Superconductor mixed oxides $La_{2-x}Sr_xCuO_{4\pm\lambda}$ for catalytic hydroxylation of phenol in the liquid–solid phase

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Superconductor mixed oxides are often used as catalysts at high temperature in gas–solid phase oxidations and considered not suitable for lower temperature reactions in the liquid–solid phase; here the catalysis of $La_{2-x}Sr_xCuO_{4\pm\lambda}$ (x = 0, 0.1, 0.7, 1) mixed oxides in phenol hydroxylation at lower temperatures are studied, and we find that the value of x has a significant effect on catalytic activity: the lower its value, the higher the catalytic activity; a mechanism is proposed to explain the experimental phenomena.

Phenol hydroxylation by H_2O_2 is a widely applied process in industrial chemistry for the preparation of diphenols (catechol and hydroquinone). Since the 1970s, phenol oxidation in the homogeneous liquid phase, with H_2O_2 as oxidant, catalysed by mineral acids,[1–3] simple metal ions and their complexes[4–6] was extensively studied. Although some of these catalysts have been used for the industrial production of diphenols from phenol and H_2O_2, the obvious shortcomings of these homogeneous reactions still prevent their wide use in diphenol production. Redox molecular sieves, TS-1,[7,8] TS-2,[9,10] zirconotitanosilicates,[11] mineral US-Y zeolite,[12] Ti-MCM-41[13] and $TAPO_4$-5, $TAPO_4$-11,[14] as heterogeneous catalysts have supplanted the homogeneous catalysts, but disadvantages such as their difficult preparation and slower reaction rates,[15] limit their wide use in industrial production. Pure metal oxides or supported oxides have also been used to catalyse phenol hydroxylation, *e.g.* MnO_2, Fe_2O_3,[16] Co_3O_4,[17] CuO/SiO_2,[18] Fe_2O_3/Al_2O,[19] V_2O_5, MoO_3[20] and TiO_2 colloidal particles,[21] but these oxides all have poor catalytic activity and undesired product selectivity for diphenol production. $La_{2-x}Sr_xCuO_{4\pm\lambda}$ is a K_2NiF_4-type solid solution characterized by the intergrowth of perovskite and sodium chloride type layers; not only are they prepared easily, but they are also very stable in different reaction environments. So far, this kind of perovskite type mixed oxide is often used in gas–solid phase oxidations at high temperature, *e.g.* in the removal of nitrogen oxides (NO_x) in automobile exhaust gases and electric power plants[22] and catalytic oxidation of carbon monoxide[23] *etc.* However, there are no reports of their catalysis in liquid–solid phase reactions at lower temperatures. In this paper, we have studied their catalysis in phenol hydroxylation, and found some of the $La_{2-x}Sr_xCuO_{4\pm\lambda}$ materials show good catalytic activity.

The catalysts $La_{2-x}Sr_xCuO_{4\pm\lambda}$ were prepared by the citrate process,[24] using $La(NO_3)_3$, $Sr(NO_3)_2$ and $Cu(NO_3)_2$ as the starting materials and calcining at 900 °C for 10 h in air. X-Ray diffraction patterns of the products are shown in Fig. 1 and are in accord with their literature spectra.

In phenol hydroxylation experiments catalyst and solvent were added successively into a 25 ml glass reactor equipped with a stirring bar and a thermostat. The reaction was initiated by adding H_2O_2 (30 mass%) at the set temperature. Decomposition measurements of H_2O_2 were also performed without addition of phenol. The gas chromatograph used for product analysis was equipped with a flexible glass capillary column coated with XE-60. The initially programmed temperature was 100 °C and the final temperature was 190 °C.

According to the analyses, the structure, average valence of copper and the nonstoichiometric oxygen (λ) of $La_{2-x}Sr_xCuO_{4\pm\lambda}$ are shown in Table 1.

Initially we studied the decomposition of H_2O_2 catalysed by $La_{2-x}Sr_xCuO_{4\pm\lambda}$ and the results are shown in Fig. 2.

Phenol hydroxylaton for our systems are compared with simple metal oxides and combinations thereof in Table 2.

After phenol hydroxylation, the XRD and IR spectra of the $La_{2-x}Sr_xCuO_{4\pm\lambda}$ catalysts were unchanged. The activity of

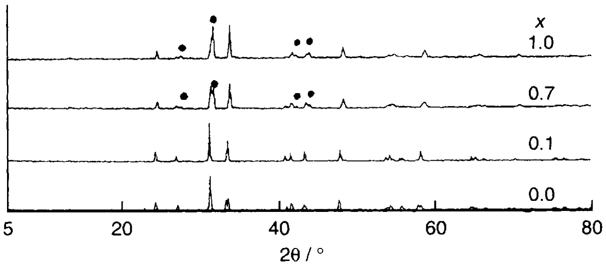


Fig. 1 X-Ray diffraction patterns for $La_{2-x}Sr_xCuO_{4\pm\lambda}$ catalysts (●, T* phase (*cf.* U. Tokura, H. Takagi and S. Uchida, *Nature*, 1989, **337**, 345)

Table 1 Characteristics of $La_{2-x}Sr_xCuO_{4\pm\lambda}$ perovskite mixed oxides*

Sample	Structure	Average Cu valence	Nonstoichiometric oxygen (λ)
La_2CuO_4	K_2NiF_4(O[a])	2.02	0.02
$La_{1.9}Sr_{0.1}CuO_4$	K_2NiF_4(T)	2.14	0.01
$La_{1.3}Sr_{0.7}CuO_4$	K_2NiF_4(T + T*)[b]	2.24	−0.22
$LaSrCuO_4$	K_2NiF_4(T + T*)	2.25	−0.38

[a] O, orthorhombic K_2NiF_4 phase. [b] T, tetraganal K_2NiF_4 phase; T*, a second tetragonal K_2NiF_4 phase in which the coordination number of oxygen at B sites is five.

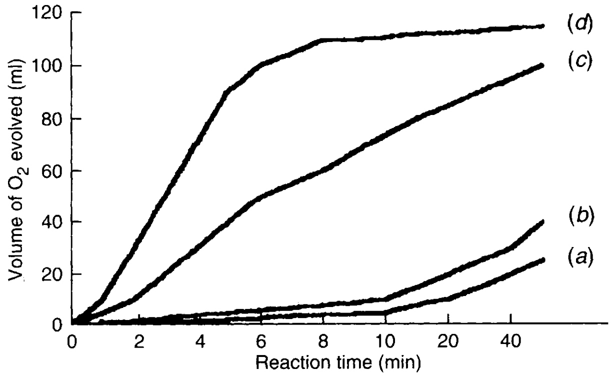


Fig. 2 Relation between reaction time and the volume of O_2 evolved during the decomposition of H_2O_2 catalysed by $La_{2-x}Sr_xCuO_{4\pm\lambda}$ [x = 0 (*a*), 0.1 (*b*), 0.7 (*c*) or 1 (*d*)]. Reaction temperature, 70 °C; solvent, water; medium pH = 7.0; H_2O_2 concentration, 0.355 mol dm^{-3}; reaction volume, 15 ml; mass of catalyst used, 0.1 g.

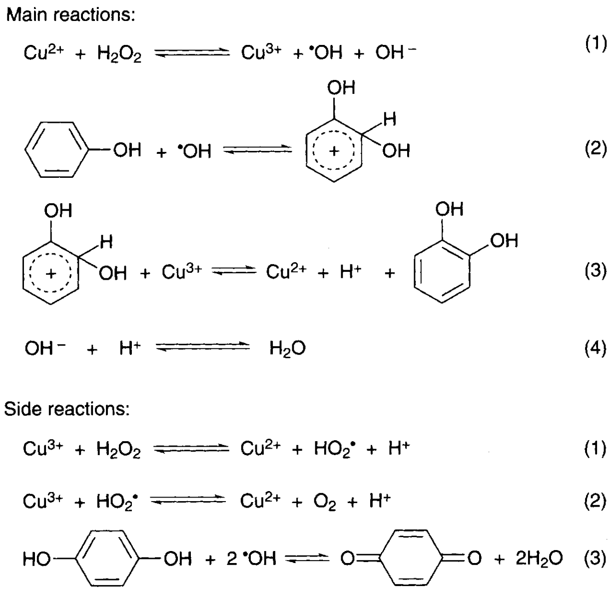
$La_{2-x}Sr_xCuO_{4\pm\lambda}$ ($x = 0, 0.1$) catalysts was monitored over ten runs of the reaction; phenol conversion was found to be unchanged indicating the high stability of the catalysts.

According to the above results, a mechanism of phenol hydroxylation and decomposition of H_2O_2 is proposed in Scheme 1.

Table 2 Activity of different catalysts in phenol hydroxylation[a]

Catalyst	Phenol conv. (%)	Product conv. (%) CAT	HQ	BQ	O_2 evolved (ml)
La_2CuO_4	50.9	29.6	20.3	1.0	12
$La_{1.9}Sr_{0.1}CuO_4$	40.8	23.2	16.6	1.0	19
$La_{1.3}Sr_{0.7}CuO_4$	10.5	6.4	4.1	0	85
$LaSrCuO_4$	2.2	1.4	0.8	0	100
CuO	11.7	7.4	2.3	2.0	78
La_2O_3	0	0	0	0	0
SrO	0	0	0	0	0
$CuO–La_2O_3–SrO$	10.5	6.0	3.5	1.0	80

[a] CAT = catechol, HQ = hydroquinone, BQ = benzoquinone. Reaction time, 2 h; reaction temperature, 70 °C; reaction medium, water; medium pH = 7.0; phenol : H_2O : H_2O (molar ratio) = 1 : 1 : 60; mass of catalyst used, 0.1 g.



Scheme 1 Proposed mechanism for phenol hydroxylation and decomposition of H_2O_2 by the $La_{2-x}Sr_xCuO_{4\pm\lambda}$ mixed oxides. Both Cu^{3+} and Cu^{2+} are found in the mixed oxides;[25] the production of hydroquinone proceeds in the same manner as for catechol.

From Tables 1 and 2 and Fig. 2, it is seen that the superconductor mixed oxides ($La_{2-x}Sr_xCuO_{4\pm\lambda}$, $x = 0.7, 1$) with higher average valence and more oxygen vacancies have high activity for the decomposition of H_2O_2 but low activity for phenol hydroxylation. According to the mechanism of Scheme 1 the presence of more copper atoms with higher valence in the mixed oxides will promote side reactions (1) and (2), to the detriment of the main reaction (1). In this way, almost all the H_2O_2 decomposes rapidly to O_2 without participation of phenol hydroxylation. Conversely for $La_{2-x}Sr_xCuO_{4\pm\lambda}$ catalysts with low values of x (0 or 0.1), the presence of more copper atoms with lower valence, favours the main reaction (1) enabling phenol hydroxylation to proceed readily giving diphenols.

In conclusion, we have established that some $La_{2-x}Sr_x$-$CuO_{4\pm\lambda}$ superconductor mixed oxides show high catalytic activity in phenol hydroxylation, and have proposed a plausible mechanism to explain the experimental observations.

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