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Catalytic behavior of $YBa_2Cu_3O_{7-x}$ in the partial oxidation of ethanol to acetaldehyde

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The partial oxidation of ethanol to acetaldehyde was performed over $YBa_2Cu_3O_{7-x}$ in a flow reactor. The catalytic characteristics of $YBa_2Cu_3O_{7-x}$ were compared with those of an individual oxide comprising the $YBa_2Cu_3O_{7-x}$. The structural change of $YBa_2Cu_3O_{7-x}$ and the other catalysts after the reaction was measured by means of XRD and XPS, and it was found that the high oxidation state of copper in $YBa_2Cu_3O_{7-x}$ was responsible for the higher activity and the higher selectivity for acetaldehyde.

Keywords: $YBa_2Cu_3O_{7-x}$ oxide superconductor; partial oxidation of ethanol; oxidation state of copper

1. Introduction

Perovskite-type oxides (ABO_3) have been studied as promising catalysts that can substitute the noble metal catalysts used in the treatment of exhaust gases from cars. However, since these oxides have been revealed to show such weak resistances to sulfur compounds, studies on perovskites for the treatment of exhaust gases have been markedly reduced. Recently, as it is disclosed that $YBa_2Cu_3O_{7-x}$, a kind of perovskite-type oxide, shows the transition temperature of 90 K, which is a higher temperature than liquid nitrogen, many studies have been focussed on the physical and electrical properties of $YBa_2Cu_3O_{7-x}$.

In the viewpoint of catalysis, $YBa_2Cu_3O_{7-x}$ is expected to show a catalytic behavior other than that of the ABO_3-type perovskite, because $YBa_2Cu_3O_{7-x}$ has less oxygen content than the conventional perovskites. For this reason, $YBa_2Cu_3O_{7-x}$ has been studied as a catalyst. It includes the total oxidation and ammoxidation of toluene [1], NO decomposition [2,3], NO reduction by CO [4],

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CO oxidation [5], the selective oxidation and dehydrogenation of methanol [6], and the partial oxidation of methane [7].

$YBa_2Cu_3O_{7-x}$ is known as the first perovskite family that is composed of Cu in the B site of ABO_3 and has an oxygen-deficient structure. Considering the oxygen deficiency of $YBa_2Cu_3O_{7-x}$, this oxide superconductor can be a candidate for a partial oxidation catalyst, differing from the ABO_3-type perovskite that has been studied as a total oxidation catalyst. In this work, $YBa_2Cu_3O_{7-x}$ has been investigated as a catalyst for the partial oxidation of ethanol to acetaldehyde. In order to supplement the catalytic behavior of yttrium serial oxide superconductors, $YBa_2Cu_4O_8$ was also studied.

The superconducting phase has been reported, in most cases, to be partially decomposed during the reaction [6–8]. Hence, it is likely that the resulting stable phases such as Y_2BaCuO_5, $BaCuO_2$, CuO, and Cu metal may be responsible for the catalytic activity.

The most important point in ethanol oxidation is to maximize the acetaldehyde or acetic acid yield. Therefore, ethanol oxidation has been carried out with mild oxidation catalysts such as Fe-molybdate [9], Mo-titanate [10], Th-molybdate [11], and Ta-oxide [12]. Nevertheless, Shimizu recently reported that $La_{1-x}Sr_xFeO_3$, a perovskite-type catalyst showing high catalytic activity for total oxidation, can facilitate the partial oxidation of ethanol [13].

The oxygen content of $YBa_2Cu_3O_{7-x}$ is closely related to the oxidation state of copper [14]. The structural change of $YBa_2Cu_3O_{7-x}$ and the oxidation state of copper in $YBa_2Cu_3O_{7-x}$ before and after the reaction were extensively investigated to find the catalytic characteristics of $YBa_2Cu_3O_{7-x}$.

2. Experimental

2.1. PREPARATION AND CHARACTERIZATION OF THE CATALYSTS

$YBa_2Cu_3O_{7-x}$ was prepared by the amorphous citrate process [15] using $Y(NO_3)_3 \cdot 5H_2O$, $Ba(NO_3)_2$, and $Cu(NO_3)_3 \cdot 3H_2O$ as starting materials and was calcined at 910°C for 5 h in air atmosphere. $YBa_2Cu_4O_8$ was also prepared by the same process with the same starting materials, but it was calcined at 835°C for 48 h in an oxygen atmosphere. The CuO catalyst (min. 99% purity) was purchased from Fluka Chemical Co. The structure of the catalysts was confirmed by means of X-ray diffraction (Rigaku, D-500), while the oxygen content and the average copper valence of the catalysts were determined by iodometric titration [16]. A four probe method was used to measure the transition temperature of $YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_4O_8$. The oxidation state of copper on the catalyst surface was characterized by X-ray photoelectron spectroscopy (VSW XPS and AES), and the measured XPS binding energies were correlated for Cu $2p_{3/2}$ of the pure copper metal.

$YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_4O_8$ catalysts after the reaction were characterized by means of XRD and XPS to determine the bulk structure and the oxidation state of the surface copper. The CuO catalyst was also characterized by XRD to investigate the structural change and the copper valence before and after the reaction.

2.2. APPARATUS AND PROCEDURE

The reaction was carried out in a flow reactor of quartz tube with 4 mm i.d., where helium was used as the carrier gas. A thermocouple connected to a PID temperature controller was used to measure and control the reactor temperature within ± 1.0°C. The thermocouple was inserted onto the catalyst bed (150 mg) placed on quartz-wool support in the reactor.

Ethanol was introduced through a microfeeder into the helium–oxygen mixture and vaporized by the heating coil around the tube at the reactor inlet. The total flow rate of the feed was adjusted to 36 ml/min. The reaction products were analyzed by gas chromatography with a column of Porapack Q (2 m) at 100°C; the reaction data were taken at steady state conditions.

3. Results and discussion

3.1. CHARACTERIZATION OF $YBa_2Cu_3O_{7-x}$

The surface area of $YBa_2Cu_3O_{7-x}$ was 1.0 m^2/g, and its transition temperature was 94 K. The average copper valence and oxygen content of the fresh catalyst (the catalyst before the reaction) determined by an iodometric titration were 2.23 and 6.85, respectively ($YBa_2Cu^{2+}_{2.31}Cu^{3+}_{0.69}O_{6.85}$).

Fig. 1 shows the X-ray diffraction patterns of $YBa_2Cu_3O_{7-x}$ before and after the reaction. The structure of the fresh $YBa_2Cu_3O_{7-x}$ was confirmed as an orthorhombic structure of a nearly pure phase. However, the XRD pattern of the used (after the reaction) $YBa_2Cu_3O_{7-x}$ showed that the original structure was partly decomposed and the oxidation state of copper was changed to Cu^{2+}, Cu^{1+}, and Cu^0.

Figs. 2 and 3 represent the XPS spectra of Cu 2p and O 1s at the surface of the fresh and used $YBa_2Cu_3O_{7-x}$ catalysts. The binding energies (BE) of Cu^0 and Cu^{1+} are the same. Hence, the distinction between Cu^0 and Cu^{1+} by XPS spectra is difficult. However, the BE of Cu^{2+} is higher than that of Cu^0 or Cu^{1+} by ≈ 1.5 eV. Furthermore, Cu^{2+} can be distinguished by the presence of shake-up satellite peaks. As shown in fig. 2, the main peak of Cu $2p_{3/2}$ at the $YBa_2Cu_3O_{7-x}$ surface is observed at 934.2 eV, while a Cu $2p_{1/2}$ main peak is observed at 954.4 eV and a satellite peak at 943.2 eV. Judging from the peak asymmetry of the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ toward the higher binding energy, it is

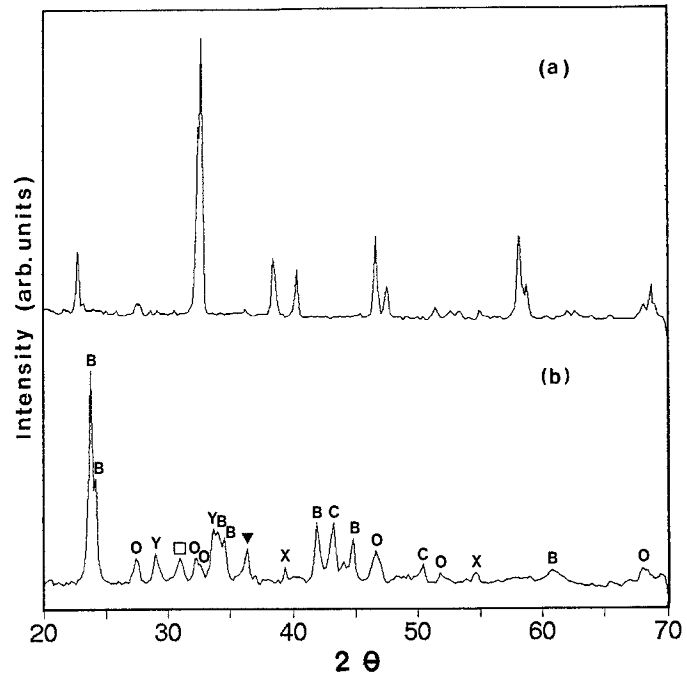

Fig. 1. X-ray powder diffraction patterns of $YBa_2Cu_3O_{7-x}$. (a) Before the reaction, (b) after the reaction, Y: Y_2O_3, B: $BaCO_3$, C: Cu, O: $YBa_2Cu_3O_{7-x}$, □: $Y_2BaCu_2O_5$, ▼: Cu_2O, X: unknown.

suggested that the fresh $YBa_2Cu_3O_{7-x}$ is composed predominantly of Cu^{2+} and partly of Cu^{3+} that contributes in shifting the peak asymmetry toward the higher binding energy. Similar observations were reported in the literature [17–19]. The data for the above XPS spectra were consistent with the BEs of Cu $2p_{3/2}$ in Cu, Cu_2O, CuO, $NaCuO_2$ and $NaCu(HIO_6)_2(H_2O)_{13}$ in the literature [20,21].

As represented in fig. 2, the BEs of Cu 2p in the used $YBa_2Cu_3O_{7-x}$ were shifted upscale about 10 eV with respect to the fresh $YBa_2Cu_3O_{7-x}$, due to the

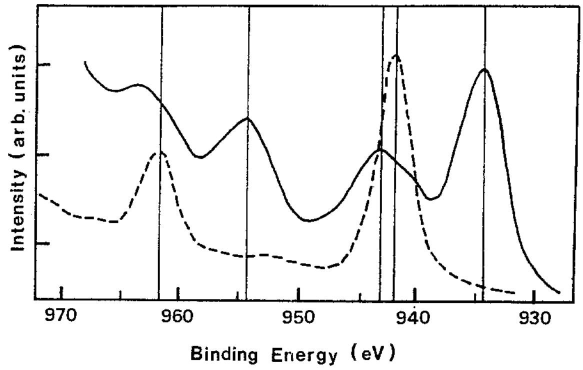

Fig. 2. X-ray photoelectron spectra of $YBa_2Cu_3O_{7-x}$ in Cu 2p region. Solid line; before the reaction, dashed line; after the reaction.

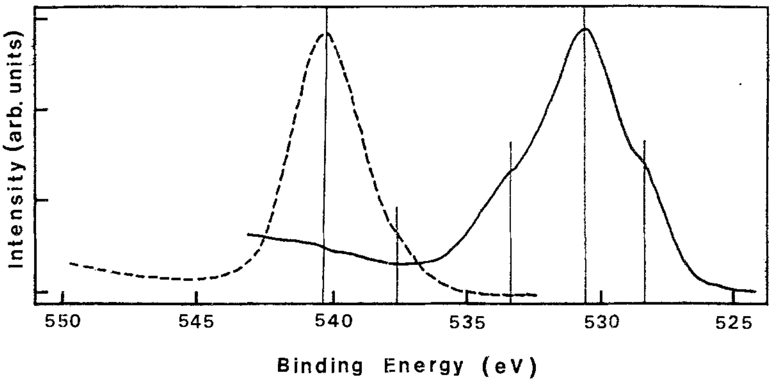

Fig. 3. X-ray photoelectron spectra of $YBa_2Cu_3O_{7-x}$ in O 1s region. Solid line; before the reaction, dashed line; after the reaction.

charging effect of the sample. Considering that the satellites representing Cu^{2+} characteristic were not observed, it was found that the oxidation state of copper at the catalyst surface was mostly changed into Cu^0 and Cu^{1+} after the reaction. This is a different point from the bulk properties of the used catalyst observed in the XRD pattern where Cu^{2+} was detected.

Fig. 3 shows O 1s XPS spectra of the fresh and used $YBa_2Cu_3O_{7-x}$. The peak at 528.4 eV in the fresh $YBa_2Cu_3O_{7-x}$ is unambiguously due to the Cu–O chain state, while the peak at 530.4 eV may be due to the contaminant species such as carbonate or hydroxide on the surface and grain boundary. The peak at 534.2 eV is probably due to the covalent mixing of the Cu 3d and O 2p states [19,22].

Fig. 3 shows that the BEs of O 1s in the used $YBa_2Cu_3O_{7-x}$ were also shifted upscale about 10 eV with respect to the fresh one, due to the charging effect of the sample. The peak observed at 537.7 eV may be due to the Cu_2O state, and the one at 540.3 eV is due to the contaminant species on the surface. The covalent mixing of the Cu 3d and O 2p state is not observed.

On the other hand, Cu 2p XPS spectra of the fresh $YBa_2Cu_4O_8$ in fig. 4 indicate that the main peaks of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ are observed at 934.2 and 954 eV, respectively and a satellite peak appears at 943 eV. This suggests that the fresh $YBa_2Cu_4O_8$ is composed predominantly of Cu^{2+} and partly of Cu^{3+} which contributes in shifting the peak asymmetry toward the higher binding energy. These values are very similar to those of the fresh $YBa_2Cu_3O_{7-x}$. However, Cu 2p XPS spectra of the used $YBa_2Cu_4O_8$ are quite different from those of the used $YBa_2Cu_3O_{7-x}$. The main peaks of Cu 2p and the satellite peak were shifted downscale about 0.4 eV and the main peak is less asymmetric in comparison to that of the fresh $YBa_2Cu_4O_8$, as shown in fig. 4. This result suggests that the oxidation state of copper in the used $YBa_2Cu_4O_8$ is mostly Cu^{2+}. The XRD pattern of the used $YBa_2Cu_4O_8$ in fig. 5 supports the XPS results. As shown in fig. 5b, although a part of the original $YBa_2Cu_4O_8$ was

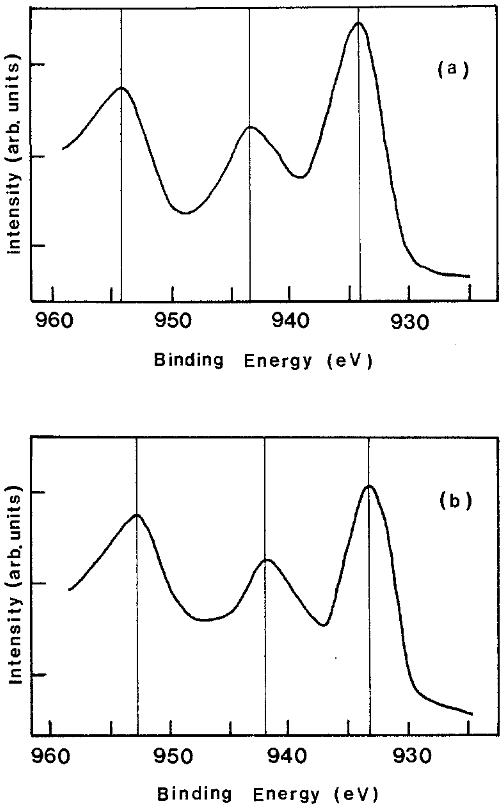

Fig. 4. X-ray photoelectron spectra of $YBa_2Cu_4O_8$ in Cu 2p region. (a) Before the reaction, (b) after the reaction.

decomposed, a large number of $YBa_2Cu_4O_8$ kept its original structure so that Cu^{2+} still mostly remained.

3.2. OXIDATION OF ACETALDEHYDE

In order to investigate the reaction route, the oxidation of acetaldehyde was carried out under the reaction condition of $C_2H_5OH = 11.8\%$, $O_2 = 10.0\%$, He = balance, and space velocity = 14400 ml/h g cat. It was confirmed that conversion of acetaldehyde was 1.8% at 300°C and 80% at 400°C. This suggests that at higher temperatures, acetaldehyde further reacts to produce CO_2.

3.3. CATALYTIC CHARACTERISTICS OF $YBa_2Cu_3O_{7-x}$ AND CuO

In order to reveal the catalytic characteristics of $YBa_2Cu_3O_{7-x}$ for ethanol oxidation, the same reaction experiments were performed over CuO, Y_2O_3, and

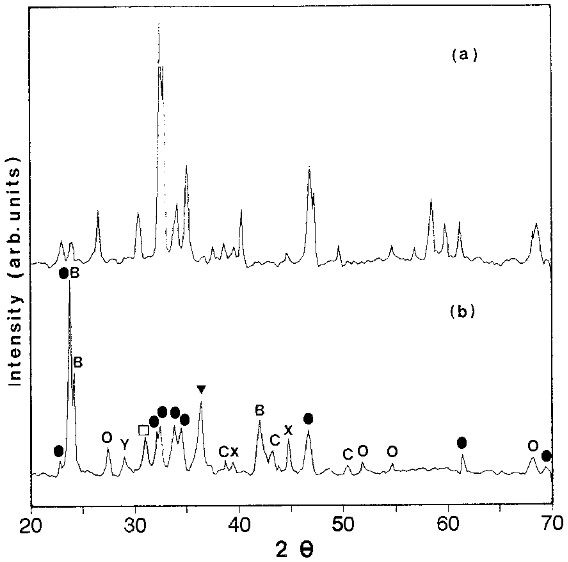

Fig. 5. X-ray powder diffraction patterns of $YBa_2Cu_3O_{7-x}$. (a) Before the reaction, (b) after the reaction, Y: Y_2O_3, B: $BaCO_3$, C: Cu, O: $YBa_2Cu_3O_{7-x}$, ●: $YBa_2Cu_4O_8$, ▼: Cu_2O, X: unknown.

$BaCO_3$, which are the key components comprising $YBa_2Cu_3O_{7-x}$, and also over $YBa_2Cu_4O_8$, one of the yttrium-serial superconductors having analogous properties to $YBa_2Cu_3O_{7-x}$. Table 1 gives the experimental results conducted at 375°C over the various catalysts including $YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_4O_8$. The catalytic activities of Y_2O_3 and $BaCO_3$ were almost negligible. In contrast with these two components. CuO showed much higher catalytic activity and selectivity for acetaldehyde. However, it is found that the selectivity for acetaldehyde of CuO is much lower than that of $YBa_2Cu_3O_{7-x}$ at nearly the same conversion over these two catalysts. On the other hand, $YBa_2Cu_4O_8$ exhibits much higher conversion than CuO. These results suggest that the catalytic characteristics of $YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_4O_8$ are related to Cu but the Cu in $YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_4O_8$ exhibits the catalytic behavior other than the Cu in CuO.

In order to investigate in detail the difference in the catalytic behavior of $YBa_2Cu_3O_{7-x}$ and CuO, ethanol conversion and selectivities for acetaldehyde and CO_2 are compared as a function of the reaction temperature in fig. 6. In the case of the CuO catalyst, the distinctive feature in fig. 6 is that the selectivity for

Table 1
Catalytic activity over various catalysts [a]

	$YBa_2Cu_3O_{7-x}$	CuO	$YBa_2Cu_4O_8$	Y_2O_3	$BaCO_3$
conversion	78.8	77.6	87.3	3.0	2.9
CH_3CHO selectivity	72.9	61.2	66.1	3.0	2.9
CO_2 selectivity	27.1	38.8	33.9	0	0

[a] Reaction conditions: $F/W = 21600$, $P_{O_2} = 9.97\%$, $P_{EtOH} = 11.77\%$, $T = 375°C$

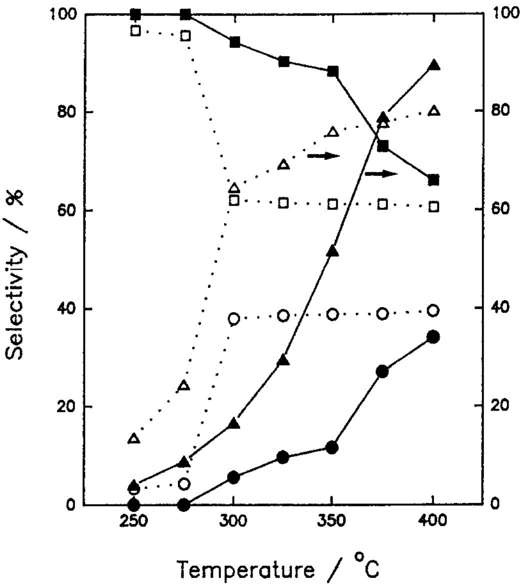

Fig. 6. Influence of reaction temperatures on ethanol conversion and product selectivities. Solid line: $YBa_2Cu_3O_{7-x}$, dotted line: CuO, $P_{O_2} = 9.97\%$, $P_{EtOH} = 11.77\%$, $F/W = 21600$ ml/hgcat., ▲ △: ethanol conversion, ■ □: CH_3CHO selectivity, ● ○: CO_2 selectivity.

acetaldehyde significantly decreases and that for CO_2 increases as the reaction temperature increases up to 300°C, while the selectivities for acetaldehyde and CO_2 stay at constant values above 300°C. On the other hand, the catalytic activity of $YBa_2Cu_3O_{7-x}$ is lower than that of CuO in the low temperature range, but exceeds the CuO activity at temperatures above 375°C, while the selectivity for acetaldehyde of $YBa_2Cu_3O_{7-x}$ is always superior to that of CuO in the experimental temperature range. Since equal amounts of CuO and $YBa_2Cu_3O_{7-x}$ were compared in this study, it is understandable that the ethanol conversion over $YBa_2Cu_3O_{7-x}$, of which the Cu content is 1/3 the Cu in CuO, was lower than that over CuO. This phenomenon strongly suggests that the differences may be due to the different oxidation states of Cu in the two catalysts. Fig. 7 gives the XRD patterns of the fresh and the used CuO measured after a series of reaction experiments from 250°C to 400°C. As represented in fig. 7b, the XRD pattern of the used CuO shows that CuO was converted to Cu_2O and Cu metal. However, the XRD pattern of the used $YBa_2Cu_3O_{7-x}$ in fig. 1b indicates that the original structure was partly decomposed but a considerable part of the original still remained. This means that there still is Cu^{2+} in the bulk of the decomposed $YBa_2Cu_3O_{7-x}$ catalyst. The presence of Cu^{2+} in the bulk of the used $YBa_2Cu_3O_{7-x}$ is the obvious difference between the two catalysts. This result suggests that the higher activity and higher selectivity of $YBa_2Cu_3O_{7-x}$ are due to the existence of Cu^{2+}. The experimental result over $YBa_2Cu_4O_8$ given in table 1 also supports the idea that

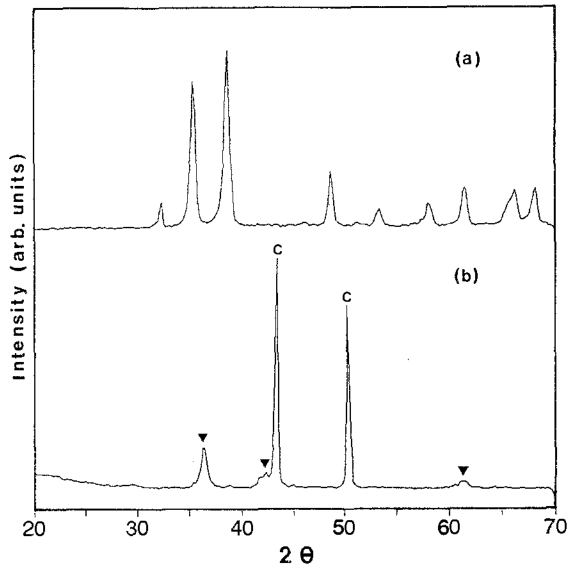

Fig. 7. X-ray powder diffraction patterns of CuO (a) before the reaction, (b) after the reaction. C: Cu, ▼: Cu_2O.

a higher Cu oxidation state enhances the catalytic activity. The selectivity for acetaldehyde over $YBa_2Cu_4O_8$ is lower than that over $YBa_2Cu_3O_{7-x}$, because ethanol conversion over $YBa_2Cu_4O_8$ is so high that a considerable amount of acetaldehyde formed under the reaction condition of low space velocity given in table 1 is converted into CO_2. As is known from figs. 4 and 5, the oxidation state of Cu in the used $YBa_2Cu_4O_8$ remains mostly Cu^{2+}.

Examining the experimental results over CuO in fig. 6 and the XRD patterns of the fresh and the used CuO, the fresh CuO seems to be gradually reduced to a lower oxidation state at temperatures up to 300°C, and then the oxidation state of Cu becomes Cu^0 and/or Cu^{1+} above 300°C. Hence, the decrease in the selectivity for acetaldehyde with the increase in reaction temperature is believed to be attributed partly to the change of the Cu oxidation state to a lower value as well as to the increase of ethanol conversion.

Integrating the experimental results for the reactions and for the catalyst characterization, it is found that the reduction of Cu in $YBa_2Cu_3O_{7-x}$ and in $YBa_2Cu_4O_8$ is more difficult than that in CuO. It is reported that the dissociation of O from CuO, which is accompanied by the reduction of Cu in CuO, is so easily proceeded that O in CuO is mostly exchanged with the gas phase oxygen [23]. However, the dissociation of the lattice oxygen from $YBa_2Cu_3O_{7-x}$ seems to be rather difficult due to the existence of an additional metal–oxygen bond (Ba–O, Y–O) in the stable perovskite structure. Accordingly, it can be presumed that the high catalytic activity of $YBa_2Cu_3O_{7-x}$ derives from the anion vacancies caused by the nonstoichiometric composition, differing from other perovskites [13].

4. Conclusion

$YBa_2Cu_3O_{7-x}$ can partially oxidize ethanol to acetaldehyde. This is a different catalytic behavior from the ABO_3-type perovskite. The catalytic characteristics of $YBa_2Cu_3O_{7-x}$ in the oxidation of ethanol were closely related to the oxidation state of copper ions and the mobility of the lattice oxygen. The difficulty of the lattice oxygen release from $YBa_2Cu_3O_{7-x}$ attributed to the less reduction of the Cu ion. It was found that Cu^{2+} was responsible for the high selectivity for acetaldehyde.

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