JOURNAL OF MATERIALS SCIENCE **32** (1997) 2895–2902

The electrical and catalytic properties of $YBa_2Cu_3O_{7-x}$ for oxidation reactions below 400 °C

M. CALDARARU*
Institute of Physical Chemistry "I.G. Murgulescu" of the Romanian Academy,
Spl. Independentei Nr. 202, Bucuresti 77208, Romania

A. OVENSTON, J. R. WALLS
Department of Chemical Engineering, University of Bradford, West Yorkshire BD1 7DP, UK

The a.c. electrical and catalytic properties of $YBa_2Cu_3O_{7-x}$ have been investigated by *in situ* dynamic experiments. The data indicate a strong dependence of surface conduction on chemisorbed species which, if loosely bound, cause fluctuations. Proton-donating compounds produce an increase in conductivity and an oscillating behaviour. Fluctuations can also be associated with instability of the basic matrix at low temperatures in various atmospheres, and may explain the somewhat erratic catalytic properties of this material. In particular, the presence of water may lead to blocking of some adsorption-active catalytic sites.

1. Introduction

The high-temperature superconductor $YBa_2Cu_3O_{7-x}$ (YBCO) is a mixed conductor at elevated temperatures, whose properties are largely dependent on the deviation from stoichiometry x, with $0 \leqslant x \leqslant 1$. It is a good oxygen ion conductor in the medium temperature range 300–500 °C, with an activation energy of about 2.6 eV above 390 °C and about 2.2 eV below 370 °C [1]. Porosities between 20% and 40% were reported to have little effect on these values.

The ease of removal of lattice oxygen has been recognized as a potentially useful property for providing oxygen for catalytic oxidation reactions [2]. A recent review of high-temperature superconductors in catalysis with a summary of the activity and selectivity of such materials and related cuprates for a wide variety of catalytic reactions, was conducted by Klissurski and Rives ([3] and references therein).

YBCO is a complex material. A tetragonal/orthorhombic phase change occurs at different x values depending on the temperature and oxygen partial pressure during annealing, as well as on the method of preparation and on the cooling rate. Methods for determining the value of x were reviewed. Temperature-programmed desorption of oxygen for YBCO has shown that the onset temperature for oxygen evolution is 390 °C, maximum evolution being attained at 500 °C [3]. Furthermore, thermogravimetric analysis (TGA) showed the uptake and release of oxygen to be smooth, reversible and rapid at temperatures as low as 400 °C.

There has also been considerable debate concerning the barium-rich phase equilibria in the phase diagram of the Y–Ba–Cu–O system. The difficulty in assigning unique stoichiometries is compounded by the fact that many of these phases have related structures and quite similar *d*-spacings [4–6] (for further details see Section 4).

In situ XRD studies have shown the steady removal of lattice oxygen (increasing x) with a gradual conversion from orthorhombic (O) to tetragonal (T) structure. Yan *et al.* [7] showed that for the composition range $0.6 > x \geqslant 0$ at room temperature, only the two orthorhombic varieties OI and OII (whose perfect structures correspond to ideal composition $x = 0$ and 0.5, respectively) exist as thermodynamically stable phases. Below 400 °C, YBCO should remain in the O state (semi-metallic, superconducting phase) in oxygen partial pressures from 0.1%–100% (in $O_2:N_2$ mixtures) [7]. Above about 350 °C, slight loss of oxygen occurs accompanied by a slow change to the tetragonal state (semiconducting, non-superconducting phase). At 350 °C, the deviation from stoichiometry, x, is about 0.04, and may rise to a maximum of about 0.13 at 500 °C. Hegde and Ramesh [8] have also recently reviewed progress with layered YBCO (123) type defect perovskites, emphasizing structure, non-stoichiometry, oxygen reactivity and catalytic behaviour for a variety of reactions. In particular, elemental substitution is presented as a chemical means to modify the catalytic activity.

---

* Author to whom all correspondence should be addressed.

The electrical properties of YBCO at elevated temperatures and the potential of this material for high-temperature catalytic oxidation reactions in a reactor in which the catalyst is heated by r.f. power have already been reviewed [9]. The link between observed behaviour for methane oxidation (both complete and partial) and the electrical properties of the catalyst have also been discussed [10]. Changes in electrical characteristics arising from the ease of removal of lattice oxygen and the effects of exposure to different atmospheres, illustrate the vulnerability of this material for use at temperatures above 400 °C [11]. For reactions in which H_2O and CO_2 are significant products, possible degradation of the catalyst may inhibit its use.

Hence, between room temperature and 400 °C, the bulk of the material should essentially remain in the orthogonal crystalline state, exhibiting semi-metallic behaviour with a negligible effect of frequency, regardless of the state of oxidation of the catalyst. However, in the surface layers, more substantial changes in oxygen content may occur, particularly when the surface is exposed to different atmospheres. Fluctuations in the powder conductivity are connected to fluctuations of local surface composition (produced by changes in composition of the gaseous atmosphere); they suggest a complex history-dependent behaviour of the surface conductivity which may also be manifested in the catalytic properties, which are reported here.

2. Experimental procedure

YBCO powder was synthesized by the solid-state reaction method from Y_2O_3, $BaCO_3$ and CuO as described previously [9]. Catalyst grains ($1.5\ cm^3$, 0.2–0.6 mm diameter) were placed between two cylindrical tantalum electrodes in a special glass reactor providing *in situ* electrical conductivity and catalytic activity measurements in a flow system, as described elsewhere [12, 13]. The a.c. electrical conductivity was measured *in situ* using a semiautomatic precision bridge Tesla BM 484 at a fixed frequency of 1592 Hz.

Various gases have been flushed ($69\ cm^3\ min^{-1}$ unless otherwise mentioned) during thermal cycling between 20 and 400 °C (with slow programmed heating at $2\ ^\circ C\ min^{-1}$ and fast cooling at about $10\ ^\circ C\ min^{-1}$ in the same atmosphere). The composition of the effluent was permanently monitored by gas chromatography (thermal conductivity detector, two parallel 1.5 m columns of Porapak Q and 0.5 nm molecular sieves).

The order of the cycled experiments was as follows: (1–3) dry argon (Dry Ar 1–3); (4) dry oxygen (Dry O_2); (5) humid oxygen with 2.5 mg $H_2O\ l^{-1}$ (Humid O_2); (6) dry argon (Dry Ar-4); (7) propylene–air (C_3H_6/air). After experiment 7, the activity for propylene oxidation was tested for 10 h in stationary conditions, then the conductivity and catalytic activity in the CO–air mixture were measured in temperature-programmed heating (experiment 8) and stationary conditions.

The mixture of propylene or carbon monoxide with air was 1 : 10 (unless otherwise mentioned). The catalytic activity was measured between 150 and 425 °C. The analysis for evaluating catalytic activity was done by periodically sampling during temperature-programmed heating experiments or by repeated sampling after temperature stabilization in some specific cases (see below).

3. Results

In order to allow for a correct understanding of the atmosphere-dependent surface dynamics, the data will be presented following the succession of the experiments; surface conditioning was performed in heating–cooling cycles (experiments 1–3) in dry argon. A rather large amount of water was found to be present in the effluent on heating the fresh YBCO up to 400 °C in argon. Much less was found in the next dry argon experiments below 350 °C but a still high amount was found above this temperature, as shown in Fig. 1a. The loss of water obviously occurs in at least two steps. One, having the maximum centred around 150 °C, is probably related to the loss of molecularly adsorbed water. Another step, above 350 °C, is still important after repeated thermal cycling in a dry inert atmosphere; it obviously accounts for surface dehydroxylation. Correspondingly, the conductivity apparently increases on dehydration in the low-temperature range (experiment 2) and for the whole temperature domain (experiment 3, Fig. 1b).

The values of the electrical conductivity in the third run are increased with respect to the fresh sample (Fig. 2) in relation to some surface reduction. However, generally, the variation of the conductivity (even in the third dry argon experiment) was rather large above 215 °C ($1000/T = 2.05$) and difficult to measure due to an apparently superimposed oscillatory behaviour; slow oscillations are still observed in dry oxygen at low temperature ($1000/T$ between 2.85 and 1.85, Fig. 2) while in humid oxygen and propylene–air flow they again appear to be increased in intensity and frequency (Fig. 3a). Still oscillating, but more stable values were measured in experiment 6 (Dry Ar-4), when some water was evolved in the effluent (Fig. 3b). Thus, the oscillations may be associated (in this low-temperature, low frequency-range, where surface effects control the electrical conductivity) with some thermally activated adsorption–desorption processes, or with some structural rearrangements of the surface layer in the presence of oxygen and water (possibly as surface OH groups) in the intergrain area.

Generally, the logarithmic plot of conductance, G, versus $1/T$ in dry argon consists of at least two parts, with different apparent activation energies, namely

Dry argon (I)	below 190 °C, 0.06 eV
	above 190 °C, 0.61 eV
Dry argon (III)	20–130 °C, 0.06 eV
	130–240 °C, 0.31 eV
	240–400 °C, 0.63 eV

As mentioned, the temperature dependence of the conductance, G, under the treatment in dry oxygen seems to be rather complex at low temperatures (Fig. 2). However, lower, but more stable values for conductance were shown above 300 °C with an activation energy of 0.93 eV.

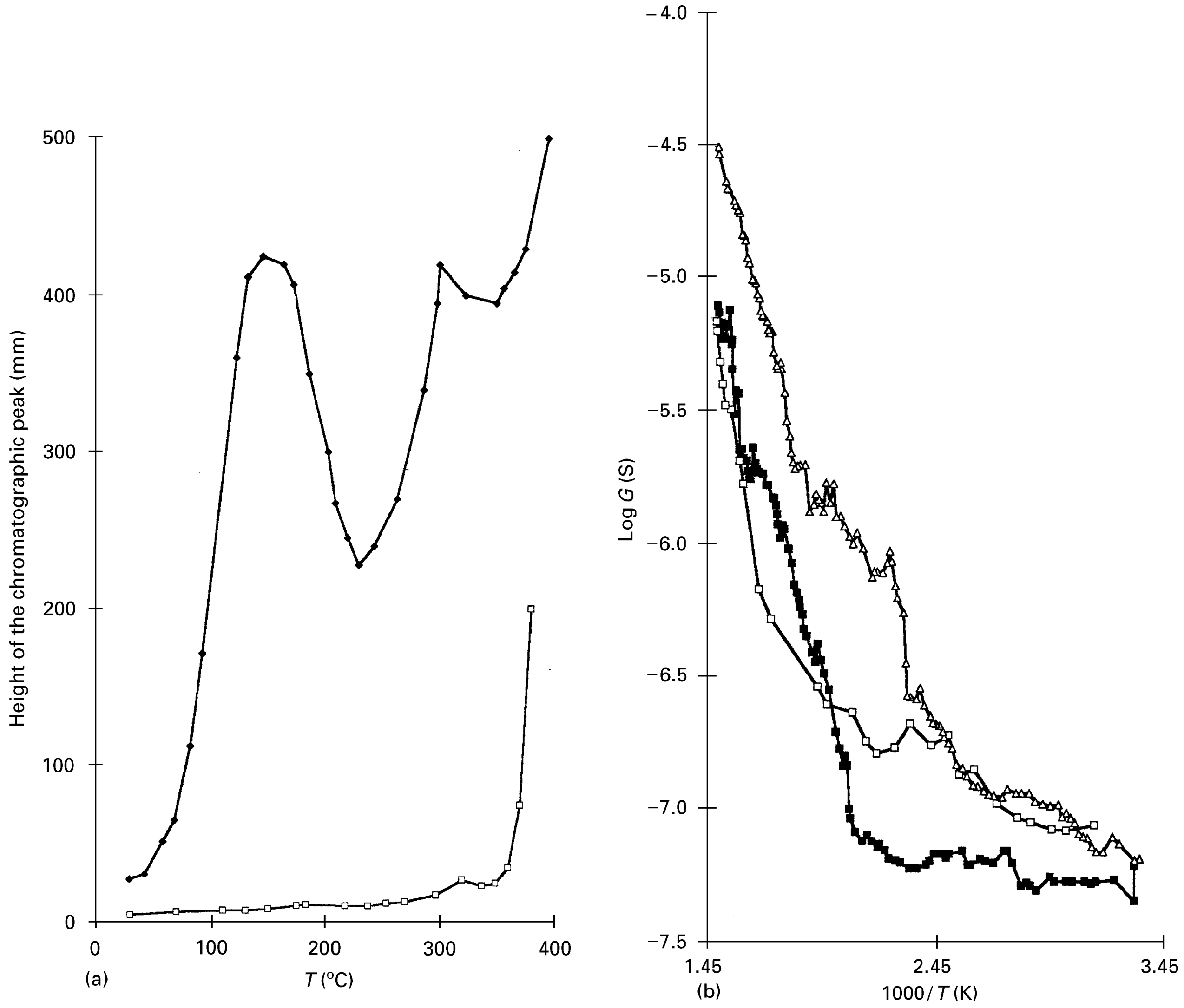

Figure 1 (a) Water evolution in the effluent on heating in dry helium. (◆) Dry Ar-1, (□) Dry Ar-3. (b) Temperature dependence of conductivity on cycling in dry argon, (■) Dry Ar-1, (□) Dry Ar-2, (△) Dry Ar-3.

The propylene–air conductivity plot (experiment 7) may be very well superposed (Fig. 3a) on the previous humid oxygen plot (experiment 5), which suggests that the propylene interaction with the YBCO surface in the presence of oxygen results in similar charge-transfer effects to those in the presence of water (see Section 4).

The catalytic activity for propylene oxidation was initially measured in the temperature-programmed heating regime by periodically sampling from the effluent. The main oxidation product was carbon dioxide which was found to appear above 250 °C. However, very small traces of other products, such as formic aldehyde, acetaldehyde and acrolein have been found at lower temperatures. The results are presented in Table I.

After cooling, and fast heating again, the temperature was maintained at a constant level and the catalytic activity was measured under stationary conditions. The results are presented in Table II.

The temperature dependence of the propylene conversion is seen to be irregular at low temperatures; this may be an indication of contamination of the surface with strongly adsorbed hydrocarbonated fragments; on the other hand, this fluctuating activity could result from consecutive adsorption/chemical interaction of the reaction products with traces of various phases possibly present in the surface layer as a result of local restructuring.

Measurements at constant temperature in propylene–air mixtures revealed faster increase of conductivity (i.e. increased reducibility) above 350 °C.

After cooling in air, electrical conductivity (Figs 3a and 4) and the catalytic activity for CO oxidation was then measured in CO : air mixtures. Water was again present in the effluent (Fig. 3b), together with traces of propylene. This seems to indicate that some water and strongly adsorbed propylene species could be removed by CO or simply on reheating (some contamination of pre-catalytic paths with propylene is also suspected). Even in these conditions (i.e. in the presence of traces of propylene), small amounts of carbon dioxide appeared only above 220 °C. This temperature corresponds to the inflexion point in the Arrhenius-type plot of the conductivity. Carbon monoxide conversion was evaluated, as shown in Table III. The activity for carbon dioxide formation increased after maintaining the temperature at about 400 °C.

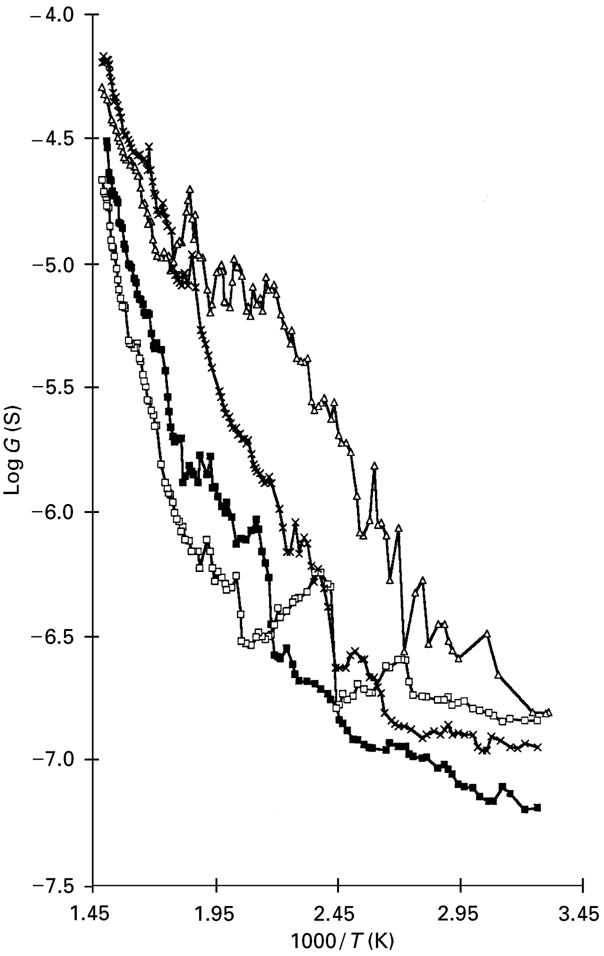

Figure 2 Effect of dry and humid oxygen on the conductance–temperature characteristics. (■) Dry Ar-3, (□) Dry O_2, (△) Humid O_2, (×) Dry Ar-4.

This was accompanied by the sharp increase of the electrical conductivity. Control experiments, repeated by decreasing the temperature, revealed higher conductivity values with respect to the previous measurement at the same conditions, which suggests some reduction and/or sintering may have occurred. A comparison of conductivity in dry conditions (in argon, in dry oxygen and in CO–air mixture) indicate surface reduction (i.e. increased conductivity) in the presence of CO (Fig. 4).

The CO tests had to be discontinued owing to a blockage in the gas flow. It is possible that this occurred due to surface contamination with carbonaceous deposits; however, the lack of improvement on prolonged heating in flowing air at 400 °C indicates that fouling is not the main cause. Sintering in reducing conditions and/or lattice expansion seem to be a more appropriate explanation for this reproducible effect.

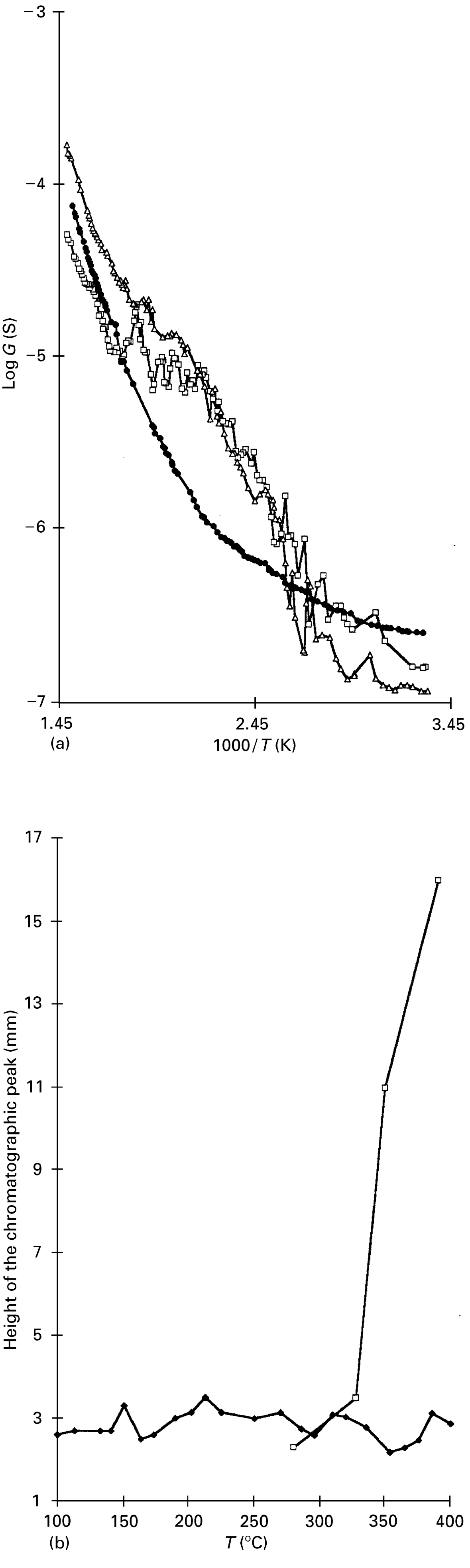

Figure 3 (a) Effect of atmospheres of C_3H_6–air and CO–air on the conductance–temperature characteristics. Humid oxygen shown for comparison. (□) Humid O_2, (△) C_3H_6–air, (●) CO–air. (b) Water evolution in the effluent on heating in dry helium following experiments in dry and humid oxygen and in CO–air (following the experiment in propylene–air). (◆) Dry Ar-4, (□) CO–air.

TABLE I Propylene oxidation, during programmed heating ($2\,^{\circ}C\,min^{-1}$) in a propylene–air mixture, 1:10, flow rate $69.3\,cm^3\,min^{-1}$, $\tau = 1.3$ s. Conversion C is evaluated from propylene consumption.

Temperature (°C)	C (%)	Products
132	4.5	Formic aldehyde, acetic aldehyde, acrolein, etc.
225	2.0	As above
315	9.8	As above plus carbon dioxide
359	8.8	Formic aldehyde, acetic aldehyde, acrolein, etc
399	12.0	As above
401	18.0	100% carbon dioxide

TABLE II The activity for propylene oxidation under stationary conditions (propylene: air 1:10). C is moles % propylene converted. S the selectivity is moles % of total product converted into a specific product as indicated.

Temperature (°C)	C (%)	S_{CO_2} (%)	S_{others} (%)
353	11.6	6.0	94.0 (acrolein 5.9)
350[a]	5.6	15.0	85.0
375	1.8	42.1	67.9 (acetaldehyde 9.1, acrolein 48.8)
400	8.2	95.0	5.0
402[b]	13.6	100	
408[c]	20.2	34.0	66.0
421	32.5	30.0	

[a] After testing for 1 h.
[b] Propylene: air = 1:19, $\tau = 1.3$ s.
[c] Propylene: air = 1:13, $\tau = 2$ s.

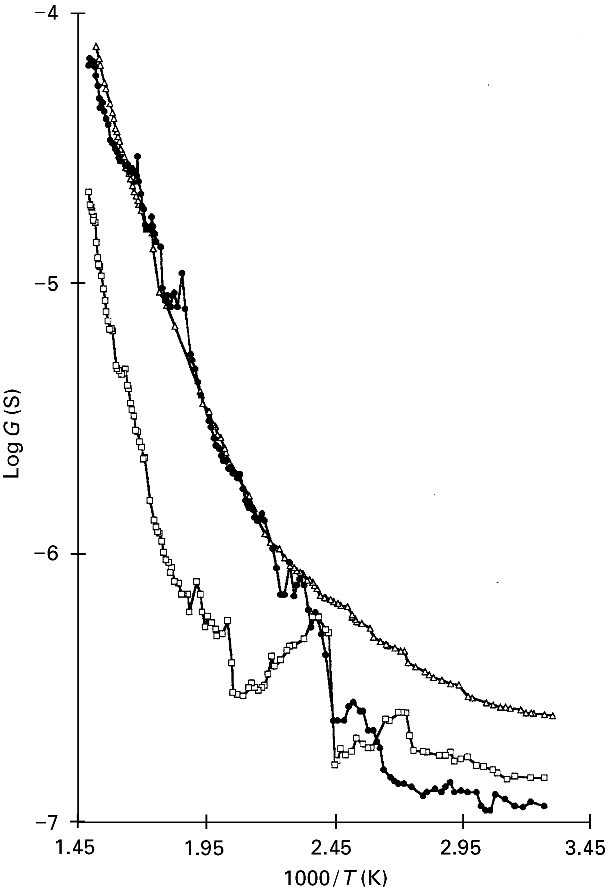

Figure 4 Comparison of conductance–temperature characteristics in dry conditions. (□) Dry O_2, (△) CO–air, (◆) Dry Ar-4.

TABLE III Catalytic activity for CO oxidation. Conversion C is percent CO converted.

Temperature (°C)	C(%)	Conditions
237	2.9	CO: air = 1:10, $\tau = 1.3$ s
256	8.3	
303	18.2	CO: air = 1:12, $\tau = 2$ s
320	44.1	
335	43.3	
350	87.2	
370	94.9	

4. Discussion

In different atmospheres, the observed changes in conductance–temperature characteristics principally arise from surface chemisorption effects which can lead to dipole relaxation phenomena [14]. These are manifested in dipolar contributions to the a.c. conductance, particularly at lower temperatures. Relaxation losses due to individual dipoles are much more frequency dependent than temperature dependent; the number of dipoles contributing to this loss process will, however, depend on thermally activated chemisorption of absorbed species. Thus temperature will play a role, but has generally been found to be less important than that of frequency. At high temperatures, the effective a.c. conductance may be governed by thermally activated bulk conduction of ions and electrons throughout the material.

The Y–Ba–Cu–O system contains three superconducting phases: $YBa_2Cu_3O_{7-x}$, $YBa_2Cu_{3.5}O_{7.5-x}$ and $YBa_2Cu_4O_8$ [4]. The low-temperature metastability of the oxidized variant of the $YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_{3.5}O_{7.5-x}$ phases has been demonstrated ([4] and references therein). Under conditions of partial pressure of oxygen of 1 atm and low temperature, the $YBa_2Cu_3O_{7-x}$ superconductor is unstable with respect to a mixture of the $YBa_2Cu_4O_8$ and the non-superconducting Y_2BaCuO_5 and $BaCuO_2$ phases; $YBa_2Cu_4O_8$ appeared to be the most stable superconductor at low temperature. It could not be prepared below 675 °C at 1 atm oxygen [5]. $YBa_2Cu_4O_8$ decomposition at low temperature in the presence of oxygen can be illustrated by the reaction

$$1/2O_2\,(g) + 2YBa_2Cu_4O_8 = Y_2O_3\,(s) + 2Ba_2Cu_3O_6\,(s) + 2CuO\,(s) \qquad (1)$$

Y_2BaCuO_5 seems to be one of the most stable high-temperature compounds in this system, but it could not be prepared at low temperatures in pure oxygen. It was also shown to be metastable below 728 °C [4].

The possible prior existence of small amounts of some different binary and/or ternary component phases (as a result of incomplete reaction of the precursors) should also be considered when analysing the temperature dependence of conductivity of the YBCO system on thermal cycling in various atmospheres. Goodenough *et al.* [6] reported that $Y_4Ba_3O_9$ undergoes a disordering transformation at 350 °C which raises the oxide ion conductivity by approximately three orders of magnitude. Based on the calculated entropy, $\Delta S = -24.7\ \mathrm{J\ mol^{-1}\ deg^{-1}}$, a very high value for an all solid-state reaction, Brosha *et al.* [4] suggested that this compound should be better viewed as a kind of "disordered liquid". In a reducing atmosphere, increased oxygen ion conductivity will be probably induced by the increased loss of lattice oxygen in this temperature range.

Much of the confusion regarding the presence of a specific phase in specific experimental conditions may also be attributed to the formation of oxycarbonates, which are particularly prone to hydration effects in an ambient atmosphere [4]. During the conditions for testing hydrocarbon oxidation when CO_2 and water are among the products, some formation of oxycarbonates must be expected. The effects of water vapour and CO_2 on YBCO at elevated temperatures have been reported previously [11]. YBCO is known to be susceptible to chemical attack from water, even at room temperature [15]. The fully oxidized form ($x = 0$) degrades less rapidly than the fully reduced one ($x = 1$) [16]. It is thought to decompose slowly to metastable Y_2BaCuO_5, copper oxides and $Ba(OH)_2$, which can further react with CO_2 to give $BaCO_3$. However, Fjellvåg *et al.* [17] report that there is no significant reaction of YBCO with CO_2 below 400 °C. Problems relating to stability are also discussed by Klissurski and Rives [3]. They report that at 300 °C the basic framework of YBCO remained preserved after 50 h exposure to water vapour, although a decrease in the intensity of the main peaks was observed indicating an "amorphization" of the catalyst. It has also been shown that the presence of CO_2 in an oxygen atmosphere during the sintering procedure is critical, because it can result in the formation of the tetragonal phase in the grain boundaries [18].

In fact, YBCO stability in the presence of water or CO_2 should also be a matter of sample history. The relative better stability of a fully oxidized compound in the presence of water should be explained by the lack of anionic vacancies acting as water adsorption sites. Thus, a lower stability in the presence of water can be expected on partially reduced surfaces or in conditions of catalysis.

This instability of phases under the influence of different gaseous atmospheres leads to questioning the true phase composition of the surface overlayer of the YBCO compound, especially when abruptly changing the atmosphere from one with a low oxygen content (or containing a reducing compound) to an oxygen-rich atmosphere. A partial decomposition of the basic matrix is to be expected.

The data in argon (experiments 1–3) showed considerable variation as moisture was desorbed from the sample. (No oxygen could be detected by using a mass spectrometer when fresh YBCO was heated in a separate experiment at $5\,^\circ\mathrm{C\,min^{-1}}$ in dry argon at $100\ \mathrm{cm^3\ min^{-1}}$.) On changing the atmosphere to dry oxygen, except for stabilization of values and a small decrease of conductivity above 300 °C (n-type behaviour), no further large changes in conductivity occurred. This seems to indicate a rather limited extent of the loss of oxygen/oxygen adsorption in dry conditions. In humid oxygen, however, the conductance increased significantly. This could be related to some structural changes of the surface resulting in an increase of the concentration of the surface OH groups and consequently in an increase of the relative contribution of protonic conduction at the expense of oxygen ion conduction. This is supported by the decrease of conductivity in the next experiment (Dry Ar-4). Indeed, the surface dehydoxylation induced by heating in dry inert conditions decreases the concentration of mobile protons participating in conduction process.

The apparent activation energy in dry oxygen above about 300 °C ($1000/T = 1.75$) is about 0.93 eV, and is probably associated with thermally activated oxygen ion conductivity. At lower temperatures, low band-gap semi-conductivity will dominate as shown by the activation energy of order 0.1 eV, which is typical for YBCO in the orthorhombic state. Apparently, the presence of water results in increased conductivity up to 340 °C. Above, its influence on conductivity is clearly diminished, partly because dehydroxylation is preferred (Figs 1a and 3b).

The propylene–air conductivity characteristic (experiment 7) can be well superimposed on that of the previous humid oxygen curve (experiment 5), suggesting that the propylene interaction with the YBCO surface occurs by a similar charge-transfer mechanism as in the presence of water (Fig. 3a). It is already well known that propylene adsorption on oxides occurs dissociatively [19–21], The loss of a hydrogen atom (ion) from the allylic position is accompanied by the formation of a π-allyl intermediate species (in radical or anion form, respectively), which must be adsorbed on to a surface cationic site. The extraction of the α- allylic hydrogen occurs via its interaction with a neighbouring lattice oxygen and produces surface OH groups. It seems that the appearance of these surface OH groups either through water adsorption, or through the surface reaction with propylene (both in the presence of oxygen) induces local thermal effects and/or irregular structural surface rearrangements producing oscillations in the conductivity (which in the conditions of the experiment are mainly controlled by the intergrain contacts). The lattice availability to accommodate the local charge deviations induced by the presence of adsorbed species should also be important at the relatively low temperature used here. Thus, a possible involvement of protonic transfer should also be considered [22, 23].

Recent reports have shown YBCO is also a good protonic conductor at moderate temperatures, e.g. 200 °C [24]. In fact, new hydrogen-containing perovskite oxide compounds of the form $H_2RBa_2Cu_3O_{7.8}$ (where R = Y, Gd, Tm, Eu or Pr) containing an increased content of both hydrogen and oxygen, have been made. Proton transfer in the lattice is believed to be accomplished by hopping through the oxygen framework, unconnected to the oxygen ion migration. It is obvious that during oxidation reactions, similar compounds may be formed on the surface. Because water vapour is a product of all oxidation reactions, surface protonic diffusion may play a part in the activity and selectivity patterns observed, while the

TABLE IV Propylene oxidation under stationary conditions (after CO tests)

Temperature (°C)	C (%)	S_{CO_2} (%)	S_{others} (%)
150	27.6	17.9	82.1 (acetaldehyde, acrolein)
314	35.0	77.0	33.0
400	78.0	92.0	8.0

possible associated thermal effects may be related to the oscillating behaviour; future work should attempt to clarify such speculations.

Owing to the very low concentration of products, the hydrocarbon conversion was evaluated only from the difference between the initial and final concentrations. However, evaluation based on the balance of carbon-containing compounds revealed somewhat lower values for the conversion data. This was only in part due to the incomplete analytical results; a possible fouling of the catalyst must also be taken into account. The latter was suggested by unusual fluctuations of propylene conversion as a function of temperature and by the blocking of the flow after some hours of testing. At the same time, the catalytic properties were apparently stabilized on diluting the propylene-containing mixture with air. As a result, the catalyst was removed to a normal tubular reactor (10 mm internal diameter). On repeating the tests in propylene–air 1 : 36, $\tau = 0.7$ s, the activity was as shown in Table IV.

The results presented in Table IV clearly demonstrate that

(i) contamination of YBCO surface occurs at higher concentration of hydrocarbon;

(ii) increased lattice oxygen mobility at high temperature is detrimental to the selectivity for partial oxidation. This can be associated with the increased extent of surface dehydroxylation/oxidation at high temperature.

Alternatively, the blockage might also have partly arisen from thermal expansion of the solid [25]. Indeed, the lattice parameters b (O region) and a (T region) decrease as the oxygen content decreases with x. On the other hand, the $c/(ab)^{1/2}$ value increases continuously with x, suggesting that bonding between layers along the c-axis becomes weaker with increasing x values. The effect is a relative expansion along the c-axis [25]. The interaction between the layers along the c-axis is the strongest for the composition $YBa_2Cu_3O_7$ and weakens with decreasing oxygen content. The thermal expansion coefficients along the a, b, c axes in the O phase between 350 and 400 °C are rather low, which may indicate low diffusivity of the oxygen ions in this temperature range. In the T phase ($x \sim 1$), the thermal expansion coefficients along the ab plane below 400 °C are much smaller than those at higher temperatures [25]. If the blocking effect at 400 °C could be attributed to the increased thermal expansion coefficient facilitated by the increase of x (which creates favourable conditions for the O to T transition), this can be taken as indirect proof for the formation of the T phase after heating the YBCO compound in the presence of a reducing gas, such as propylene or carbon monoxide. Thus, it is to be expected that around 400 °C, increased mobility of the surface lattice oxygen results in reduction of the solid in the presence of reducing gases, increasing x and consequently, increasing the rate of conversion to the T structure in the intergrain area. This statement is also supported by the increased catalytic activity for oxidation in this temperature range.

Whatever the cause, the blocking effect was found to be reversible, because, on stopping the reducing gas, and eventually cooling, the gas flow was unimpeded and on re-introducing the reducing gas and progressively heating, the blockage was re-established very rapidly.

As suggested by the conductivity data, the reducing effect of carbon monoxide in the presence of oxygen seems to be weaker than that of propylene (the conductivity was lower in the CO–air mixture with respect to the previous experiment in the propylene–air mixture). This indicates that the rates of reduction/reoxidation of the surface in our experimental conditions are comparable. By taking into account the perfect superposition in the high-temperature range with Dry Ar-4 data, it can be speculated that a rather limited extent of surface reduction can be obtained in dry conditions. Also, the temperature variation of conductivity was without fluctuations (Fig. 4). This again supports the assumption that the oscillations in the conductivity are related to the presence of water or of another proton-donating compound (and/or of the corresponding hydroxyl groups) in the inter-grain (surface) area. Because water is one of the main oxidation products of propylene oxidation, its interaction with the YBCO compound should be important, and must also be related to the increase of conductivity in the presence of propylene. On reheating in a dry atmosphere (as in the CO–air mixture), some of the surface sites are freed for oxygen adsorption which will, furthermore, result in simultaneous decreases of protonic and electronic conductivity. This suggests competition between water and oxygen for adsorption at the same adsorption sites.

In the case of YBCO, the presence of water or CO_2 or especially the mixture of these gases, decomposition to Y_2BaCuO_5, CuO, $BaCO_3$ and $Ba(OH)_2$ is likely [11]. Thus, due to surface contamination with degradation products resulting from reaction with atmospheric water and carbon dioxide, YBCO may partially decompose during catalytic reaction, leading to insulating, stable phases such as Y_2BaCuO_5 and $BaCuO_2$. Some of these decomposition products are also catalytically active; in particular Y_2BaCuO_5 when mildly reduced has an activity 60 times larger than for oxidized YBCO with the activity levels comparable with the best CO oxidation catalysts such as CuO, Co_3O_4, Pt [26]. The surface is likely to contain islands of phases nucleated as a result of decomposition of the main matrix or reformed under thermal cycling in various oxidizing/ reducing atmospheres, in accordance with thermodynamic considerations. Small amounts of new phases play the role of dopants and change the catalytic/conductivity properties of the surface accordingly. Such small amounts of contaminant phases cannot be detected by XRD or by XPS, so this possibility can at present only be postulated.

Otamiri and Andersson [27] studied the kinetics for CO oxidation between 160 and 200 °C. The higher activity of the oxygen-deficient samples (in comparison with the oxygen-rich ones) was attributed to a higher concentration of surface vacancies and defects. The presence of water reversibly reduced the activity, which was suggested to be the result of competitive adsorption with the CO or possibly with oxygen. Pickering and Thomas [2] report that the rate of production of CO_2 decreased rapidly in the absence of gaseous oxygen (due to removal of available lattice oxygen), but only very slowly when gaseous oxygen was added.) Bansal [28] compared TGA curves for YBCO powders heated and cooled in atmospheres of air, O_2 and N_2, sintered and annealed in oxygen. On heating, weight gain started at about 280 °C in air and at 265 °C in pure O_2. A maximum weight gain of about 0.3% occurred at about 425 °C. Above this temperature the samples continuously lost weight.

The change of activation energy of conduction in dry conditions observed above 220 °C, coupled with the appearance of oxidation products is indicative for the onset of the increased lattice mobility, which will result in diffusion of vacancies and an increased rate of oxidation. Dehydoxylation–oxidation effects coexist in the presence of water, and their relative importance will depend on the temperature range. Based on the conductivity data presented above, we suggest that the deactivating role of water in the case of CO oxidation stems from two simultaneous effects: the transformation of surface lattice oxygen (necessary for oxidation) in OH groups, and the competition with CO for the same adsorption sites (cationic sites).

As observed by Klissurski and Rives [3], a decrease in the oxygen content of YBCO leads to an increase in the binding energy of oxygen; the activation energy for oxygen desorption from the T phase is almost double that for the O phase, hence the T structure should exhibit a higher selectivity in partial oxidation in comparison with the O structure. For selective oxidation and ammoxidation of hydrocarbons, optimum catalytic behaviour was found for largely reduced or slightly oxidized material; total reduction or oxidation leads to poorer catalysts. Hence the catalytic activity and selectivity are highly dependent on the pre-history of the catalyst.

5. Conclusion

The data presented above reveal the extreme sensitivity of conductivity of YBCO on the history of the sample compared with other catalysts investigated in the same fashion. This sensitivity indicates a strong dependence of surface conduction on chemisorbed species, which if loosely bound, will cause fluctuations. This can also be associated with instability of the basic matrix and related phases at low temperatures in various atmospheres, and will explain the rather diverse catalytic properties of this material. In particular, the presence of water may lead to blocking of the hydrocarbon/carbon monoxide adsorption sites (surface cationic sites) or of surface lattice oxygen which normally participates in the oxidation reaction. Monitoring of the surface and bulk chemical and phase composition during catalytic tests in the presence of CO_2 and/or water vapour should be included in future experiments.

References

1. W. CARRILLO-CABRERA, H. D. WIEMHÖFER and W. GÖPEL, *Solid State Ionics* **32–33** (1989) 1172.
2. I. J. PICKERING and J. M. THOMAS, *J. Chem. Soc. Farad. Trans.* **87** (1991) 3067.
3. D. KLISSURSKI and V. RIVES, *Appl. Catal. A:Gen.* **109** (1994) 1.
4. E. L. BROSHA, F. H. GARZON, I. D. RAISTRICK and P. K. DAVIES, *Am. Ceram. Soc.* **78** (1995) 1745, and references therein.
5. E. L. BROSHA, E. SANCHEZ, P. K. DAVIES, N. COPPA, A. THOMAS and R. SALOMON, *Physica C (Amsterdam)* **184** (1991) 353.
6. J. B. GOODENOUGH, A. MANTHIRAM, M. PARANTHAMAN and Y. S. ZHEN, in "Proceedings of the International Conference on Advanced Materials".
7. Y. YAN, M-G. BLANCHIN, C. PICARD and P. GERDANIAN, *J. Mater. Chem.* **3** (1993) 603.
8. M. S. HEGDE and S. RAMESH, *Proc. Indian Acad. Sci. (Chem. Sci.)* **106** (1994) 1363.
9. A. OVENSTON, J. R. WALLS, A. ALLEN and W. ARMSTRONG, *J. Mater. Sci.* **29** (1994) 1358.
10. A. OVENSTON, J. R. WALLS and D. SPRÎNCEANA, *J. Mater. Sci. Lett.* **14** (1995) 311.
11. A. OVENSTON, D. QIN, L. SHIELDS and J. R. WALLS, *J. Mater. Sci.* **30** (1995) 5405.
12. M. CALDARARU, D. SPRÎNCEANA and N. I. IONESCU, *Ber. Buns. Phys. Chem.* **97** (1993) 369.
13. M. CALDARARU, D. SPRINCEANA, V. T. POPA and N. I. IONESCU, *Sensors Actuators* **B30** (1996) 35.
14. A. OVENSTON and J. R. WALLS, *J. Catal.* **140** (1993) 464.
15. I. M. LOW, S. S. LOW and C. KLAUBER, *J. Mater. Sci. Lett.* **12** (1993) 1574.
16. J-P. ZHOU and J. T. MCDEVITT, *Solid State Commun.* **86** (1993) 11.
17. H. FJELLVÅG, P. KAREN, A. KJEKSHUS, P. KOFSTAD and T. NORBY, *Acta Chem. Scand.* **A42** (1988) 178.
18. G. SELVADURAY, C. ZHANG, U. BALACHANDRAN, Y. GAO, K. L. MERKLE, H. SHI and R. B. POEPPEL, *J. Mater. Res.* **7** (1992) 283.
19. R. K. GRASSELLI, J. D. BURRINGTON and J. F. BRAZDIL, *Farad. Disc. Chem. Soc.* **12** (1982) 205.
20. N. I. IONESCU and M. CALDARARU, "Heterogeneous Selective Oxidation of Lower Olefins" (Romanian Academy Printing House, Bucharest, 1993).
21. A. W. SLEIGHT, in "Solid State Chemistry of Compounds", edited by A. K. Cheetham and P. Day (OUP, Oxford, 1992) Ch. 5, p. 166.
22. K-D. KREUER, *Chem. Mater.* **8** (1996) 610.
23. T. NORBY, *Adv. Ceram.* 23 (1987) 107.
24. Y. M. BAIKOV, *ISSI Lett.* **6** (1995) 1.
25. J. MIZUSAKI, H. TAGAWA, K. HAYAKAWA and K. HIRANO, *J. Am. Ceram. Soc.* **78** (1995) 1781.
26. I. HALASZ, A. BRENNER, M. SHELEF and K. Y. S. NG, *J. Catal.* **134** (1992) 731.
27. J. C. OTAMIRI and S. L. T. ANDERSSON, *Appl. Catal.* **73** (1991) 267.
28. N. P. BANSAL, *J. Mater. Res.* **3** (1988) 1304.

Received 24 June 1996
and accepted 7 January 1997