THE CATALYTIC OXIDATION OF CO ON SUPERCONDUCTOR Ba$_2$YCu$_3$O$_{7-8}$

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The measurements of MS-TPD, TPRS, the electrical conductivity and kinetics on Ba$_2$YCu$_3$O$_{7-8}$ 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$_2$YCu$_3$O$_{7-8}$ have drawn the attention of a number of scientists since its discovery [1–3]. As Ba$_2$YCu$_3$O$_{7-8}$ 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$_2$YCu$_3$O$_{7-8}$ 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$_2$YCu$_3$O$_{6.92}$) 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
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catalysts was 20–40 mesh. The specific surface area determined by the BET method was 0.65 m$^2$/g. The Ba$_2$YCu$_3$O$_{6.92}$ 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 $\delta$ 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 $\delta$ 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$_2$YCu$_3$O$_{7-\delta}$

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 $1 \times 10^{-6}$ Torr, and the detection part with a pressure of $1 \times 10^{-9}$ 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 $4 \times 10^{-5}$ Torr and the actual quantities of CO, O$_2$ and CO$_2$ were detected individually while the temperature was being raised programatically.

2.5. MEASUREMENTS OF THE ELECTRICAL CONDUCTIVITIES OF Ba$_2$YCu$_3$O$_{7-\delta}$

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 $\mu$V. The measurements were made in the temperature range from 25 to 200°C. The electrical conductivity ($\sigma$) and the activation energy for conduction ($\Sigma$) were then calculated using the following equations

$$\sigma (\text{m}$\Omega^{-1}$ mm$^{-1}) = I/(2\pi s \cdot V_{2.3})$$

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