Continuous Reactions in Supercritical Water: A New Route to La_2CuO_4 with a High Surface Area and Enhanced Oxygen Mobility**

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Perovskite-type complex oxides have been investigated intensively in recent years because of their potential as catalysts for oxidation processes.[1, 2] Their catalytic properties are principally associated with oxygen nonstoichiometry, oxygen storage capacity, oxygen mobility, and the electronic properties of the perovskites themselves.[3] The attraction of such materials is that these properties can be tuned through variation of the metals within the structure. Additionally, they have high thermal stability and relatively low cost compared to noble metal oxidation catalysts.[1]

La_2CuO_4 is an important, catalytically active perovskite. It has the K_2NiF_4 structure with alternating layers of the ABO_3 perovskite and the AO salt.[3] La_2CuO_4 and its derivatives catalyse a wide variety of reactions including the oxidation of CO[4–7] and CH_4,[5], decomposition of NO and N_2O,[8, 9] and NO reduction with CO.[3, 10, 11] Furthermore, catalysts such as $La_{2-x}Sr_xCuO_{4-\delta}$ and $La_2Cu_{1-x}Pd_xO_4$ exhibit a catalytic activity comparable to that of Pt-Rh/CeO_2-Al_2O_3 for three-way automotive catalysis.[3, 8]

Usually, single-phase perovskites are synthesized by annealing stoichiometric mixtures of metal oxides or other suitable precursors at very high temperatures.[4–6, 8, 12] For example, La_2O_3 heated with CuO at 1000–1200 °C leads to the formation of La_2CuO_4 but its surface area[4, 6, 12] is $\leq 1\,m^2\,g^{-1}$ and too low for use as a catalyst. However, surface areas as high as $13\,m^2\,g^{-1}$ [13] can be obtained through a number of "wet chemical" routes including sol–gel processes,[3, 13] coprecipitation,[7, 9, 11] inverse microemulsion techniques,[14] and combustion synthesis,[15] all of which involve lower annealing temperatures, about 600–800 °C. Unfortunately, these "wet" routes are often complicated or involve large quantities of toxic or inflammable compounds.

Herein, we describe a relatively simple route to La_2CuO_4, the initial stage of which involves the simultaneous hydrolysis of lanthanum(III) and copper(II) acetates in supercritical water, scH_2O. There has been a considerable amount of research into the reactions of metals in scH_2O,[16] while Arai and co-workers have pioneered the use of scH_2O for hydrolysis of metal salts.[17–18] They showed that continuous hydrolysis of metal nitrates in scH_2O ($T > 374\,°C$) generated the corresponding metal oxides for a wide range of different metals. Recently, we showed that decomposition of metal acetates in scH_2O was an even more facile route to metal oxides.[19] Here, we report how the decomposition of $La(CH_3COO)_3$ and $Cu(CH_3COO)_2$ in a continuous scH_2O reactor leads to the formation of an intimate mixture of $La(OH)_3$ and CuO, which can then be sintered to form single phase La_2CuO_4 with a high surface area.

Our continuous reactor is shown schematically in Figure 1. Briefly, a cold solution, which contained both La^{III} and Cu^{II} acetates, was mixed with scH_2O at 400–500 °C and at 25 MPa. The resulting colloidal suspension of $La(OH)_3$ and CuO was quenched and evaporated (see the Experimental Section). The gray, solid product was then annealed at 600 °C and La_2CuO_4 formed within 5 h.

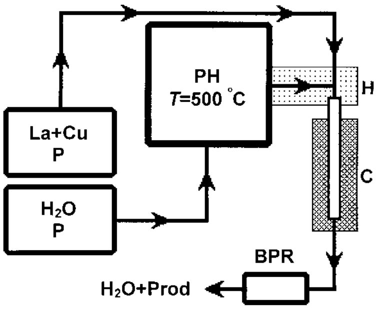

Figure 1. Continuous, supercritical water flow reactor. Abbreviations are backpressure regulator (BPR), cooling area (C), heating area (H), pumps (P), water preheater (PH), and hydrolysis products (Prod). The reactor is constructed from 316 stainless steel components (Swagelok).

X-ray diffraction (XRD) spectra showed the product, $(La_2CuO_4)_{sc}$ to be of a single phase;[11, 13, 14] see Figure 2. Brunauer-Emmet-Teller (BET) surface area measurements gave surface areas of up to $19\,m^2\,g^{-1}$, very high for this type of material. By comparison, only $0.4\,m^2\,g^{-1}$ was obtained with ceramic La_2CuO_4 prepared from La_2O_3 and CuO (see the Experimental Section). A scanning electron microscopy (SEM) examination of $(La_2CuO_4)_{sc}$ and ceramic La_2CuO_4

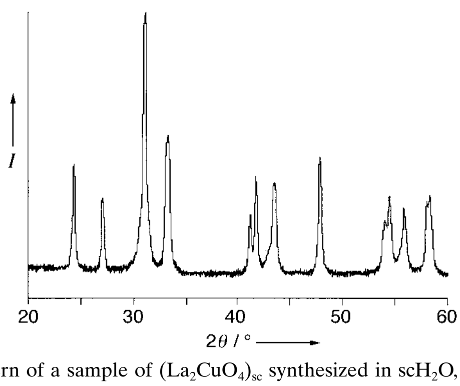

Figure 2. XRD pattern of a sample of $(La_2CuO_4)_{sc}$ synthesized in scH_2O, which shows the absence of reflections attributable to other phases or to the $CuO/La(OH)_3$ precursors.

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[**] We thank Ms. E. P. Chinennikova, Dr. A. Cabañas, Dr. J. A. Darr, Dr. D. A. Graham, and Mr. M. Guyler for their help. We are grateful to EPSRC (grant no. GR/K84929), the Royal Society, NATO, the Royal Academy of Engineering, and the Russian Foundation for Basic Research for support.

showed that the $(La_2CuO_4)_{sc}$ material has much smaller and more uniform particle sizes (Figure 3a). More detailed SEM studies showed that the morphology of the $La(OH)_3/CuO$ precursor was largely unaffected by annealing to 600°C. Energy-dispersive X-ray microanalysis (EDX) of both La_2CuO_4 samples confirmed the correct 2:1 La:Cu ratio. La_2CuO_4 may possibly be formed by annealing the supercritical hydrolysis product at temperatures as low as 400°C but the XRD peaks are so broadened by the small particle size that positive identification of La_2CuO_4 has not been possible.

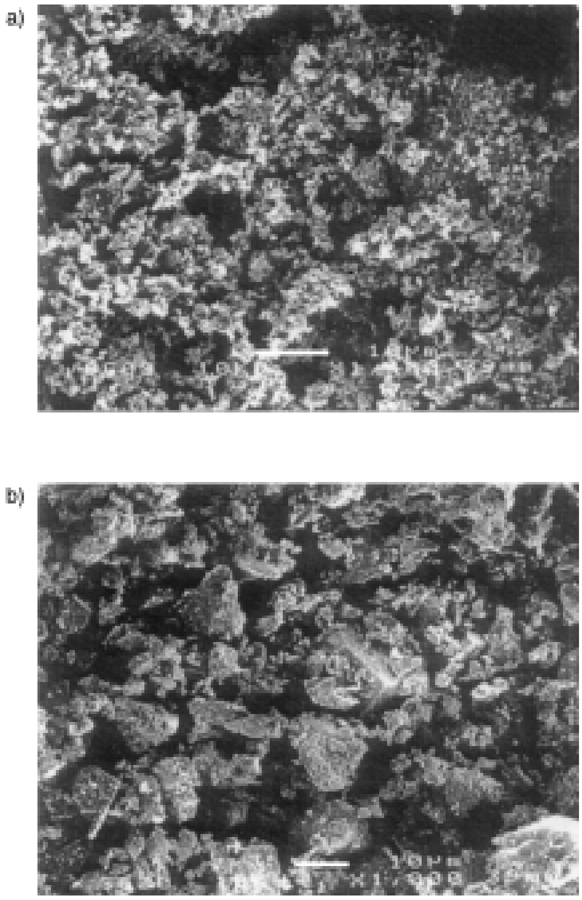

Figure 3. SEM micrographs for La_2CuO_4 samples prepared using the a) scH_2O or b) conventional ceramic method. Scale bars = 10 µm.

Temperature programmed reduction (TPR) is a key indicator of potential catalytic activity and Figure 4 compares the TPR profiles for the La_2CuO_4 samples prepared using scH_2O or the ceramic method. The higher temperature peak in both traces corresponds to bulk reduction with the formation of a mixture of Cu, CuO, and La_2O_3 phases, which occurs at almost the same temperature for both samples. In contrast, the first reduction peak, assigned to loss of weakly bound oxygen, occurs 100 K cooler for $(La_2CuO_4)_{sc}$. This shift towards a lower temperature indicates a much increased bulk oxygen mobility, a crucial factor for effective oxidation catalysis. This striking difference in the TPR occurred even though the overall hydrogen takeup for the two samples was essentially identical, 5.747 and 5.736 $mmol\,g^{-1}$ for the scH_2O and ceramic samples, respectively.

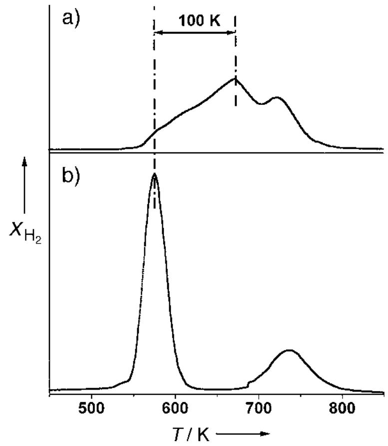

Figure 4. TPR curves for La_2CuO_4 samples prepared using the a) conventional ceramic method or b) scH_2O. x_{H_2} = hydrogen consumption.

The higher catalytic activity of $(La_2CuO_4)_{sc}$ was demonstrated by the oxidation of CO. Two independent series of pulsed microcatalytic experiments were carried out. First, with a stoichiometric $CO:O_2$ mixture, we found that the efficiency of the $(La_2CuO_4)_{sc}$ catalyst was about 2.5 times higher per unit mass compared to the ceramic sample. Second, the O_2 and CO pulses were separated in time with the catalyst heated to 270°C, where, according to the TPR data (Figure 4), the weakly bound oxygen is mobile in $(La_2CuO_4)_{sc}$ but still inactive in the ceramic phase. Both $(La_2CuO_4)_{sc}$ and ceramic La_2CuO_4 were oxidized initially by a pulse of O_2, which was then followed by alternating pulses of CO and O_2. The rates of CO oxidation reaction were 73.5 and 9.1 $\mu L\,s^{-1}m^{-2}$ for the scH_2O and ceramic catalysts, respectively. Thus, the $(La_2CuO_4)_{sc}$ is eight times more effective per unit area of surface. However, this difference in reaction rates may not be solely due to higher rates of oxygen diffusion in $(La_2CuO_4)_{sc}$. The large difference in the surface areas between the samples of La_2CuO_4 means that the reaction conditions are not identical and the higher "total" surface area of the $(La_2CuO_4)_{sc}$ sample may result in significant O_2 adsorption by the surface with consequently higher concentrations of active oxygen for the subsequent CO oxidation. Nevertheless, $(La_2CuO_4)_{sc}$ is a more effective catalyst.

In conclusion, our supercritical water method has produced, at a cooler reaction temperature, high surface area La_2CuO_4 with enhanced oxygen mobility, probably because the $La(OH)_3/CuO$ precursor was produced as an intimate nanoparticulate mixture. The preliminary catalytic tests showed the activity of $(La_2CuO_4)_{sc}$ towards CO oxidation is considerably higher compared to the ceramic La_2CuO_4 phase. A detailed study of the catalytic activity in other oxidation reactions, as well as the investigation of the oxygen adsorption kinetics, for $(La_2CuO_4)_{sc}$ is currently in progress.

Experimental Section

Caution: These experiments involve high pressures.

The synthesis of La_2CuO_4 was performed using a particle flow reactor (Figure 1). To obtain supercritical conditions ($T_c = 374$°C, $P_c = 22.1$ MPa), water was pumped continuously through a preheater and oven to reach a final temperature of 400–500°C before mixing with a solution of La^{III} and

Cu^{II}. A backpressure regulator at the end of the system maintained the system pressure close to 25 MPa. At the mixing point, a cold solution of stoichiometric amounts of Cu^{II} and La^{III} acetates (0.01 M each) was rapidly hydrolysed by scH_2O stream. The temperature at the mixing point was in the range of 350 – 400 °C and the residence time was only a few seconds. The hot water and dispersed hydrolysis products (CuO and $La(OH)_3$) were cooled and collected after the BPR. A gray solid was recovered from the mixture by complete evaporation of water and was annealed at 600 °C for 5 h to form single-phase La_2CuO_4.

Ceramic La_2CuO_4 was synthesized by annealing a stoichiometric mixture of CuO and La_2O_3 at 1100 °C for 48 h with two intermediate grinding sessions.

The phase composition of all the materials was determined by XRD (Phillips XPERT, $Cu_{K\alpha}$ radiation), at a scan rate of 1 min^{-1} over the range $20 < 2\theta < 60°$. The microstructure of the samples was investigated by SEM (JEOL Winsem JSM-6400, acceleration voltage 10 kV) after the deposition of a gold layer (15 nm thick) on the specimen. The BET surface area was measured by N_2 adsorption at 77 K. TPR profiles were recorded at a heating rate of 10 K min^{-1}; prior to the TPR experiments, the samples were pretreated in an O_2 flow at 600 °C for 1 h and allowed to cool in oxygen until, when at room temperature, the O_2 flow was replaced with an Ar/H_2 flow (95 %/5 %).

The catalytic activity of La_2CuO_4 towards CO oxidation was studied by a pulsed microcatalytic technique over the temperature range 200 – 400 °C.[20] The composition of the gas phase was monitored by an LHM-8MD gas chromatograph (Carbosieve-B column, $l = 1$ m, $\phi = 2$ mm) with a catharometer detector and He carrier gas (70 mL min^{-1}, $P = 1$ atm). The reactant pulse was 1 mL, which contained 7.5 % v/v of the stoichiometric $CO:O_2$ mixture. Before the activity measurements, the catalysts were pretreated in a He flow.

Received: February 15, 2000 [Z 14712]

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Evidence for Dangling Bond Mediated Dimerization of Furan on the Silicon (111)-(7×7) Surface**

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The binding of organic molecules on silicon surfaces has recently become an increasingly important aspect of surface modification in microelectronics and sensing technology.[1, 2] To gain the control needed for incorporating organic functionalities into existing technologies, there are growing efforts dedicated to the fundamental understanding of molecular adsorption on silicon surfaces.[3, 4] One central focus in this area is the covalent attachment of olefins to the Si dangling bonds at silicon surfaces.[5–7]

Experimental and theoretical results suggest that [4+2] or [2+2] cycloadditions of conjugated dienes with Si=Si dimers proceed by a diradical mechanism on the Si(100) surface.[6, 7] Recently, we showed that the radical nature of the electron-deficient Si dangling bonds plays an essential role in the [4+2] cycloaddition of thiophene to the Si(111)-(7×7) surface.[8] These studies implied that the Si dangling bonds can be alternatively viewed as reactive "free radicals" involved in the surface-attachment reactions. On the other hand, organic radical based C−C bond formation[9] was recently shown to be highly selective in enantioselective synthesis[10] or preparation of controlled macromolecular architectures.[11] Therefore, it is of significant interest to investigate whether this radical-based C−C formation is feasible on silicon surfaces in association with Si dangling bonds. Such a study may offer new insight into the covalent attachment of molecular functionalities onto the silicon surface.

We report here on the Si dangling bond mediated dimerization of furan molecules on the Si(111)-(7×7) surface. Through the use of thermal desorption spectroscopy (TDS) and vibrational high-resolution electron energy loss spectroscopy (HREELS), the structure and bonding of the adsorbed furan species on Si(111)-(7×7) have been investigated. The structure of the Si(111)-(7×7) unit cell (Figure 1) is well known,[12] and the unique Si(111)-(7×7) surface offers an excellent opportunity to examine the surface chemistry associated with the Si dangling bonds at the silicon surface. Furan was chosen for this study because it is one of the basic building blocks for conducting polymers.[13, 14]

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[**] This work was supported by the National University of Singapore (grant no. 3970612).

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