AMMOXIDATION OF TOLUENE OVER Y-Ba-Cu-Co-O PEROVSKITES

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Ammoxidation of toluene over the perovskites $YBa_2Cu_3O_{6.1}$, $YBa_2Cu_2CoO_{6.7}$ and $YBaCuCoO_{4.9}$ was investigated at 400°C. At low partial pressures of O_2 benzonitrile was selectively formed, while CO_2 was the main product at high pressures of O_2. Systematic differences in activity were observed for the three phases and are related to the crystal contents of Cu and Co. At low O_2 pressures, Cu-sites are active for nitrile formation, while Co-sites give CO_2. At high O_2 pressures, the activity for CO_2 of Cu-sites increases more than that of Co-sites due to filling of near-surface oxygen vacancies.

1. Introduction

Since the discovery that $YBa_2Cu_3O_{6+x}$, $x = 1$, is a superconductor with a critical temperature of about 90 K [1], a vast amount of data has been collected concerning the physical and chemical properties of this new material. Several studies, e.g. [2–11], have been made of the performance of this perovskite phase as a catalyst for a variety of chemical reactions. In our previous works [3,7], $YBa_2Cu_3O_{6+x}$ was used for the ammoxidation of toluene. We found a reversible and sharp transition in product selectivity over a catalyst with x close to zero. Benzonitrile is selectively formed at low O_2 pressure, while CO_2 is the main product when the O_2 pressure is high. The activity and selectivity for nitrile formation of $YBa_2Cu_3O_6$ is superior to that of V_2O_5, at low O_2 pressures. Co can replace Cu in $YBa_2Cu_3O_{6+x}$ to a limiting composition of $YBa_2Cu_2CoO_{6+x}$ [12]. This substitution affects the amount of oxide ions in the structure, since the limits $0 < x < 1$ apply to the undoped phase. In the phase with maximum cobalt content, the range is $0.7 < x < 1.3$ [12]. At temperatures above 200°C some oxide ions become mobile and the content of lattice oxygen in the structures becomes dependent on the atmosphere surrounding the crystals [12,13]. Recently we have prepared the perovskite phase $YBaCuCoO_5$ [14]. Chemical analysis and X-ray powder diffraction data indicate that it is isostructural with $YBaCuFeO_5$ [15] and that the content of lattice oxygen is more or less constant.

$YBa_2Cu_3O_{6+x}$, $YBa_2Cu_2CoO_{6+x}$ and $YBaCuCoO_5$ (hereafter termed 1230, 1221, 1111 for short) are three Y-Ba-Cu-Co-O perovskites which represent a substantial variation in crystal chemistry. Due to their crystal structures, these materials can expose low-index surfaces, i.e. $\{100\}$ and $\{001\}$, of very different chemical compositions depending on the actual position of the surface within the unit cell. Consequently, an important issue concerns the nature of the catalytically active sites that are present and comparative studies of 1230, 1221 and 1111 can give important clues in this regard. The present study reports about the ammoxidation of toluene over these perovskites.

2. Experimental

PREPARATION OF PHASES

Samples of $YBa_2Cu_3O_{6+x}$, $YBa_2Cu_2CoO_{6+x}$, and $YBaCuCoO_5$ were prepared from stoichiometric amounts of Y_2O_3 (Ventron, 99.99%), $BaCO_3$ (Merck, > 99%), CuO (Merck, > 99%) and Co_3O_4 (Merck, p.a.), ground together with acetone in a mortar of porcelain. The mixture was dried and reground in an agate mortar and the powder was pressed into tablets, which were placed in alumina boats. The samples were fired in air at 900°C for a period of 17 h using a tube furnace. After regrinding, new tablets were pressed and the final heating was performed in flowing N_2 (Aga Plus, < 5 ppm O_2 and < 5 ppm H_2O) for a period of 17 h. The tablets were then allowed to cool for about 5 h in the stream of N_2. The temperature was below 200°C when the samples were exposed to air and removed from the furnace. BET-surface areas of the prepared samples are in table 1.

ACTIVITY MEASUREMENTS

The catalytic activity of samples was studied in the ammoxidation of toluene by measuring the rates for formation of products in a differential and isothermal plug-flow reactor. For each experiment, about 350 mg of sample diluted with

Table 1
BET surface areas and titrimetric lattice oxygen content

Sample	Surface area [a] (m^2/g)	Oxygen content	
		before use	after use
1230	0.14	6.10	6.18
1221	0.18	6.76	6.70
1111	0.37	4.94	4.82

[a] The values were the same for fresh and used catalysts.

quartz was charged into the reactor and heated to the reaction temperature of 400°C in N_2 atmosphere. Preheated mixture of NH_3, toluene and O_2 was introduced and the partial pressure of O_2 was varied from low to high, while keeping the pressures of NH_3 and toluene constant at 2.58 and 0.77 kPa, respectively. After the experiments, the samples were rapidly cooled down in N_2 and then characterized by chemical analysis and X-ray powder diffraction. The main products, benzonitrile, CO_2 and CO were analyzed on a Varian Vista 6000 gas chromatograph as described before [16].

IODOMETRIC TITRATION

The oxygen content before and after reaction was determined by iodometric titration. The weighed sample, about 100 mg, was dissolved in a solution consisting of 15 ml of 10% KI and 5 ml of 3.5 mol l^{-1} HCl, which was diluted with 10 ml of distilled water before titration with 0.1 mol l^{-1} $Na_2S_2O_3 \cdot 5H_2O$. The end-point was determined with fresh starch solution after adding about 2–3 grams of KSCN towards the end of the titration.

POWDER X-RAY DIFFRACTION

Small portions of the catalyst samples were ground together with silicon powder, which was used as an internal standard, and then mounted on adhesive tape. Powder X-ray diffractograms were recorded with $CuK_{\alpha 1}$ radiation, wave length 1.54056 Å, in a Guinier-Hägg camera equipped with a quartz monochro-

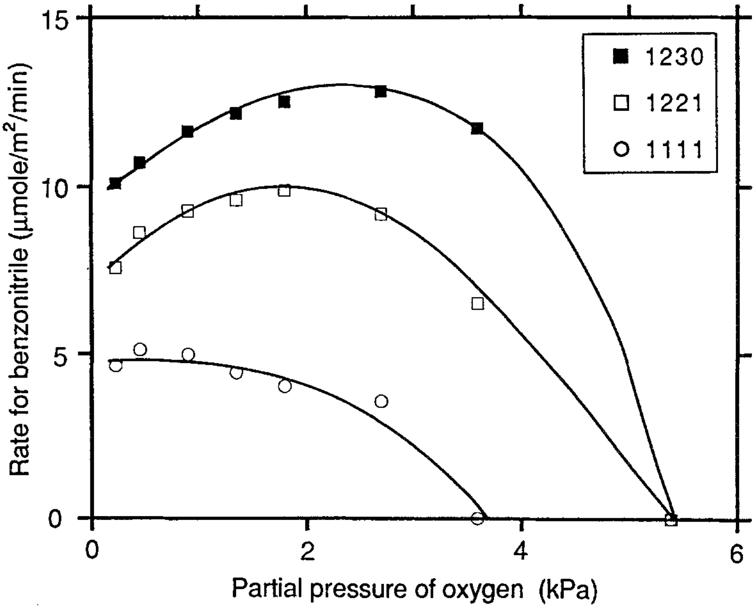

Fig. 1. The rate for formation of benzonitrile as a function of the partial pressure of O_2.

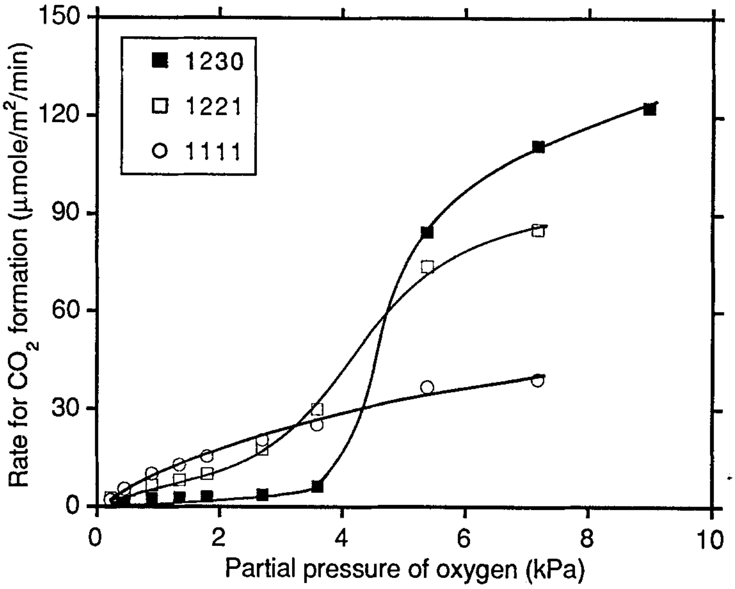

Fig. 2. The rate for formation of CO_2 as a function of the partial pressure of O_2.

mator. The camera constant was determined from the Si scattering angles and the lattice parameters of the perovskite phase were refined by the method of least-squares.

3. Results

CATALYTIC PERFORMANCE

Fig. 1 shows the rate for formation of benzonitrile over the various samples. The rates pass over broad maxima with O_2 pressure, especially for the 1230 and 1221 catalysts. In the case of the 1111 catalyst, the maximum is less obvious. A comparison of rates shows that they vary in the order 1230 > 1221 > 1111. The position of the maximum shifts towards lower O_2 pressure in the same order.

In fig. 2, the rate for formation of CO_2 is shown. At low O_2 pressures, the rate is highest for the 1111 catalyst, followed by 1221 and 1230. However, as the pressure of O_2 is increased above 4 kPa there is a transition in the rates over the 1230 and 1221 catalysts, which is sigmoidal in shape. For the 1111 catalyst a monotonous increase in rate is observed and consequently there is a reverse in the order of activity. The rate for formation of CO_2 at high pressures of O_2 varies in the sequence 1230 > 1221 > 1111.

The rate for CO formation over the three catalysts is given in fig. 3. The figure shows the same trend as in the case of benzonitrile formation, i.e., that the activity for CO formation varies in the order 1230 > 1221 > 1111 for all investi-

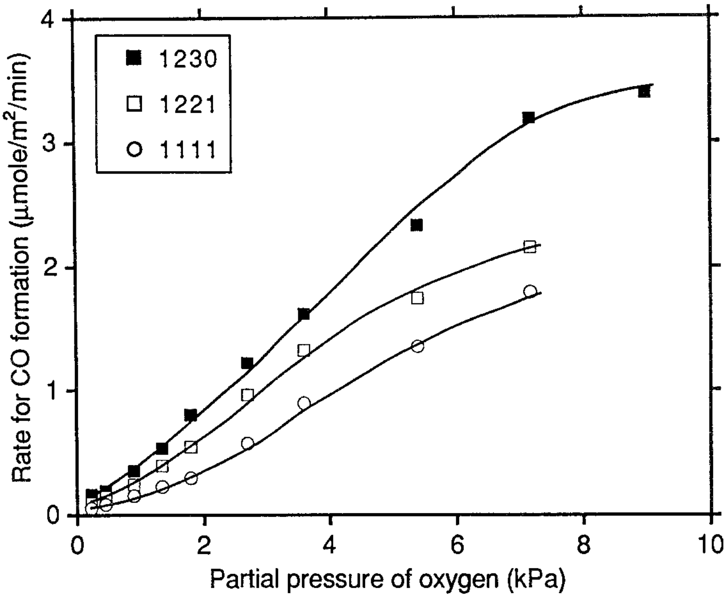

Fig. 3. The rate for formation of CO as a function of the partial pressure of O_2.

gated partial pressures of O_2 The variations of selectivity for nitrile formation with the partial pressure of O_2, fig. 4, show clear differences between the samples. The selectivity over the 1230 catalyst exceeds 70% over a range of about 3 kPa at low O_2 pressure. The selectives over the 1221 and 1111 catalysts, on the other

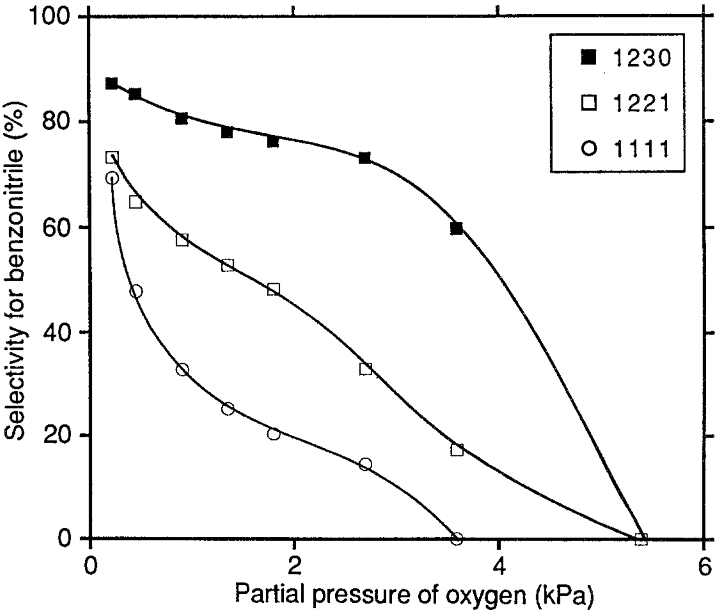

Fig. 4. The selectivity for benzonitrile formation as a function of the partial pressure of O_2.

Table 2
Tetragonal unit cell parameters determined by powder X-ray diffraction. Numbers in parenthesis are estimated standard deviations

Sample	Before use		After use	
	a(Å)	c(Å)	a(Å)	c(Å)
1230	3.8594(2)	11.819(1)	3.8580(2)	11.823(1)
1221	3.8835(3)	11.728(1)	3.8836(3)	11.731(1)
1111	3.8699(5)	7.558(2)	3.8704(3)	7.558(1)

hand, more rapidly decrease with increase in O_2 pressure. For all samples, at high O_2 pressures, the selectivity for nitrile formation is zero.

LATTICE OXYGEN STOICHIOMETRY

The iodometric titration results, table 1, show that the catalyst phases are present in a reduced state both before and after use in the catalytic experiments where the pressure of O_2 was varied from low to high. The unit cell parameters in table 2 indicate that the changes in lattice parameters are small, when the values for a fresh catalyst prepared in N_2 atmosphere, are compared to those of the used phase. It is known that the c parameter of the 1230 phase varies with the content of lattice oxygen [13,17] and the same applies for the 1221 phase [18]. The c axis repeat of 11.82 observed for the 1230 catalyst in the present study, corresponds to a lattice oxygen content of 6.15 according to the lattice parameter vs composition diagram of Rao [17]. This value is in agreement with the oxygen contents determined by titration, cf. table 1. Both titration and X-ray results thus indicate that the content of oxygen ions in the bulk of the crystals remains almost constant during the catalytic experiments.

4. Discussion

The crystal structures of 1230 [19], 1221 [12,20] and 1111 are depicted in fig. 5. The structure of $YBaCuCoO_5$ is assumed to be analogous to that of $YBaCuFeO_5$ [15]. The structures are derived from the cubic perovskite structure ($a = 3.9$ Å, unit cell content ABX_3) by ordering of the large cations (Y, Ba) along c and by introduction of vacancies in the yttrium plane. The positions in the yttrium layer are always empty, in contrast to the oxygen positions in the planes marked CuO_x and CoO_x in the 1230 and 1221 structures, respectively. Oxide ions in the CuO_x and CoO_x planes are mobile at elevated temperatures and they can leave and enter the bulk of the crystal depending on surface reactions and the composition of the surrounding gas phase. The situation in the 1111 compound is completely different, since the segment of the structure with mobile oxygens is absent in this

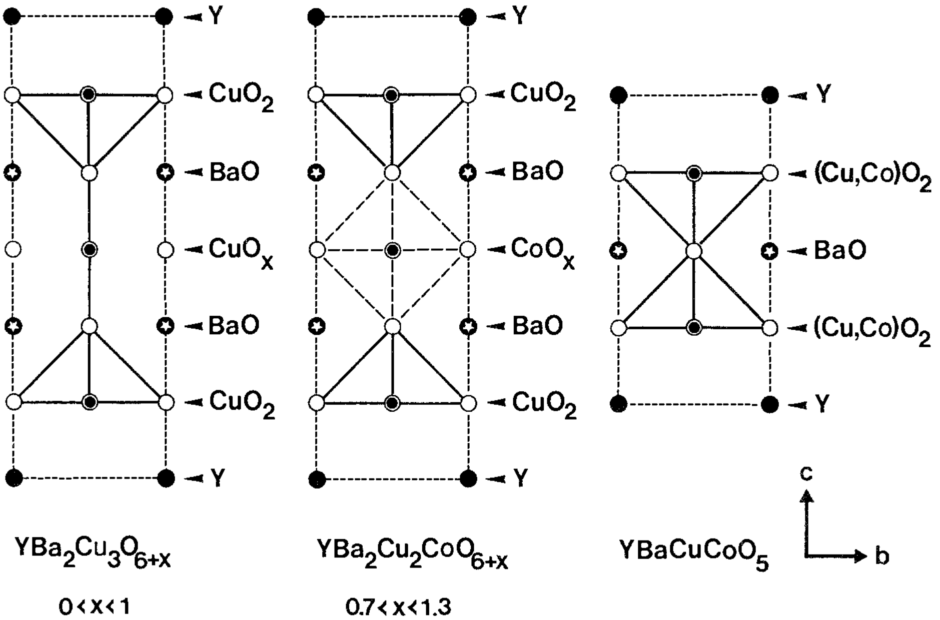

Fig. 5. Crystal structures seen along *a*. Oxygen ions are designated by unfilled circles.

type of structure, as can be seen in fig. 5, though a slight oxygen deficiency, as compared to the ideal value of 5 oxygen atoms per unit cell, is consistently observed in 1111. In order to facilitate a comparison, the normalized catalyst compositions are presented in table 3. The anion vacancies have been divided into to two categories: (i) those in the yttrium plane, and (ii) those in the rest of the structure. A systematic variation in the content of active metals (Cu, Co) and bulk vacancies is observed.

A comparison of the catalytic activities, measured at low and high partial pressures of O_2, and the catalyst composition is made in table 4. Considering the normalized contents of Y and Ba, cf. table 3, it is obvious that there is no correlation between any of these and any rate for formation of products. The rate variations are best correlated to the differences in contents of Cu and Co of the samples. This finding is not surprising since it is known that Cu and Co oxides

Table 3

Actual catalyst composition normalized to ABX_3 stoichiometry, where A designates large cations and B small cations, while X stands for oxide ions and vacancies

Phase	A	B	X_3 [a]
1230	$Y_{0.33}Ba_{0.67}$	$Cu_{1.00}Co_{0.00}$	$O_{2.05}[\ ]_{0.33}(\ )_{0.62}$
1221	$Y_{0.33}Ba_{0.67}$	$Cu_{0.67}Co_{0.33}$	$O_{2.24}[\ ]_{0.33}(\ )_{0.42}$
1111	$Y_{0.50}Ba_{0.50}$	$Cu_{0.50}Co_{0.50}$	$O_{2.44}[\ ]_{0.50}(\ )_{0.06}$

[a] Anion vacancies are symbolized by ( ), except those in the yttrium plane, which are symbolized by [ ].

Table 4
Comparison of catalyst composition and rates for formation of products, r (μmol m^{-2} min^{-1})

Phase	Cu	Co	( ) [a]	at low $P(O_2)$ [b]		at high $P(O_2)$ [c]
				r(nitrile)	$r(CO_2)$	$r(CO_2)$
1230	1.00	0.00	0.62	13	2	109
1221	0.67	0.33	0.42	10	11	85
1111	0.50	0.50	0.06	4	18	40

[a] Anion vacancy, cf. table 3.
[b] 2 kPa.
[c] 7 kPa; r(nitrile) = 0.

are active for combustion of toluene at comparatively high partial pressures of O_2 [21]. Also, it has been found that copper oxide is active and selective for partial oxidation of propene to acrolein on the condition that its surface is in a reduced state, i.e. at low partial pressures of O_2 [22,23]. From table 4 it is seen that at low O_2 pressure, there is a relationship between the rate for formation of benzonitrile and the sample content of Cu. The modest rate for formation of CO_2 at low O_2 pressures seems to strongly depend on the content of Co, while at high O_2 pressures, this rate can primarily be correlated to the content of Cu. Possible correlations between rates and the concentration of type (ii) oxygen vacancies in the bulk are of less significance, since we found that the bulk content of vacancies is almost constant during the transition in selectivity, see table 1. It is reasonable to assume though, that the concentration of surface oxygen vacancies is variable, as long as the reservoir of mobile bulk oxygens is almost empty as in the case of the 1230 and 1221 catalysts in this study. However, when the concentration of mobile oxygen in the bulk is high, it is impossible to have large number of vacancies in the surface region. This is in agreement with our earlier finding, that total combustion is obtained when $x > 0$ in $YBa_2Cu_3O_{6+x}$ [3,7].

The observation that the rates for formation of benzonitrile and CO_2, at low and high partial pressures of O_2, respectively, are related to the Cu-content, suggests that the same Cu-sites are involved in the formation of both products. Comparison of the rates for formation of CO_2 over the samples, fig. 2, shows that the degree of transition, from low to high partial pressure of O_2, increases with the Cu-content of the sample. This relationship infers that the structure and selectivity of the active Cu-site is dependent on the pressure of O_2, and indicates filling of nearby vacancies with increase in O_2 pressure. However, this filling must be confined to the surface and near-surface regions, since it could not be confirmed by determination of the bulk oxygen content, cf. tables 1 and 2. In order to propose a model of active site, it is also necessary to consider that imido and oxo species have been implicated in partial (amm)oxidation mechanisms [16,24,25]. For combustion, on the other hand, it has been established that electrophilic oxygen species, O^-, are involved [16,24,26]. These species attack the adsorbed hydrocarbon in its region of highest electron density, i.e. the aromatic ring, leading to degradation and, eventually, formation of carbon oxides. Thus, from the above considerations, the formation of nitrile at low partial pressures of O_2 can be proposed to occur on cu-sites surrounded by a relatively large number of surface vacancies, i.e. on a reduced surface. At high partial pressures of oxygen, low NH_3/O_2 ratios, the filling of vacancies in the near-surface region changes the character of the active oxygen species of Cu-sites from O^{2-} to electrophilic O^- type, because Cu has to share its valence electrons with additional oxygen species. This oxidized surface is selective for the formation of CO_2.

The finding that the rate for formation of CO_2 primarily depends on the Co-content at low pressures of O_2 and on the Cu-content at high O_2 pressures, does not mean that Co-sites are inactive for combustion at high O_2 pressures. Contrarily, it shows that there is a normal pressure dependency for formation of CO_2 over the Co-sites (no transition), inferring that with increase in O_2 pressure no change occurs in the electronic character of the oxygen species at the Co-site.

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