HaiQing and DENG JingFa

Chemistry Department, Fudan University, Shanghai, P.R. China

Received 10 March 1989; accepted 20 July 1989

CO oxidation on $Ba_2YCu_3O_{7-\delta}$

The measurements of MS-TPD, TPRS, the electrical conductivity and kinetics on $Ba_2YCu_3O_{7-\delta}$ show that the catalytic activity of CO oxidation is closely related to properties such as the amounts and sites of oxygen, and electrical conductivity. Based on the experimental results a reaction mechanism has been suggested.

1. Introduction

The properties of high-Tc superconductor $Ba_2YCu_3O_{7-\delta}$ have drawn the attention of a number of scientists since its discovery [1–3]. As $Ba_2YCu_3O_{7-\delta}$ has the ability to relieve and to adsorb oxygen reversibly, which is similar to adsorption and desorption properties of other types of oxide catalysts [4], it is reasonable to consider high-Tc superconductors as a new type of oxidation-reduction catalysts.

2. Experimental

2.1. PREPARATION OF $Ba_2YCu_3O_{7-\delta}$ SAMPLES

A mixed solution of $Y(NO_3)_3$ (A.R.), $Ba(NO_3)_2$ (A.R.), $Cu(NO_3)_2$ (A.R.), with relative mole proportions of 1 : 2 : 3 was precipitated by NH_3 (excessive NH_3 must be avoided). The precipitation was dried, grounded, thermo-decomposed, heated at 800 ° C, and calcined at 950 ° C in an oxygen atmosphere for 8 h, then the obtained black powder ($Ba_2YCu_3O_{6.92}$) was pressed into pellets and calcined in oxygen again in order to get a single phase superconductor with Tc of 91 K. This sample was shown to be of single phase by the powder XRD. The content of oxygen was measured by TG as well as hydrogen reduction. The size of the catalysts was 20–40 mesh. The specific surface area determined by the BET method was 0.65 m^2/g. The $Ba_2YCu_3O_{6.92}$ catalysts were put into a pipe furnace with a flow of N_2 for 1 h at deoxidizing temperature of 400 ° C, 500 ° C, 600 ° C and 700 ° C respectively. The deoxidized samples with different δ values were identified by TG as 0.37, 0.78, 0.95, 1.15 respectively. XRD showed that the structure of the samples with different δ had not been changed significantly. Furthermore the TG and XRD showed that the samples had not been changed after the catalytic reaction.

2.2. MEASUREMENTS OF THE CATALYTIC ACTIVITIES OF $Ba_2YCu_3O_{7-\delta}$

A mixture of CO ($>$ 99.5%) and air with total CO concentration of ca. 3% in volume was passed through a continuous-flow system at 1 atm. The reactor was a stainless steel pipe of 6 mm i.d. The compositions of the gases before and after the reaction were analyzed by gas chromatography.

2.3. MEASUREMENTS FOR THE KINETICS

The reacting gases CO, O_2 and carrier gas N_2 were mixed and then passed through a continuous-flow reactor. The temperature and space velocity were fixed. The conversion of CO was kept less than 5%. The proportion of CO and O_2 of the reacting gas can be changed in demand. In the present experiments the influence of internal and external diffusions can be neglected.

2.4. THE HIGH VACUUM MASS SPECTROMETER-TPD AND TPRS

Both apparatuses consist of two parts, the reaction part with a pressure of 1×10^{-6} Torr, and the detection part with a pressure of 1×10^{-9} Torr. The product of the reaction can leak into the detection part by a leak valve and analyzed by Q.M.S.. In TPRS experiments, the pressures of the flowing gases CO, O_2 and CO_2 were all kept at 4×10^{-5} Torr and the actual quantities of CO, O_2 and CO_2 were detected individually while the temperature was being raised programmatically.

2.5. MEASUREMENTS OF THE ELECTRICAL CONDUCTIVITIES OF $Ba_2YCu_3O_{7-\delta}$

The four-probe method was used in our measurements. The applied current was controlled to be less than 10 mA and the voltage measured was precise to 1 μV. The measurements were made in the temperature range from 25 to 200 ° C. The electrical conductivity (σ) and the activation energy for conduction (Σ) were then calculated using the following equations

$$\sigma(\mathrm{m}\Omega^{-1}\ \mathrm{mm}^{-1}) = I/(2\pi s \cdot V_{2,3})$$

$$\Sigma = -k \cdot \mathrm{d} \ln \sigma / \mathrm{d}(1/T)$$

where I is the current passing through a sample. S (mm) the distance between two probes. $V_{2,3}$ (μV) is the voltage between the tested two probes. After catalytic reaction the samples were powered and the σ could not be measured.

3. Results

3.1. THE CATALYTIC ACTIVITIES OF THE OXIDATION OF CO ON $Ba_2YCu_3O_{7-\delta}$

Figure 1 presents the results of the catalytic activity measurements. It shows that $Ba_2YCu_3O_{7-\delta}$ is such a good catalyst to the oxidation reaction of CO that the reaction already processed significantly at 180 ° C and the conversion reached 90% with CO_2 selectivity of 100% at 260 ° C.

At 400 ° C the catalytic activity of the initial sample ($Ba_2YCu_3O_{6.92}$) is close to those of the deoxidized samples. With increasing deoxidizing temperature the value of δ increases and the activity decreases gradually. At 700 ° C the activity (represented by the reaction temperature at CO conversion of 50%, see fig. 1) of the deoxidized sample is increased by 80 ° C in comparison to that of the initial sample.

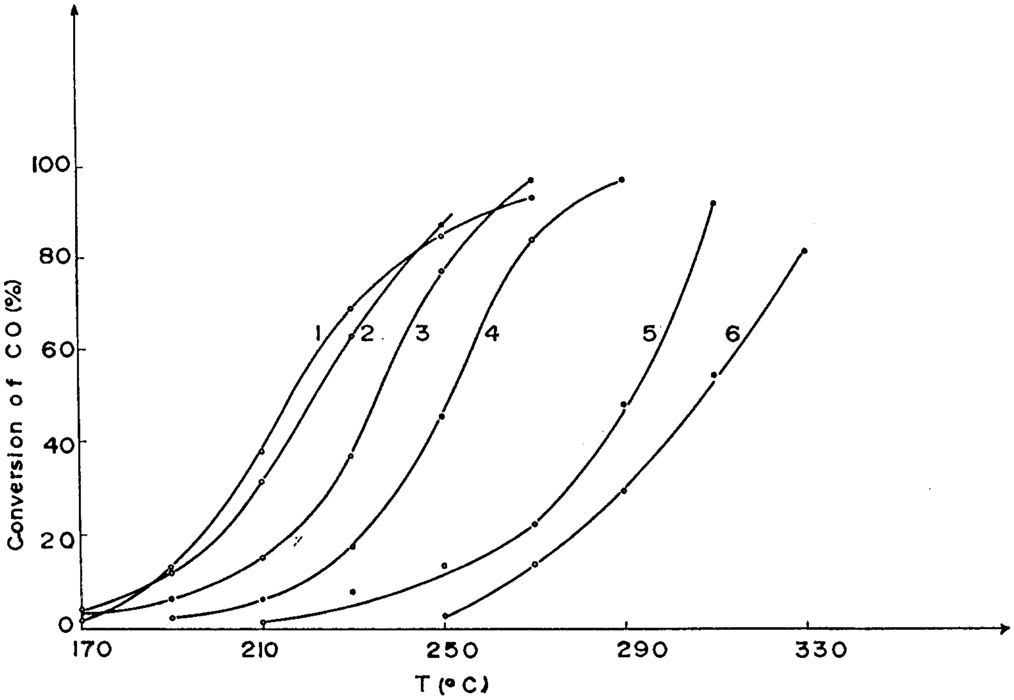

Fig. 1. The conversion of CO on $Ba_2YCu_3O_{7-\delta}$. Condition: $W/F = 1.0 \cdot 10^{-3}$ g·h/ml, CO, 3.2% another reacted gas is air. 1. $Ba_2YCu_3O_{7-\delta}$ ($\delta = 0.08$), 2. 400 ° C, $\delta = 0.37$, 3. 500 ° C, $\delta = 0.78$, 4. 600 ° C, $\delta = 0.95$, 5. 700 ° C, $\delta = 1.15$, 6. 900 ° C.

3.2. RESULTS OF KINETICS MEASUREMENTS

By varying the partial pressure of either CO or O_2 while keeping the other constant over $Ba_2YCu_3O_{6.92}$ (see fig. 2), the rate equation can be written as:

$$r = KP_{CO}P_{O_2}$$

The reaction order is zero for oxygen and near one for carbon monoxide. By applying the formula of the collision theory with values of k at various temperatures:

$$\ln k/T^{1/2} = C - E/RT \ [5]$$

the activation energy is found to be 115 kJ/mol.

3.3. RESULTS OF GAS CHROMATOGRAPHY-TPD, MS-TPD AND MS-TPRS MEASUREMENTS

The results of GC-TPD and MS-TPD measurements reveal that O_2, CO, CO_2 are not adsorbed on $Ba_2YCu_3O_{6.92}$ at room temperature. The MS-TPRS measurements show that when the temperature is programmed to 170 °C (fig. 3) CO_2 is

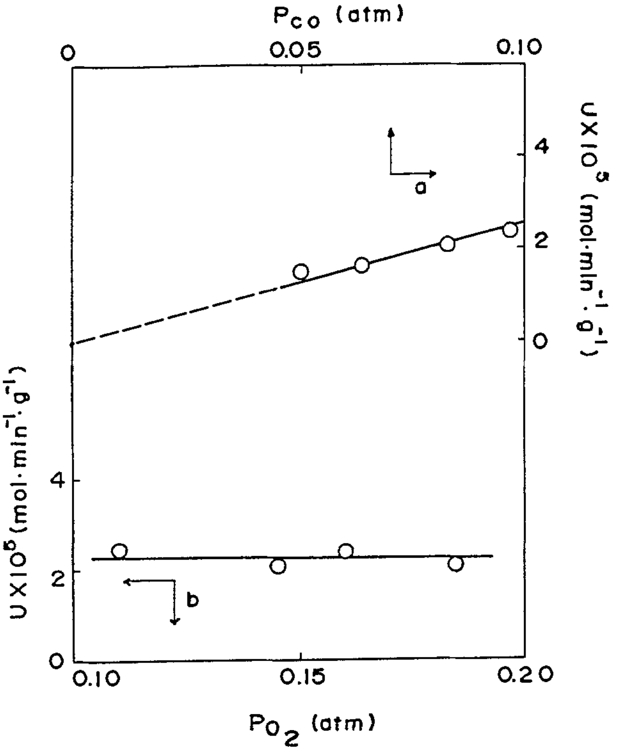

Fig. 2. Rate of oxidation as a function of partial pressure a, P_{CO} (P_{O_2} = constant); b, P_{O_2} (P_{CO} = constant).

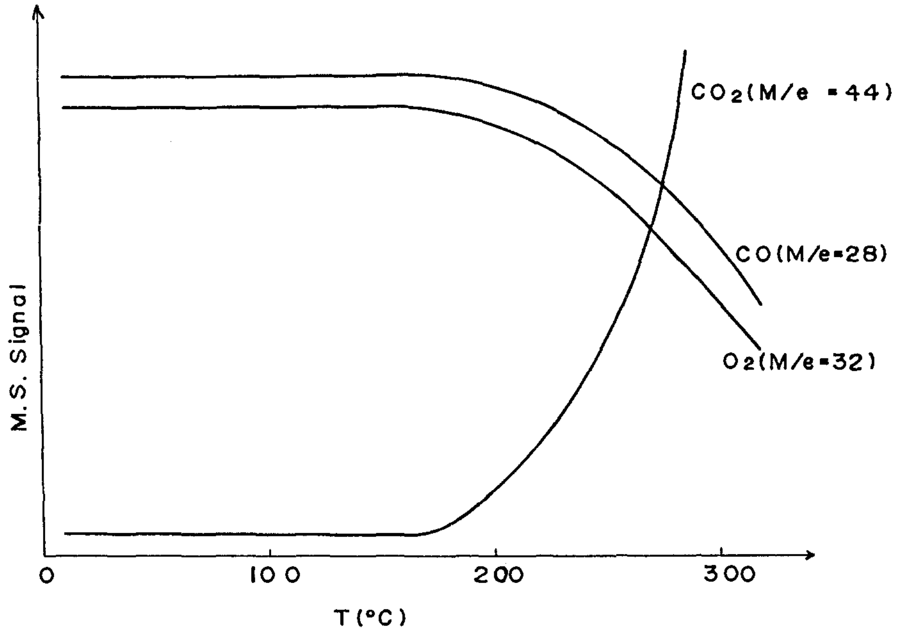

Fig. 3. MS-TPRS results of CO on $Ba_2YCu_3O_{6.92}$. Condition: CO, $4 \cdot 10^{-5}$ Torr; O_2: $4 \cdot 10^{-5}$ Torr.

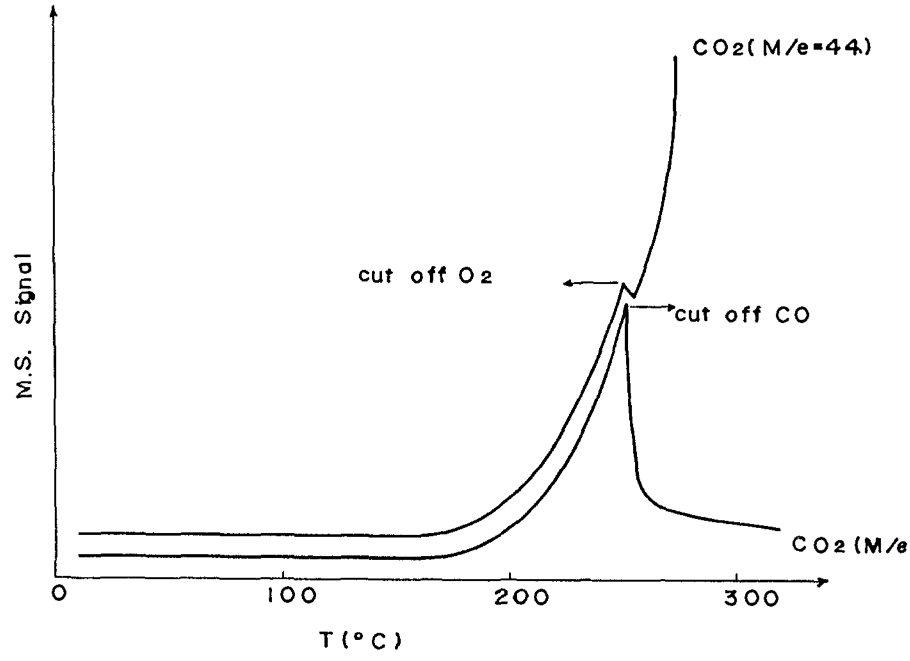

Fig. 4. Transient response results of CO on $Ba_2YCu_3O_{6.92}$ detected by MS-TPRS. CO: $4 \cdot 10^{-5}$ Torr; O_2: $4 \cdot 10^{-5}$ Torr.

detected; when the temperature is further increased the conversion of CO and the yield of CO and the yield of CO_2 increases dramatically. If the CO inlet is suddenly closed the amount of the product CO_2 decreases rapidly. Under the same condition, however, if the O_2 inlet is closed, the amounts of CO_2 still increase markedly (fig. 4). These results imply that the catalyst can supply sufficient oxygen for the oxidation of CO, i.e. it is the oxygen in the $Ba_2YCu_3O_{7-\delta}$ that reacts with the gaseous CO.

3.4. RESULTS OF CONDUCTIVITY MEASUREMENTS FOR $Ba_2YCu_3O_{7-\delta}$ AT VARIOUS TEMPERATURES

Figure 5 gives the plot of equilibrated ln σ vs $1/T$ for $Ba_2YCu_3O_{7-\delta}$ in air. The conductivity of a non-deoxidized $Ba_2YCu_3O_{6.92}$ ($\delta = 0.08$) sample, is similar

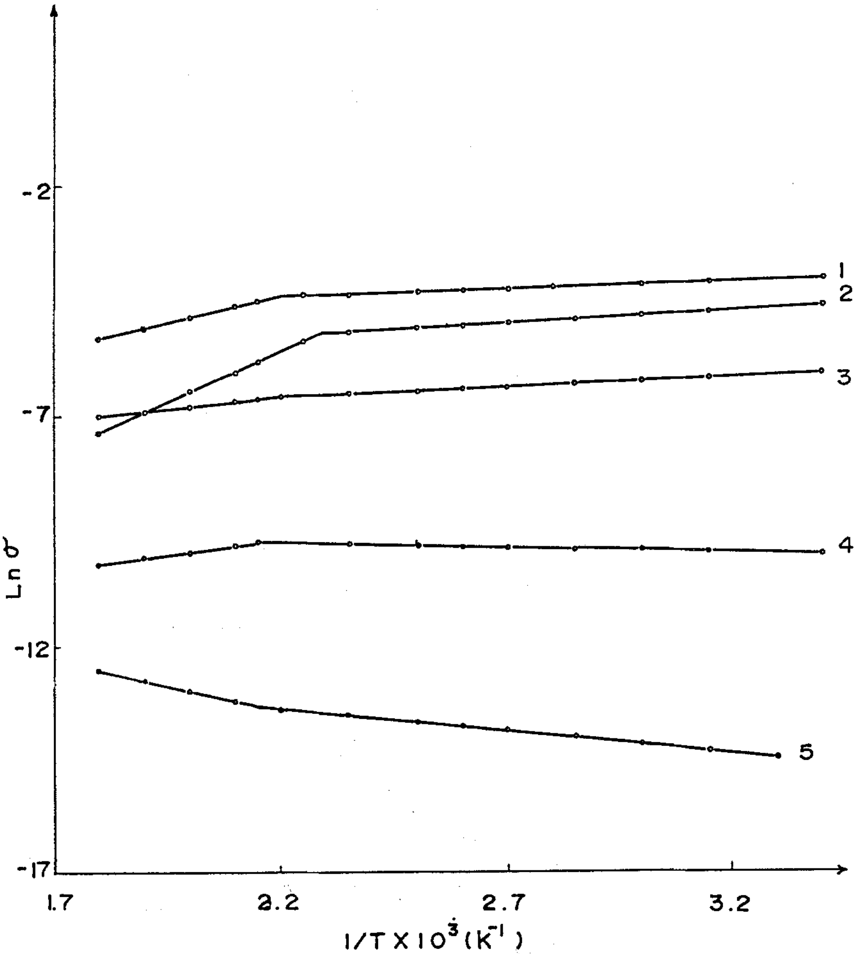

Fig. 5. Relationship between electrical conductivity and temperature for $Ba_2YCu_3O_{7-\delta}$. 1: $Ba_2YCu_3O_{7-\delta}$ ($\delta = 0.08$), 2: 400 °C, $\delta = 0.37$, 3: 500 °C, $\delta = 0.78$, 4: 600 °C, $\delta = 0.95$, 5: 700 °C, $\delta = 1.15$.

to those samples deoxidized at 400 °C ($\delta = 0.37$) and at 500 °C ($\delta = 0.78$) respectively. But the conductivities of samples with $\delta = 0.95$ (deoxidized at 600 °C) and $\delta = 1.15$ (deoxidized at 700 °C) are about 2 and 5 orders of magnitude lower than those of samples with $\delta = 0.08$ respectively. By comparing these results with those of the catalytic activities, it can be seen that the bigger the conductivities of the samples, the better the activities. The tendency of the conductivity decreasing with rising δ value is similar to that of the catalytic activity in relation to δ values. Figure 5 also shows that the slope of the straight line decreases with rising δ and eventually becomes negative, that is, the activation energy for the conduction changed gradually from negative to positive. This indicates that the properties of the $Ba_2YCu_3O_{7-\delta}$ system have changed from metal-like to semi metal-like with a decrease of the oxygen content within the temperature range studied.

4. Discussion

4.1. THE REACTION MECHANISM AND KINETICS

Following the experimental results presented above, a reaction mechanism can be suggested:

$$CO(g) + O_{\square} \dashrightarrow CO_2(g) + \square \qquad (1)$$

with which the gaseous carbon monoxide reacts with oxygen atoms located in the surface lattice point of $Ba_2YCu_3O_{7-\delta}$ to form gaseous carbon monoxide.

It has been suggested that the O-sites at the surface are different from the bulk-sites [6]. J. Haber [7] pointed out that surface lattice oxygen of metal oxide catalysts can be supplied in two ways, gaseous oxygen occupying the oxygen vacancy site and the bulk lattice oxygen diffusing to the surface and entering the oxygen vacancy site. It can be considered that the consumed surface lattice oxygen during the oxidation of CO can be compensated by both gaseous and bulk lattice oxygen so that the oxidation of CO may take place continuously. According to eq. (1), the reaction rate can be expressed by

$$r = k_1[CO] \cdot [O]_I$$

Assuming that the supplement of surface lattice oxygen is fast and the concentration of surface lattice oxygen ($[O]_I$) can be regarded constant, the rate expression becomes

$$r = k[CO] \quad (k = k_1[O]_I).$$

This is well consistent with the results from the kinetic measurements.

In the case of $Ba_2YCu_3O_{7-\delta}$, the peak temperature of the revealing oxygen obtained from MS-TPD measurements varies with the δ value. With increasing δ

the peak position shifts to higher temperature which means that the partial pressure of equilibrium oxygen (P_{O_2}) becomes lower at a fixed temperature. It can be seen from the equation $\mu = \mu^0 + RT \ln P_0$, that the smaller the P_0, the smaller the chemical potential of lattice oxygen is, and the activity of lattice oxygen weaker. Since it is the surface lattice oxygen that the gaseous CO reacts with, it can be inferred that the catalytic activity of $Ba_2YCu_3O_{7-\delta}$ would decrease with an increasing δ value. This is in fact confirmed by the activity results obtained from deoxidized $Ba_2YCu_3O_{7-\delta}$ samples at various temperatures (see fig. 1).

4.2. THE RELATIONSHIPS BETWEEN OXYGEN CONTENTS AND OXYGEN SITES, AND CATALYTIC ACTIVITY AND ELECTRICAL CONDUCTIVITY

In the process of catalytic oxidation of CO the oxygen is supplied with $Ba_2YCu_3O_{7-\delta}$ by the surface lattice oxygen and the oxygen vacancies thus formed are compensated by both gaseous oxygen and bulk lattice oxygen. This result is consistent with the reversibility of absorption and desorption of oxygen onto and from $Ba_2YCu_3O_{7-\delta}$. The desorption curve when heating is given in fig. 6(a) and the absorption curve when cooling is given in fig. 6(b). It can be deducted that the oxygen in the desorption and the absorption curves are in the same sites. Different sites of oxygen in the crystal have different thermostability depending on the crystal structure of $Ba_2YCu_3O_{6.92}$ (see fig. 7) [3,4,8]. The oxygen of the O_I site corresponding to the first peak in fig. 6(a) is the most active, while the oxygen

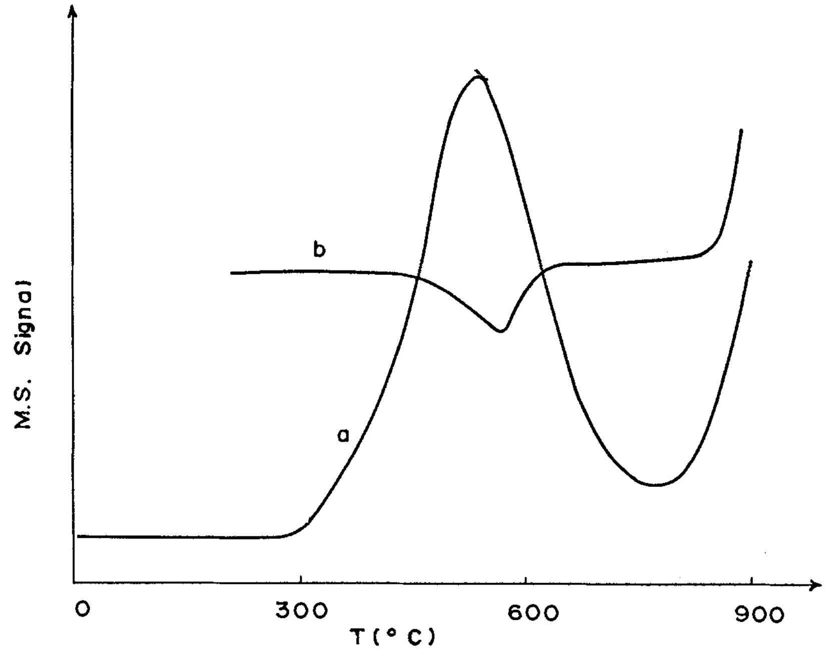

Fig. 6. TPD spectra of oxygen derived from $Ba_2YCu_3O_{6.92}$. a. heating-releasing oxygen; b. cooling-absorbing oxygen.

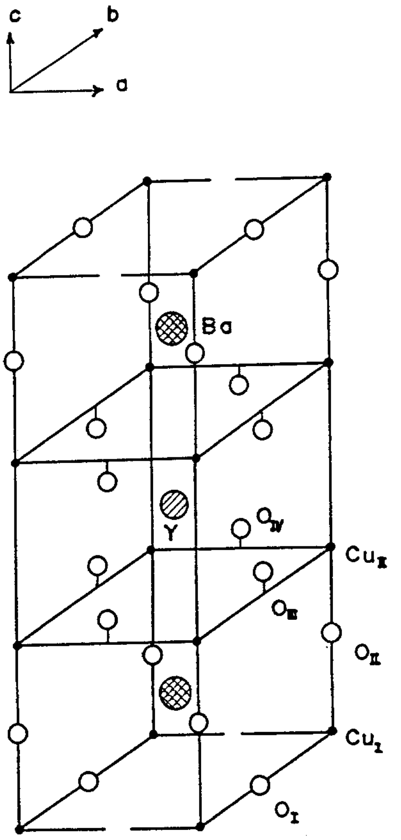

Fig. 7. The crystal lattice of $Ba_2YCu_3O_{7-\delta}$.

of the O_{III} and O_{IV} sites desorbing at above 900 °C in fig. 6(a) are much more stable. Thus it is considered that the active center of $Ba_2YCu_3O_{6.92}$ is oxygen of the O_I site.

The reaction temperature (at a conversion of 50%) representing the activity of CO oxidation is plotted with δ (see fig. 8). It can be seen from the figure that the catalytic activity of CO oxidation decreases with increasing value of δ. The value of δ has no obvious influence on the catalytic activity when δ is less than 0.9, but when δ is larger than 0.9, the effect of δ on the catalytic activity is greatly strengthened. The existence of the turning point at $\delta = 0.9$ is due to the occupation of oxygen on O_I sites being 0.92 per unit cell. The fact that the catalytic activity of CO oxidation decreases notably at $\delta > 0.9$ can be explained in the way that the oxygen taking part in the catalytic reaction is oxygen of O_{III} and O_{IV} sites only which are of lower activities.

It is generally accepted that electrons in the $Ba_2YCu_3O_{7-\delta}$ system move two-dimensionally in the x–y plane [9]. The electrical conductivity in this system may be determined by the numbers of deficiency in O_{III} and O_{IV} sites at the

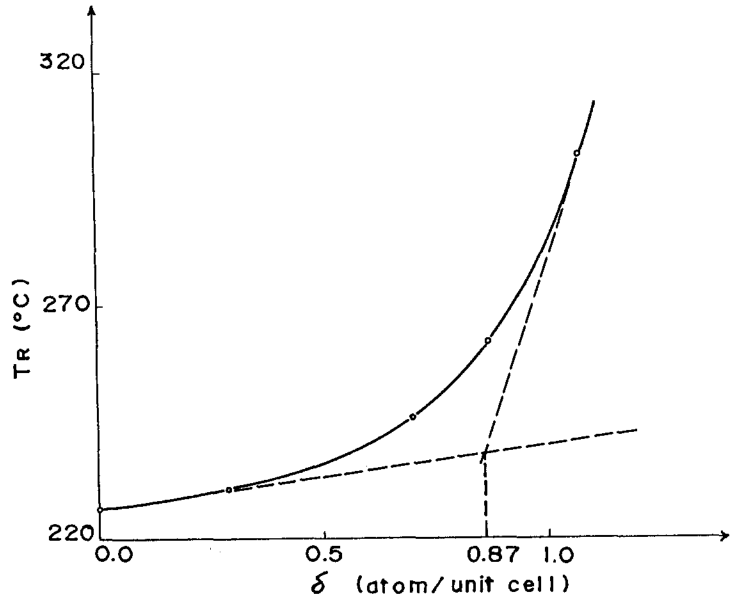

Fig. 8. The reaction temperature (when conversion = 50%) versus the value of δ.

same degree because the oxygens of the O_{III} and O_{IV} sites are in the x–y plane. It can be seen from our experimental results that the electrical conductivity of $Ba_2YCu_3O_{7-\delta}$ has no clear variation when δ is less than 0.9 because the oxygen vacancies are only located at the O_I site and no deficiency on O_{III} and O_{IV} sites at this time, but the electrical conductivity of $Ba_2YCu_3O_{7-\delta}$ decreases rapidly when δ is larger than 0.9 because there are some vacancies of oxygen in the O_{III} and O_{IV} sites now.

The essential factor which relates the catalytic activity to the electrical conductivity is that there are different amounts of oxygen in different lattice sites in the crystal of $Ba_2YCu_3O_{7-\delta}$.

Acknowledgment

This work was supported by The National Center for Research & Development on Superconductivity.

References

[1] C.W. Chu et al., Phys. Rev. Lett. 58 (1987) 405.
[2] R.T. Cava, B. Batlogg, C.H. Chen, E.A. Rietman, S.M. Zahurak and D. Werder, Nature 329 (1987) 423.
[3] W.I.F. David et al., Nature 327 (1987) 310.

[4] Q.W. Zhou, A.R. Jiang et al., Acta Physico-chimica Sinica 4 (1988) 229.
[5] W.J. Moore, *Physical Chemistry* (second edition) (Prentice-Hall Inc. Englewood Cliffs) 549.
[6] T. Nakamura, M. Misono and Y. Yoneda, Bull. Chem. Soc. Jpn. 55 (1982) 394.
[7] J. Haber, Z. Chem. 13 (1973) 241.
[8] P. Bordet et al., Nature 327 (1987) 687.
[9] T.K. Worthington, W.J. Gallagher and T.R. Dinger, Phys. Rev. Lett. 59 (1987) 1160.