Role of Copper in the Characterization of Copper(II)-Promoted Tin(IV) Oxide Catalysts for the Catalytic Oxidation of Carbon Monoxide

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$Cu(II)/SnO_2$ catalyst materials with Cu:Sn ratios in the range 0.02−0.30 have been prepared by three routes: coprecipitation from aqueous solutions containing Cu^{2+} and Sn^{4+} ions, sorption of Cu^{2+} ions on to tin(IV) oxide gel, and destabilization of choline-stabilized tin(IV) oxide colloidal sols by the addition of aqueous copper(II) nitrate solution, and their constitution after thermal treatment in the temperature range 333−1273 K has been investigated by powder X-ray diffraction and EXAFS. Materials obtained by coprecipitation or impregnation are similar in nature irrespective of the Cu:Sn ratio with particle sizes <5 nm even after calcination at 673 K. Calcination at 873 K results in larger particles, but at temperatures ≥1073 K sintering to give very large particles occurs. EXAFS data show that the initial Cu(II) species from the coprecipitation or impregnation routes are hexaaqua $\{Cu(H_2O)_6\}^{2+}$ ions sorbed onto the surface of the tin(IV) oxide particles but calcination at temperatures of 873 K and above causes the phase separation of CuO. EPR shows that only surface copper(II) is readily reduced on exposure to carbon monoxide. Copper(II)-promoted tin(IV) oxide catalysts effect the catalytic oxidation of CO for stoichiometric CO/O_2 mixtures under at 328 K. The mode of operation of the catalysts appears to be synergistic in nature with the principal role of Cu(II) being mainly in electron transfer, i.e., it abstracts the negative surface charges (formed in the oxygen vacancies following desorption of CO_2) to form Cu(I), which is then oxidized back to Cu(II) by reaction with oxygen. The activity of catalysts deactivated by running under highly reducing conditions can be restored completely by heating in a flow of air at 355 K. Irreversible deactivation occurs on processing at very high temperatures due to sintering and the phase separation of copper(II) oxide.

Introduction

That the incorporation of copper(II) ions into tin(IV) oxide has a dramatic effect on the ability of these materials to catalyze the oxidation of carbon monoxide using either dioxygen or nitric oxide has been know for some time.[1,2] However, the nature of these catalyst materials and the role which copper plays in the catalytic processes are not well understood. We have previously studied extensively the adsorption of carbon monoxide, carbon monoxide/dioxygen mixtures and carbon dioxide onto both tin(IV) oxide itself[3−6] as well as transition metal-modified tin(IV) oxide materials.[7−9] Three surface species were observed on the surface of tin(IV) oxide alone: unidentate and bidentate carbonate as well as a surface carboxylate species. The adsorption of carbon monoxide onto tin(IV) oxide is very fast, but that of carbon dioxide is much slower; however, the same three species are formed in both cases. All three species are associated with surface oxygen generated by dehydroxylation of the surface at high calcination temperatures.[5,6] Increasing the adsorption temperature causes a slow transformation of the latter two into the unidentate carbonate.[6] Infrared studies of the transition metal-modified tin(IV) oxide materials showed adsorbed CO and different carbonate species adsorbed at the metal sites, some of which were the same as those observed for tin(V) oxide alone.[7,8] Although the observed ν(CO) frequency of the adsorbed CO correlated with the electric field strength at the metal adsorption site for different transition metals, it was not possible to

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(1) Fuller, M. J.; Warwick, M. E. *J. Catal.* **1974**, *34*, 445.

(2) Fuller, M. J.; Warwick, M. E. *J. Catal.* **1976**, *42*, 418.

(3) Thornton, E. W.; Harrison, P. G. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 461.

(4) Harrison, P. G.; Thornton, E. W. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2597.

(5) Harrison, P. G.; Willett, M. J. *Nature* **1988**, *332*, 337.

(6) Harrison, P. G.; Guest, A. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1897.

(7) Harrison, P. G.; Thornton, E. W. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2703.

(8) Harrison, P. G.; Thornton, E. W. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 1487.

(9) Matar, K.; Zhao, D.; Goldfarb, D.; Azelee, W.; Daniell, D.; Harrison, P. G. *J. Phys. Chem.* **1995**, *99*, 9966.

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establish unambiguously whether species of the types $M-CO$ and/or $M-O^{-}\cdots O$ were present.[8] The implication of the infrared data is that the catalytic oxidation of carbon monoxide over tin(IV) oxide occurs by initial adsorption of CO at isolated or neighboring surface oxygen atoms to generate the surface carboxylate species and bidentate or bridging carbonate, followed by conversion of the species into unidentate carbonate and the desorption of carbon dioxide. The surface oxygen vacancies are replenished by the dissociative chemisorption of dioxygen. The role of copper would appear to be to provide a facile adsorption site for CO, catalytic conversion proceeding via spillover onto tin(IV) oxide. However, in the absence of corroborating evidence, this mechanism is only speculative and the possibility remains that the surface species observed in the infrared are merely “spectator” species and may not even participate in the catalytic conversion process.

In general, Cu(II)/SnO_2 catalysts may be prepared by two methods: (i) coprecipitation of a mixed-oxide gel from an aqueous solution containing both copper(II) and tin ions, and (ii) the sorption of copper(II) ions from aqueous solution onto preformed tin(IV) oxide gel. The principal difference in these procedures is that in the latter the copper ions should be distributed only on the surface of the tin(IV) oxide particles, whereas in the former some incorporation into the bulk of the tin(IV) oxide may occur. Our earlier[9] EPR and electron spin–echo envelope modulation (ESEEM) studies of very dilute Cu(II)/SnO_2 catalysts prepared by both routes have demonstrated that different types of Cu(II) species are generated, the relative abundance of which depends on the preparative method and the calcination history of the material. Calcined samples of both types of material contained two species with well-defined EPR parameters, one of which was assigned to Cu(II) in substitutional sites in the bulk oxide while the other was thought to be in an interstititial site also coordinated by oxygen atoms. Prior to any thermal treatment the major species in both materials appears to be a hydrated Cu(II) ion adsorbed on the oxide particulate surface, although the material prepared by coprecipitation also contains some bulk-substituted copper(II).

To understand the nature of the catalytic conversion process it is, therefore, necessary to investigate (a) the nature of the copper(II)-promoted tin(IV) oxide catalyst materials themselves and the effect of thermal treatment on their constitution, and (b) the environment at the copper centers in the catalyst materials and the processes which occur at these sites. To this end we here present details of the characterization of Cu(II)/SnO_2 catalysts prepared by different methods, data for the catalytic oxidation of CO, and an EPR study of the role of the paramagnetic copper(II) centers.

Experimental Section

Preparation of Catalyst Materials. *(a) Tin(IV) Oxide Gel.* Tin(IV) oxide gel was precipitated by the dropwise addition of concentrated 33% w/w AnalaR aqueous ammonia solution to a cold, vigorously stirred solution of 0.1 M (75 g, 33.69 mL by volume) tin(IV) chloride (Aldrich) in triply distilled water (~500 mL) to a final pH of 4, to give an average particle size of 2.0 nm (TEM). The gelatinous precipitate formed was washed free of chloride ion by repeated centrifuging and redispersing in triply distilled water. This was confirmed by a simple negative chloride ion test using silver nitrate solution. The solid, white gel obtained was then allowed to air-dry at 333 K for 2–3 days. At this stage the gel was of a granular appearance, and approximately one-tenth of its initial volume. These large granules were then broken down by pouring a small amount of triply distilled water over them, and then allowed to air-dry further at 333 K for 24 h. The dry colorless gel was then ground into a fine white powder.

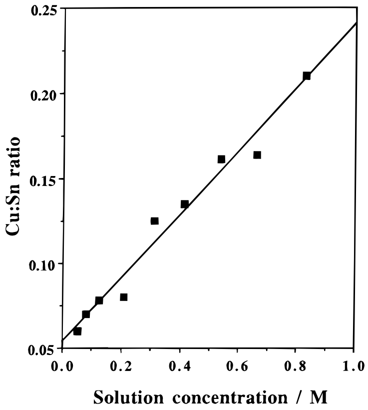

Figure 1. Plot of resultant Cu(II):Sn ratio in the final Cu(II)/SnO_2 catalyst material versus $Cu(NO_3)_2$ solution concentration. The solid line represents the best least-squares fit $\{Cu:Sn\} = 0.186[Cu(II)] + 0.054$ ($R^2 = 0.973$).

Transformation of this gel into a sol gel modification was accomplished by the use of choline hydroxide (Aldrich) as the peptizing agent as follows. To a suspension of tin(IV) oxide gel (12.5 g) in triply distilled water (60 mL) was added choline hydroxide (12 mL) and the suspension stirred for 24 h until a clear, brown dispersion was obtained. The dispersion was then air-dried at 333 K for 24 h to yield a brown-glassy solid.

(b) Preparation of Copper(II)-Promoted Tin(IV) Oxide Catalyst Materials. (i) By Impregnation. To a suspension of tin(IV) oxide gel (10 g) was added an aqueous solution of $Cu(NO_3)_2\cdot 2.5H_2O$ (Aldrich) dissolved in triply distilled water. These mixtures were kept stirred for 18 h and the resultant suspension was filtered to yield the blue Cu(II)/SnO_2 mixed-oxide gel. The Cu:Sn atomic ratio in the catalyst could be controlled by modifying the initial solution concentration of the copper(II) nitrate solution. Figure 1 shows the linear relationship between the initial solution concentration and the Cu:Sn ratio in the Cu(II)/SnO_2 gel over the solution concentration range of 0.1–0.8 M after the materials had been dried in air at ambient temperature. Targeting a specific loading was reproducible under the same preparative conditions. However, washing the impregnated materials with triply distilled water during the filtration stage results in a marked decrease in the overall loadings. For example, washing the Cu(II)/SnO_2 (Cu:Sn 0.08) material reduces Cu:Sn ratio progressively to 0.065. The resultant pale blue precipitate was then air-dried under ambient conditions for 24 h.

(ii) By Coprecipitation. This was achieved by a modification of the precipitation method above. $Cu(NO_3)_2\cdot 2.5H_2O$ was allowed to dissolve and homogenize in the vigorously stirred solution of tin(IV) chloride prior to addition of base. The subsequent workup was as above, affording a pale blue gel.

(iii) By Destabilization of Tin(IV) Oxide Sols. Copper(II) nitrate solution was added dropwise to a colloidal dispersion of choline-stabilized tin(IV) oxide sol prepared as described above. At Cu:Sn ratios >0.025 the tin(IV) oxide sol is destabilized and precipitation occurs. Addition was continued until Cu:Sn ratios of 0.08 and 0.30 were achieved. The resultant greenish gelatinous precipitate were then dried at 333 K, yielding a dark green solid.

(c) Copper(II) Oxide. To a solution of copper(II) nitrate hexahydrate (50 g) in triply distilled water was added dropwise sodium hydroxide solution (5 M, 200 mL) to produce a blue precipitate. The mixture was stirred overnight and washed with triply distilled water, and the solid was separated by

centrifugation. The washing procedure was repeated four times and the product dried in air at 333 K to yield a fine light blue powder of basic copper(II) nitrate (infrared) which was converted to copper(II) oxide as a black powder by calcination at 673 K. Powder XRD showed this material to be the tenorite syn monoclinic phase of copper(II) oxide with no other phase present up to calcination at 1273 K.

Catalyst Thermal Pretreatment. Copper(II)-promoted tin(IV) oxide catalyst materials (~2 g aliquots) were calcined in an alumina boat for 24 h using a Vecstar 91e tube furnace at temperatures of 573, 673, 873, 1073, and 1273 K. Several color changes were observed (573 K green, black 873 K, gray/black 1273 K).

Physical and Spectroscopic Measurements. Photon correlation spectroscopy data were obtained using a Malvern 3700 system equipped with a type K7025 correlator Infrared spectra were obtained from KBr disk samples using a Nicolet 20SXC spectrometer. A total of 32 scans were recorded for each sample at a resolution of 1 cm^{-1}. EPR measurements were performed on a Varian E-12 EPR spectrometer at 9.0−9.3 GHz. The spectra were recorded at 100−120 K, and the frequency and the magnetic field were measured with a HP5350B microwave frequency counter and a NMR Gaussmeter (Bruker ER035M), respectively. The *g*-factor was determined using DPPH as reference. Catalyst stoichiometries were determined by atomic absorption and X-ray fluorescence (Philips PW1480 wavelength dispersive instrument).

Powder X-ray diffraction data was acquired using a Philips X-pert system fitted with a PW 1710 diffractometer control unit with Cu Kα radiation ($\lambda = 1.5405$ Å). Representative diffractograms were acquired over 5−80° 2θ with 0.02° steps and 0.4-s acquisition times per step. DICVOL91[10] was used for indexing. Data for Rietveld refinement[11] were acquired between values of 5−120° 2θ with 0.02° steps and 9.5-s acquisition times per step.

EXAFS measurements were performed on station 8.1 at the Daresbury laboratory, Warrington, U.K., which operates at an energy of up to 2.0 GeV, and a maximum beam current of 200 mA. The X-rays are vertically collimated producing a beam of less than 1 mrad divergence. A Si(111) double-crystal monochromator was used to select a single wavelength beam of X-rays, the tunable energy range that can be achieved using this monochromator is 2−10 keV. A total of 40−50% of the X-ray beam was rejected to filter out the undesired harmonics while retaining 50−60% of the primary beam intensity.

Data were collected at the Cu K-edge (kiloelectronvolts) in fluorescence mode utilizing a Ge-13 channel solid-state detector. The sample was positioned at ~45° to the incident beam so as to maximize the solid angle seen by the detector. A total of 6 scans recorded for each catalyst sample, and refinement was achieved using EXBACK, EXCALIB, and EXCURV92.[12] The scans were coaligned, spikes due to noise removed, and the total number of scans added together to produce a single output data set with an improved signal-to-noise using EXCALIB. Background X-ray absorption was removed from the summed data set in two stages using the program EXBACK. Initially the preedge background was determined by fitting this region to a polynomial usually of order 1. The background absorption was then removed from the postedge region by a series of linked polynomial curves (normally 2 or 3) of order 3. With both the preedge and postedge background absorption removed from the data, the *x* axis was converted from energy to *k* space ($k = 2\pi/\lambda$, where λ is the electron wavelength) to give the EXAFS oscillations form $k = 0$. The EXAFS were then multiplied to k^3 so as to increase the amplitude of the oscillations at high values of *k*. Finally, radial distribution spectra were obtained via Fourier transformation of the EXAFS data. EXCURV92 was used to simulate EXAFS spectra of radial shells of neighbors around the central atom. For a more detailed description of the curved wave theory used in the program to calculate theoretical backscattering amplitudes and phase shifts, the reader is directed to the publications of Gurman[13] and Lee.[14]

The fit correlation parameter *R* between the calculated and observed data fall in the very acceptable range 20−40. Values of $R < 50$ are very reasonable for this type of sample, and values of $R < 20$ are unobtainable except for crystalline structures of clearly defined geometries. The estimated levels of accuracy in the refinements made by the EXCURV92 program arising from imperfect transferability of phase shifts and the fitting procedures are coordination number (50%), Debye−Waller factor, $2\sigma^2$ (50%), and radii (0.02 Å).

EPR Measurements. Three types of Cu/SnO_2 catalyst materials were prepared for the EPR experiments using modifications of the methods detailed above to afford materials with very low loadings of copper(II) to differentiate between the behavior of surface copper and copper which is incorporarted in the bulk material: (a) Cu(II) introduced by coprecipitation, (b) sorption of Cu(II) on to SnO_2 gel (impregnation), and (c) sorption of Cu(II) on to crystalline SnO_2. Here Cu(II) was introduced as described in b but after calcination of the SnO_2 gel at 873 K. The atomic ratio of copper to tin in all these materials was 0.0008.

The CO adsorption EPR experiments were performed as follows: the calcined materials were loaded into 3 mm o.d. quartz tubes and in the course of 4 h the temperature was gradually increased from 673 to 773 K under vacuum ($<10^{-4}$ Torr). After 2 h the samples were cooled to room temperature and exposed to 200−400 Torr CO. Some of the samples were then immediately immersed in liquid nitrogen, sealed, and kept in liquid nitrogen to prevent any reaction. The effect of the temperature was studied on samples which were heated at the desired temperature for 1 h after the exposure to CO and were then cooled to room temperature.

Catalysis Measurements. Catalytic conversion data for the oxidation of carbon monoxide were obtained using a custom-built horizontal geometry continuous flow microreactor. The furnace consisted of a stainless steel tube surrounded by a cylindrical stainless steel heating block. The sample tube, which sits inside the stainless steel tube, is made of Pyrex glass 1 cm in diameter with a glass sinter in the middle. The catalyst sample was packed on the inlet side of the sinter, supported by a dry silica pellet and held in place with glass wool. The outlet side of the sinter was packed with a dry silica pellet also held in place with glass wool. Catalyst samples (0.5 g) were sieved to a particles size in the range 38−63 μm, and diluted with silica gel of particle size 100 μm. Catalyst samples were activated by preheating in situ in the microreactor at 573 K for 2 h under a flow of air, and then allowed to cool also under a flow of air prior to examination. Catalyst temperatures were measured using a thermocouple located as close to the catalyst as possible. Gas flows were controlled by mass flow controllers, and concentrations of gas-phase components were measured using precise integration of characteristic infrared peaks. Initial compositions of the gas mixtures were 5.00% CO, 20.00% O_2, and 75.00% N_2 using a flow rate of 98 mL min^{-1}, corresponding to a space velocity of ~18 000 h^{-1}.

Results

Photon Correlation Spectroscopy. Stable SnO_2 colloidal sols can be readily made using choline as the stabilization agent. Previous studies have shown that the average particle size in choline-stabilized SnO_2 sols increases with increase in concentration.[15] The effect of the presence of Cu(II) cations on the state of aggregation in tin(IV) oxide colloidal sol is shown in Figure 2

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[10] DICVOL91: Boultif, A.; Louer, D. *J. Appl. Crystallogr.* **1991**, *24*, 987.

[11] PC-Rietveld Plus, Philips, June 1993.

[12] EXBACK, EXCALIB, and EXCURV92, Daresbury Computer programs, Daresbury Laboratory, Cheshire, U.K.

[13] Gurman, S. J.; Binstedt, N.; Ross, I. *J. Phys. C* **1984**, *17*, 143; **1986**, *19*, 1845.

[14] Lee, P. A.; Pendry, J. B. *Phys. Rev. B* **1975**, *11*, 2795.

[15] Harrison, P. G.; Azelee, W. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 813.

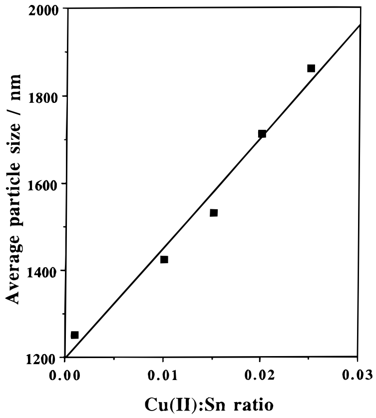

Figure 2. Plot of average particle size (APS) versus the Cu(II):Sn ratio in choline-stabilized SnO_2 sols (sol concentration 0.720 M). The solid line represents the best least-squares fit $\{APS\} = 2.549 \times 10^4\{Cu:Sn\} + 1195$ ($R^2 = 0.980$).

in which it can be seen that the particle size is strongly dependent on the quantity of Cu(II) present. At the lowest Cu:Sn ratio (0.001), the particle size is ~1252 nm, significantly larger than the particle size observed in the choline-stabilized tin(IV) oxide sol alone (~520 nm) at the same concentration of tin.[15] As the Cu(II):Sn ratio is increased and at ratios of Cu:Sn > 0.02 the average particle size is greater than 1800 nm. At Cu:Sn ratios > 0.025 the tin sol is destabilized and precipitation occurs.

X-ray Diffraction Studies. Catalysts comprising tin(IV) oxide promoted with copper(II), prepared by coprecipitation (Cu:Sn atomic ratios 0.02 and 0.25), impregnation (Cu:Sn atomic ratios 0.06, 0.12, and 0.21) and sol-destabilization (Cu:Sn atomic ratios 0.08 and 0.30) were analyzed by XRD after drying at 333 K as well as after calcination at 573, 673, 873, 1073, and 1273 K. All three types of catalyst material exhibited similar behavior. Prior to calcination the Cu(II)/SnO_2 catalyst materials exhibit diffractograms comprising four very broad peaks due to very small particulate SnO_2. The intensities of these peaks increase and sharpen with a progressive increase in calcination temperature, indicating an increase in crystallinity of the SnO_2 phase (Figure 3). The patterns after calcination at 1273 K are dominated by the characteristic pattern of tin(IV) oxide. No other phase is observed on heating to 873 K. However, after calcination at 873 K, Bragg reflections for CuO are observable. Monoclinic CuO is identifiable after calcination at 1273 K, with the most intense peaks at interplanar spacings (d) of {002} (2.530 Å), $\{\bar{1}11\}$ (2.523 Å), {111} (2.323 Å), {200} (2.312 Å), $\{\bar{2}02\}$ (1.866 Å), {202} (1.581 Å), and $\{\bar{1}13\}$ (1.505 Å).[16] For thermal treatments below 873 K, no information concerning phase can be gained as the diffraction patterns are very broad, indicative of small particle size and amorphous characteristics. Cu(II)/SnO_2 materials obtained by coprecipitation exhibit patterns where the phase-separated CuO peaks are considerably more intense than materials prepared by impregnation.

The possibility of copper incorporation in the tetragonal SnO_2 lattice was investigated using the DICVOL91 indexing program together with Rietveld refinement. Indexed values and refinement parameters for both impregnated and coprecipitated Cu(II)/SnO_2 materials after calcination at 1273 K are shown in Table 1 and are in good agreement with the literature with high figures of merit and acceptable R_{wp} values. The figures of merit, M(13), for indexing decrease for materials subjected to thermal treatments at temperatures lower than 1273 K due to a lesser degree of SnO_2 crystallinity. It can be concluded that after calcination at elevated temperatures the copper(II) exists solely as phase-separated CuO with no thermally induced incorporation into the SnO_2 lattice.

Mean particle sizes (D) calculated using the Scherrer equation for Cu(II)/SnO_2 catalyst materials prepared by all three methods for various copper loadings over a range of calcination temperatures are listed in Table 2. Figure 4 illustrates that the same general behavior is shown by all materials essentially irrespective of preparative route. Uncalcined materials just dried at 333 K comprise ~2 nm particles. Very little increase in size

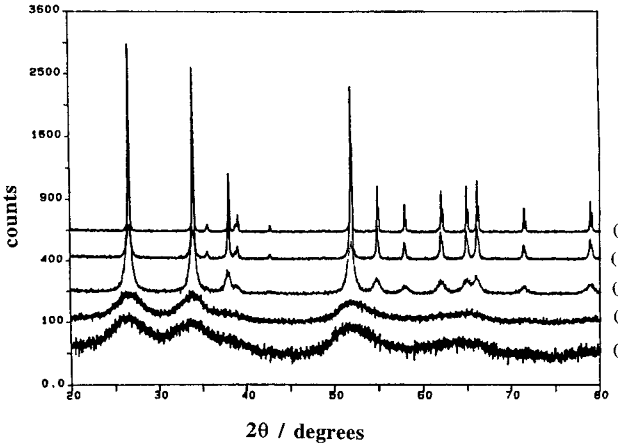

Figure 3. Powder X-ray diffractograms of Cu(II)/SnO_2 (Cu:Sn 0.30) prepared by sol destabilization after calcination at 333 K (a), 573 K (b), 873 K (c), and 1273 K (e). The corresponding diffractogram for a similar sample also prepared by sol destabilization and calcined at 1273 K but with a Cu:Sn atom ratio of 0.08 is shown in part d.

Table 1. Lattice Parameters for SnO_2 by Indexing and Rietveld Refinement of the Cu(II)/SnO_2 Materials at Various Calcination Temperatures

catalyst sample/ calcination temp	unit cell parameters,[a,b] Å	figure of merit M(13)	unit cell parameters,[a,c] Å	R_{wp}
Cu(II)/SnO_2 (imp) Cu:Sn 0.21)				
873 K	$a = 4.740(0)$ $c = 3.184(1)$	140	$a = 4.735(1)$ $c = 3.184(1)$	9.11
1073 K	$a = 4.729(1)$ $c = 3.182(1)$	68	–	–
1273 K	$a = 4.733(1)$ $c = 3.183(0)$	58	–	–
Cu(II)/SnO_2 (cop) Cu:Sn 0.25)				
873 K	$a = 4.736(0)$ $c = 3.184(0)$	310	$a = 4.736$ $c = 3.186$	5.25
1073 K	$a = 4.733(0)$ $c = 3.184(0)$	127	–	–
1273 K	$a = 4.736(1)$ $c = 3.186(0)$	36	–	– a

[a] Compare, values for tin(IV) oxide[17] are $a = 4.739$ Å and $c = 3.186$ Å. [b] Using DICVOL91.[10] [c] Using Rietveld.[11]

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(16) JCPDS pattern no. 5-661.

Table 2. Calculated Values of Mean Crystallite Size (*D*) of the SnO_2 Particles Derived from from X-ray Line Broadening in the Diffraction Patterns of Cu(II)/SnO_2 Catalyst Materials after Thermal Processing[a]

material/Cu:Sn atomic ratio	mean particle size (*D*), nm					
	333 K	573 K	673 K	873 K	1073 K	1273 K
Cu(II)/SnO_2 (imp)						
0.06	2.2	3.0	4.4	9.1	53.7	186.7
0.12	2.0	3.0	3.8	9.9	64.2	205.3[b]
0.21	1.8	2.7	4.4	13.2	81.7	207.9[b]
Cu(II)/SnO_2 (sol destab)						
0.08	2.4	3.0		9.3		204.1
0.30	2.5	3.0		8.6		204.4[b]
Cu(II)/SnO_2 (cop)						
0.02	1.9	4.2	4.6	6.9	52.2	170.0
0.25	2.0	4.2	5.0	6.7	52.9	176.8[b]

[a] Corresponding data for SnO_2 gel (nm): 2.4 (333 K), 6.6 (473 K), 8.2 (573 K), 33.7 (773 K), 81.6 (1073 K), and 207.6 (1273 K). [b] CuO observed, average particle size 14 nm.

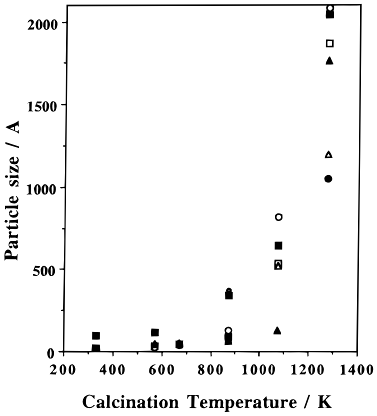

Figure 4. Variation in mean particle size with calcination temperature for Cu(II)/SnO_2 catalyst materials determined by X-ray line broadening for Cu(II)/SnO_2 prepared by impregnation Cu:Sn 0.06 (○), 0.12 (●), and 0.21 (+), Cu(II)/SnO_2 prepared by sol destabilization Cu:Sn 0.08 (▲) and 0.30 (■), and Cu(II)/SnO_2 prepared by coprecipitation Cu:Sn 0.02 (□) and 0.25 (×). Corresponding data for SnO_2 gel obtained by precipitation is denoted by △.

occurs on calcination at temperatures up to 673 K, but calcination at 873 and 1073 K results in significant progressive increases in particle size. Very large particles are formed in all materials on calcination at 1273 K. Although the particle size in SnO_2 gel dried at 333 K is the same as that in the Cu(II)/SnO_2 materials, the particle size increases significantly at relatively low calcination temperatures (×2.7 at 473 K, ×3.4 at 573 K), and it would appear that the presence of Cu(II) exercises an inhibiting effect on SnO_2 particle size growth. This inhibition is even more startling at higher calcination temperatures, for example the particle size of SnO_2 is 33.7 nm after calcination at 773 K compared to 6.7−13.2 nm for Cu(II)/SnO_2 after calcination at 873 K. Similar inhibition has also been observed for sol−gel-derived Cu(II)/SnO_2.[18] After calcination at very high temperatures, the presence of copper(II) has a lesser effect, and large SnO_2 particles are seen in both unpromoted and copper(II)-promoted materials.

EXAFS Studies. Representative fits for impregnated Cu(II)/SnO_2 (Cu:Sn = 0.21) dried at 333 K and after calcination at 873 and 1273 K are shown in Figure 5, with the numerical data tabulated in Table 3. Fits for the coprecipitated Cu(II)/SnO_2 (Cu:Sn = 0.25) material dried at 333 K and after calcination at 1273 K are presented in Figure 6 with the accompanying coordination data tabulated in Table 4.

For both the uncalcined impregnated and coprecipitated Cu(II)/SnO_2 materials, the major sorbed copper species are hexaaqua $\{Cu(H_2O)_6\}^{2+}$ ions sorbed onto the surface of the tin(IV) oxide particles. Jahn−Teller distortions (4 + 2 coordination) characteristic of copper(II) d^9 ($t_{2g}{}^6 e_g{}^3$) is observed for these adsorbed Cu^{2+} species with the four (equatorial) oxygen atoms in the octahedral coordination sphere at a Cu···O distance of ∼1.95 Å, and two at a slightly longer distance of ∼2.1 Å for both material types. The fit correlations were improved with the inclusion of two oxygen atoms in a third shell at a radial distance of ∼3.7 Å from the Cu absorber for both material types.

Scans of the Cu(II)/SnO_2 materials which had been calcined at 573 K were not obtained. However, data for the related Cu(II)/CeO_2 material calcined at 573 K, which is believed to behave in a similar way similar to the analogous Cu(II)/SnO_2 material, have been discussed by Daniell.[19] However, no theoretical model could be fitted to the experimental data due to the averaging of the EXAFS signal between bulk incorporated Cu(II) sites, probably existing as small amorphous aggregates, and surface adhered Cu(II) species probably coordinated by five water molecules and a surface oxygen. With increased calcination, particle size growth accompanied by Cu(II) migration increases with the formation of monoclinic CuO. After calcination at 873 K, phase-separated CuO can be identified (Table 3) for impregnated Cu(II)/SnO_2. The coordination parameters are in good agreement with literature values.[21,22] After calcination at 1273 K the fit parameters are in even better agreement with the literature, reflected by the lower fit correlation of $R = 22.6$. The higher R value observed after calcination at 873 K, may also be attributed to an averaging effect in the EXAFS between the CuO phase and the small amount of Cu(II) species near to or at the external surface of the particles Table 4 shows data for CuO in the coprecipitated Cu(II)/SnO_2 material calcined at 1273 K.

EPR Studies. The EPR spectrum of Cu(II)/SnO_2 (Cu: Sn 0.0008) prepared by impregnation and calcined at 673 K (Figure 7, top trace) exhibits broad nonresolvable resonances due to Cu(II) species with a distribution of parameters upon which is superimposed the resolved spectra of the species which we have previously identified as Cu(II) species occupying substitutional positions in the tetragonal tin(IV) oxide lattice.[17] These unresolved EPR resonances we attribute to a range of broadly similar Cu(II) species located on the surface of

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(17) Baur, W. H. *Acta Crystallogr.* **1956**, *9*, 515.

(18) Davis S. R.; Chadwick, A. V.; Wright, J. D. *J. Phys. Chem. B* **1997**, *101*, 9901.

(19) Daniell, W., Ph.D. Thesis, University of Nottingham, **1998**.

(20) Maercera, P. D. L.; Ommen, J. G.; Doesburg, E/B. M.; Burgraaf, A. J.; Ross, J. R. H. *Appl. Catal.* **1991**, *71*, 363.

(21) Åsbrink, S.; Norrby, L. J. *Acta Crystallogr. B* **1970**, *26*, 8.

(22) Blake, A. J. Private communication, 1997.

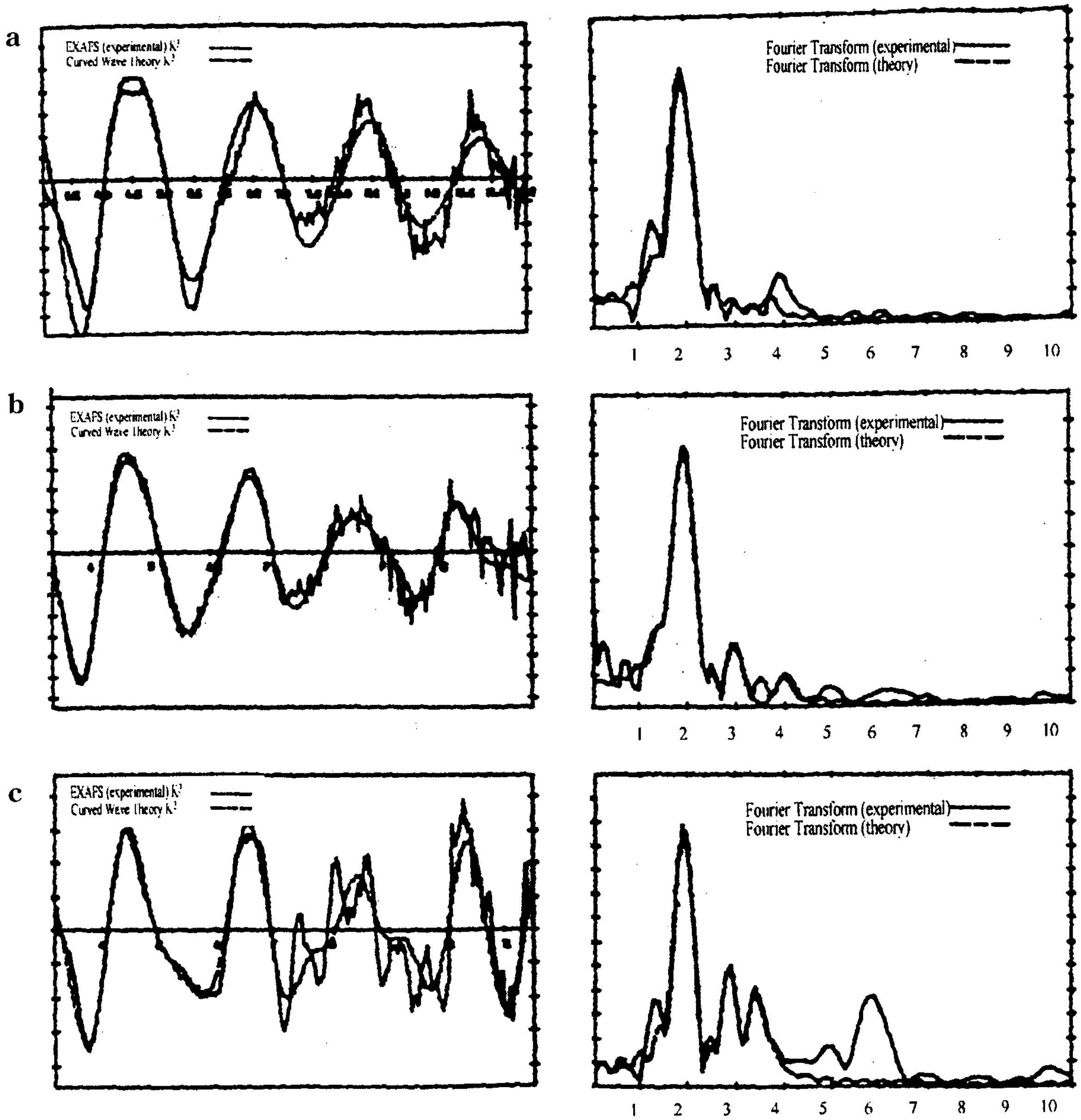

Figure 5. Experimental (solid line) and theoretical (dashed line) normalized EXAFS data and the corresponding Fourier transforms for Cu(II)/SnO_2 prepared by impregnation (Cu:Sn 0.21): (a) after drying at 333 K, and after calcination at 873 K (b) and 1273 K (c).

the tin(IV) oxide particles. EPR spectra of an otherwise identical sample which was prepared by first calcining the tin(IV) oxide to 873 K prior to impregnation with Cu(II) and calcination at 773 K is shown in Figure 8 (top trace). This sample exhibits mostly the broad unresolved features due to surface Cu(II) species with very little of the resolved spectra due to bulk incorporated Cu(II).

Also shown in Figure 8 are EPR spectra recorded after exposure of the postcalcined (873 K) Cu(II)-impregnated sample to 400 Torr of CO at different temperatures. Room temperature adsorption results in only a slight decrease in the intensity of the Cu(II) signals, indicating that at room temperature the Cu(II) reduction is very slow. A narrow anisotropic signal with maximum at $g = 2.004$ is also generated which is attributed to an oxygen species.[23-25] This species could be $O_2^-{}_{ads}$ which is generated upon the adsorption of O_2 on slightly reduced SnO_2.[23] Although O_2 was not introduced intentionally to the sample, small amounts of oxygen are probably present as an impurity in the CO. The Cu(II) signals were drastically reduced in intensity on heating to 373 K as reduction to EPR-silent Cu(I) occurs. By 573 K most of the Cu(II) signals had disappeared, and Cu(II) could no longer be detected after 1 h at 673 K. The $O_2^-{}_{ads}$ signal which appears after exposure to CO at room temperature vanishes on heating. Heating to 673 K results in the appearance of new signal at $g = 1.89$, which may be attributed to singly ionized oxygen vacancies[26] but is more probably due to a surface Sn(III) species.[27]

Somewhat different behavior was exhibited by the sample prepared by impregation of uncalcined tin(IV)

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(23) Meriaudeau, P.; Naccache, C.; Tench, A. J. *J. Catal.* **1971**, *21*, 208.

(24) Volodin, A. M.; Cherkashin, A. F. *React. Kinit. Catal. Lett.* **1981**, *17*, 323, 329.

(25) Chang, S.-C. *J. Vac. Sci. Technol.* **1980**, *17*, 366.

Table 3. Refined Structural Parameters from Cu K-edge EXAFS Data for the Cu(II)/SnO_2 (Cu:Sn 0.21) Catalyst Material Prepared by the Impregnation Route after Calcination at Various Temperatures in the Range 333−1273 K[a]

calcination temperature	atom type	coord no.	Debye−Waller factor $2\sigma^2$/Å^2	radial distance, Å	copper species present	lit. values, Å
333 K	O	4	0.010	1.959	$\{Cu(H_2O)_6^{2+}\}$[b]	1.980
	O	2	0.082	2.120		2.005
	O	2	0.019	3.751		
873 K	O	2	0.003	1.866	CuO[c]	1.951
	O	2	0.014	1.966		1.960
	O	2	0.050	2.710		2.784
	Cu	2	0.018	2.900		2.905
	Cu	2	0.012	3.078		3.083
	Cu	1	0.005	3.245		3.173
	Cu	1	0.016	3.853		3.748
1273 K	O	2	0.008	1.951	CuO[c]	1.951
	O	2	0.007	1.961		1.960
	O	2	0.011	2.782		2.784
	Cu	2	0.001	2.905		2.905
	Cu	2	0.006	3.080		3.083
	Cu	1	0.006	3.177		3.173
	Cu	1	0.010	3.797		3.748

[a] *R* values 31.6 (333 K), 35.5(873 K), and 22.6 (1273 K). [b] Reference 20. [c] References 21 and 22.

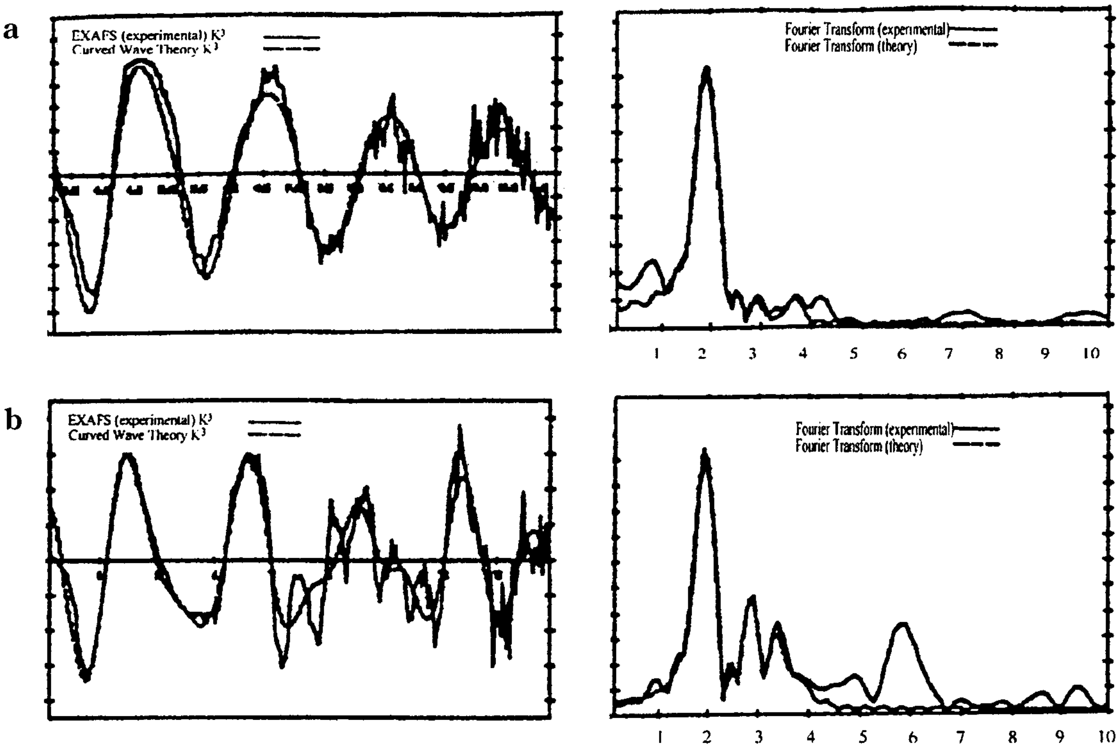

Figure 6. Experimental (solid line) and theoretical (dashed line) normalized EXAFS data and their Fourier transforms for Cu(II)/SnO_2 (Cu:Sn 0.25) prepared by coprecipitation(a) after drying at 333 K and (b) after calcination at 1273 K.

oxide in a similar series of CO adsorption experiments (Figure 7). Room-temperature adsorption generates the same narrow anisotropic signal at $g = 2.004$ attributed to $O_2^-{}_{ads}$ species, accompanied by a similar slight decrease in the intensity of the Cu(II) signals. Increasing the sample temperature to 373 K leads to the disappearance of the $O_2^-{}_{ads}$ signal and to a significant decrease in the intensity of the Cu(II) signal due to reduction to Cu(I). Further increase of the temperature to 573 K causes an additional decrease in the intensity accompanied by an enhancement in the resolution along with the appearance of a signal at $g = 1.89$. A similar but significantly narrower species is observed after further heating to 673 K for 1h. Spectra of samples recorded after heating to temperatures ≥573 K exhibit signals due to lattice-incorporated Cu(II) species and no surface Cu(II) species is apparent. Reduction of lattice-incorporated Cu(II) could be accomplished only after exposing the sample to CO at 623 K overnight. Evacuation of the fully reduced sample and exposure to oxygen (200 Torr) at 723 K for 4 h restored the original EPR spectrum. All spectra show a small isotropic signal at $g = 1.983$ which appeared also in SnO_2 samples without Cu(II). We assign it to an impurity of negligible amount and therefore will not be discussed further.

Cu(II)/SnO_2 samples prepared by coprecipitation and calcined at 773 K exhibited the same behavior upon reduction with CO. The Sn(III) signal appeared only

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(26) Di Nola, P.; Morazzoni, F.; Scotti, R.; Narducci, D. *J. Chem. Soc., Faraday Trans. 1* **1993**, *89*, 3711.

(27) Ishiguro, K.; Sasaki, T.; Arai, T.; Imai, I. *J. Phys. Soc. Jpn.* **1958**, *13*, 296.

Table 4. Refined Structural Parameters from Cu K-Edge EXAFS Data for the Cu(II)/SnO_2 (Cu:Sn 0.25) Catalyst Material Prepared by the Coprecipitation Route after Calcination at 333 and 1273 K[a]

calcination temperature	atom type	coord no.	Debye−Waller factor $2\sigma^2$/Å^2	radial distance, Å	copper species present	lit. values, Å
333 K	O	4	0.009	1.946	$\{Cu(H_2O)_6^{2+}\}^b$	1.980
	O	2	0.118	2.180		2.005
	O	2	0.017	3.720		
1273 K	O	2	0.009	1.940	CuO[c]	1.951
	O	2	0.007	1.955		1.960
	O	2	0.015	2.759		2.784
	Cu	2	0.005	2.892		2.905
	Cu	2	0.011	3.051		3.083
	Cu	1	0.007	3.101		3.173
	Cu	1	0.010	3.821		3.748

[a] *R* values 34.0 (333 K) and 39.0 (1273 K). [b] Reference 20. [c] References 21 and 22.

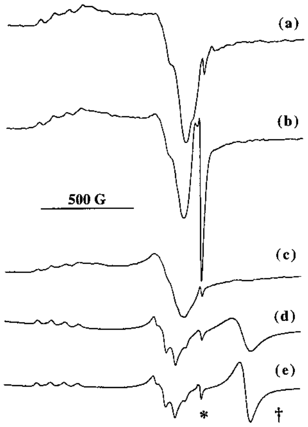

Figure 7. CW-EPR spectra (recorded at 120 K) of Cu(II)/SnO_2 (Cu:Sn 0.0008) prepared by impregnation and precalcined at 773 K (a) after dehydration at 673 K, and after exposure to 400 Torr of CO at (b) ambient temperature, (c) 373 K, (d) 573K, and (e) 673 K for 1 h. The resonance at $g = 2.004$ is denoted by an asterisk (*) and that at $g = 1.89$ by a dagger (†).

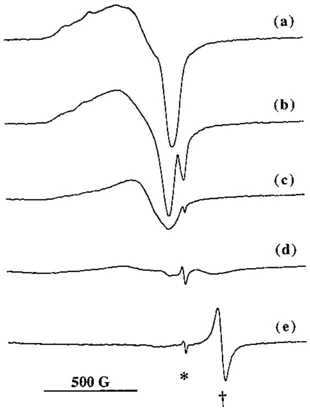

Figure 8. CW-EPR spectra (recorded at 120 K) of Cu(II)/SnO_2 (Cu:Sn 0.0008) prepared by impregnation of Cu(II) onto precalcined SnO_2 at 873 K followed by calcination at 773 K (a) after dehydration at 673 K, and after exposure to 400 Torr of CO at (b) ambient temperature, (c) 373 K, (d) 573 K, and (e) 673 K for 1 h. The resonance at $g = 2.004$ is denoted by an asterisk (*) and that at $g = 1.89$ by a dagger (†).

after reduction at 573 K and lattice-incorporated Cu(II) could be reduced only after exposure to CO at high temperature for a prolonged time.

The Activity of Copper(II)-Promoted Tin(IV) Oxide Catalysts toward the Catalytic Oxidation of Carbon Monoxide. Catalysts obtained by all three methods of preparation were active for the oxidation of carbon monoxide, and showed similar behavior for light-off and T_{100} temperatures (the temperature required for 100% conversion of CO) irrespective of the preparative route. Because of this similarity, only data for the Cu(II)/SnO_2 (Cu:Sn 0.30) catalyst obtained by the sol-destabilization route are described in detail. Light-off and T_{100} values (the temperature required for the complete oxidation) for the oxidation of CO for this catalyst are summarized in Table 5 with conversion plots illustrated in Figure 9.

Table 5. Conversion Data for the Catalytic Oxidation of CO over Cu(II)/SnO_2 (Cu:Sn 0.30) Catalyst Prepared by Sol Destabilization

catalyst	pretreatment temp, K	light-off temp, K	T_{100}(CO), K
SnO_2	673	373	613
CuO	673	490	533
Cu(II)/SnO_2	333	350[a]	405[a]
	673	300	355
	873	320	487
	1273	470	727
commercial Pt/Al_2O_3	573	433	623

[a] Light-off and T_{100}(CO) temperatures for this sample decrease to 300 K and 385 K after thermal pretreatment in situ at 573 K.

The freshly prepared uncalcined Cu(II)/SnO_2 (Cu:Sn 0.30) calcined in situ at 573 K gives 100% conversion of CO at 374 K under oxygen-rich conditions (5% CO + 20% O_2 + 75% N_2). However, when this catalyst is calcined at 673 K 100% conversion is achieved at an even lower temperature (355 K). For the 673 K ex situ precalcined catalyst, only 95% conversion of CO is observed on cooling to 333 K, but 100% conversion is again achieved on heating to 349 K. Furthermore, if under these conditions (349 K), the input gas mixture composition is changed to stoichiometric (30% CO + 15% O_2 + 55% N_2)), 100% CO conversion is still achieved. In addition, even when the furnace is switched off reaction is self-sustaining and proceeds with 100% conversion, the exotherm of the reaction keeping the furnace warm (328 K). Complete CO conversion was maintained over 24 h period under these conditions. Subsequent removal of this catalyst sample from the microreactor and strorage at ambient temperature for more than one week followed by reexamination in the microreactor gave an identical activity performance for both oxygen-rich and stoichiometric input gas mixture compositions.

The T_{100} value observed for the Cu/SnO_2 catalyst for after activation in situ at 673 K is substantially lower (355 K) than that exhibited by both copper oxide (533

K) (Figure 9B) and tin(IV) oxide alone (613 K) as well as a commercial Pt/Al_2O_3 catalyst (623 K) under the same conditions (Table 5).

Ex situ precalcination of the Cu/SnO_2 catalyst at higher temperatures results in a decrease in activity with increased light-off temperatures and T_{100} values rising to 573 and 723 K after precalcination at temperatures of 873 and 1273 K, respectively (Figure 9A and Table 5). The catalyst is also deactivated completely by running under very lean conditions (high CO, low O_2) (e.g., 50% CO + 11% O_2 + 39% N_2). However, the activity of the catalyst can be restored completely by heating in a flow of air at 573 K (Figure 9C).

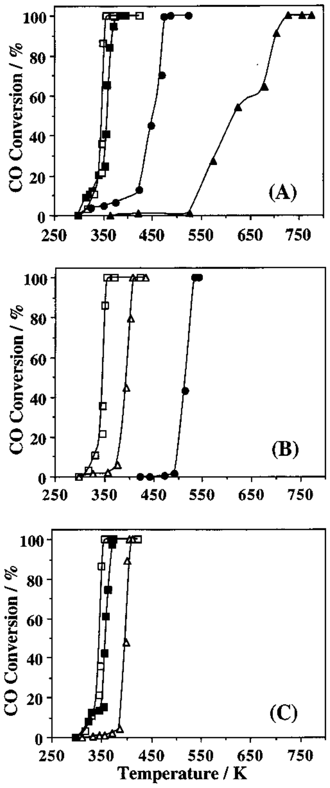

Figure 9. Percentage conversion versus temperature plots for the catalytic oxidation of CO over $Cu(II)/SnO_2$ (Cu:Sn 0.40): (A) after precalcination treatment ex situ at 333 K (■), 673 K (□), 873 K (●), and 1273 K (▲) followed by in situ activation at 573K. Part B shows the comparative behavior of a precipitated CuO catalyst which has been precalcined ex situ at 673 K followed by activation in situ at 573 K (●) with the $Cu(II)/SnO_2$ (Cu:Sn 0.30) catalyst after the same treatment (□) and without the in situ activation treatment at 573K (△). Part C illustrates the reactivation of the $Cu(II)/SnO_2$ (Cu:Sn 0.30) precalcined at 673 K and activated in situ at 573 K (□) following deactivation by CO and treatment in a stream of air at 355 K (△) and 573 K (■).

Discussion

The initial report[1] of the activity of Cu/SnO_2 catalysts prepared by the coprecipitation method and activated at 723 K toward the oxidation of carbon monoxide indicated empirically that the optimum performance resulted from a composition of $0.55CuO\cdot SnO_2$. The activity was attributed to the sorption of copper(II) ion on the surface of hydrous SnO_2 particles, with no evidence for the formation of any mixed oxide up to temperatures of 1273 K. In the present study, catalysts obtained by all three methods, coprecipitation, sorption, and sol-destabilization, showed similar behavior for light-off and T_{100} temperatures irrespective of the preparative route and which is also similar to that of the initial report.[1] For all, optimum catalytic activity appeared to be induced by thermal pretreatment at ~673K, and the Cu:Sn atomic ratio appeared to have less influence on the activity. Pretreatment of the catalysts at higher temperatures reduced progressively the catalytic activity, a trend which was irreversible. However, catalysts which had been activated at 673 K are very active, and their activity was self-sustaining by the exotherm of the reaction resulting in an equilibrium reaction temperature under these conditions of 328 K. Further, these active catalysts are deactivated by exposure to highly reducing atmospheres, but the activity is restored completely by thermal reactivation in a flow of air at 573 K.

A number of conclusions may be drawn from the catalytic activity data: (1) The "active" catalyst results from thermal activation processing at ~673 K of the initial products obtained from a variety of preparative procedures. (2) Thermal processing at higher temperatures results in irreversible deactivation. (3) Reversible deactivation of the "active" catalyst occurs on exposure to reducing atmospheres. (4) The activity of the composite $Cu(II)/SnO_2$ catalyst toward the oxidation of carbon monoxide is greater than for either of the two individual oxides. These observations indicate the occurrence of both chemical and physical changes which affect the nature of the catalyst material.

We have employed three methods for the preparation of $Cu(II)/SnO_2$ catalyst materials: (i) coprecipitation from aqueous solutions containing Cu^{2+} and Sn^{4+} ions, (ii) sorption of Cu^{2+} ions on to preformed tin(IV) oxide gel, and (iii) destabilization of choline-stabilized tin(IV) oxide colloidal sols by the addition of aqueous copper(II) nitrate solution. Coprecipitation is expected to produce a gel material in which copper(II) is incorporated into the tetragonal lattice of the microparticulate tin(IV) oxide. However, such incorporation of copper(II) ions into lattice sites will occur only to a relative small extent, and any additional copper ions would be expected to sorb to the exterior of the tin(IV) oxide particles. In contrast, no incorporation of copper(II) ions into tin(IV) oxide lattice sites would be expected by either of the other two methods. Rather, both of these routes would be expected to yield gel materials in which all copper(II) ions are present as surface species sorbed onto the tin(IV) oxide particulate, irrespective of the level of copper loading. Thus, both the method of preparation and the level of copper loading are important in determining the nature of the products. Our previous[9] EPR and ESEEM studies of very dilute $Cu(II)/SnO_2$ (Cu:Sn 0.0008) materials prepared both by coprecipitation and inpregnation/sorption routes show that the sorption route does indeed afford only surface-sorbed hexaaqua $\{Cu(H_2O)_6\}^{2+}$ ions. In contrast, even at these low levels of copper doping by the coprecipitation method results in two types of copper(II), the same surface-sorbed hexaaqua $\{Cu(H_2O)_6\}^{2+}$ ions as observed by the sorption route and also lattice-incorporated copper(II). Incorporation of copper(II) into lattice sites only occurred after thermal treatment for the doped sample derived by sorption. In the present study, EXAFS data indicate that the major copper(II) species present in freshly prepared Cu(II)/SnO_2 materials obtained by both the impregnation of preformed tin(IV) oxide gel using aqueous copper(II) nitrate solution and coprecipitation is the same hexaaqua $\{Cu(H_2O)_6\}^{2+}$ ion. That no lattice copper(II) is observed in the EXAFS is not surprising since the copper(II) loadings in these materials is high (Cu:Sn ~0.21−0.25) and indicates that the level of lattice-incorporated copper(II) is relatively low. This conclusion is in accord with other recent EXAFS studies on copper-doped tin(IV) oxide materials prepared in similar ways with varying amounts of copper loading.[28] In this study it was shown that the limit of solubility of copper in nanocrystalline tin(IV) oxide is ~1%. This figure is about 1 order of magnitude lower than previously determined,[18] which suggests that the precise experimental preparative conditions play an important part in the level of dopant incorporation into the tin(IV) oxide lattice.

Coprecipitation reproduces the same Cu:Sn ratio in the catalyst material as in the initial solution. However, targeting a specific loading by the impregnation method depends on various criteria: initial solution concentration, exposure time, reflux temperature, and washing conditions. Both routes, however, give tin(IV) oxide nanoparticles of ~2 nm. It is perhaps noteworthy that the color of the materials obtained by sol-destabilization (green) is different from the other materials (pale blue), indicating that the copper is initially present as a different complex rather than hexaaqua $\{Cu(H_2O)_6\}^{2+}$ ions. Nevetheless, this material, like that produced by sorption, is not expected to have copper in lattice sites.

Thus, we may conclude that the copper dopant in the Cu(II)/SnO_2 materials examined in the present study is present as copper(II) ions adsorbed on the surface on tin(IV) oxide nanocystallites, with no lattice incorporation except in via coprecipitation where a low level (~5% of the total copper loading) occurs.

The thermal processing of these materials, which is important in their activation as CO oxidation catalysts, induces significant changes. Crystallite growth is slow initially, but nevertheless involves a 50% increase in size by 573 K, a doubling in size by 673 K and a 5-fold increase by 873 K. Processing at temperatures in excess of this leads to a much more rapid crystal growth and the phase separation of copper oxide crystallites. In materials calcined at 1273 K, the copper is segregated as copper(II) oxide crystallites of ~14 nm in size together with very large (~180−200 nm) particles of tin(IV) oxide. It is clear from the precise determination of unit cell parameters from powder X-ray data for materials calcined at temperature ≥ 873 K that there is no significant incorporation of Cu(II) into the tin(IV) oxide lattice. This is consistent with previous observations that the lattice-incorporated copper(II) in Cu(II)/SnO_2 gels prepared by coprecipitation migrates from the metastable gel to the crystallite surface at relatively low temperatures.[18]

The process by which particle growth occurs is by initial loss of physisorbed/hydrogen-bonded molecular water, thereby exposing surface hydroxyl groups which can then condense forming interparticular "necks". Loss of water by these processes is essentially complete by ~723 K. Simultaneously two other processes occur, the dehydration of the adsorbed hexaaqua $\{Cu(H_2O)_6\}^{2+}$ ions and the migration of copper(II) ions in substitutional lattice sites in the bulk to superficial surface sites. These processes lead to a material after treatment at 573−673 K comprising small (~4 nm) particles of tin(IV) oxide which have a superficial amorphous oxide layer which has a disordered structure containing both tin(IV) and copper(II) ions. At this stage no phase separation of copper(II) oxide crystallites has yet occurred, and the copper(II) ions are dispersed in the superficial oxide layer. This composite material derived by calcination of the gel materials obtained initially by all three routes exhibits the highest activity for carbon monoxide oxidation.

The surface concentration [M] of the promoter on the surface particles of a support oxide, assuming spherical, fully dense particles, is given by the expression:

$$[\mathrm{M}] = \frac{\rho A d(n \times 10^2)}{6M} \text{ atoms nm}^{-2} \tag{1}$$

where ρ is the bulk density of the support oxide (grams per cubic cetimeter), A is Avogadro's number, d is the diameter of the support oxide particles (nanometer), M is the formula mass of the support oxide, and n is the fractional metal atom ratio of the promoter metal to support oxide. For copper-promoted tin(IV) oxide catalyst materials, this expression becomes

$$[\mathrm{Cu}] = 4 \times 26(dn) \text{ atoms nm}^{-2} \tag{2}$$

After thermal activation at 573−673 K the tin(IV) oxide particle size is ~4 nm, essentially independent of the copper loading level and preparative route (Table 2). Hence, for a Cu:Sn loading of 0.2, the surface [Cu] concentration on the surface of the tin(IV) oxide particles will be 3.4 Cu atoms nm^{-2}, and for a Cu:Sn loading of 0.3 the surface [Cu} concentration will be 5.1 Cu atoms nm^{-2}. These data correspond to a spacing of the copper atoms on the surface of 0.54 and 0.44 nm, respectively; i.e., even at these typical loadings the copper atoms are fairly well spaced apart in the thermally activated catalysts.

It is open to speculation what role copper(II) plays in catalysts which have been thermally activated in the temperature range 573−673 K to give optimum performance. Both tin(IV) oxide and copper(II) oxide exhibit catalytic activity for the oxidation of carbon monoxide on their own account. However, temperatures for light-off and complete conversion are considerably higher than for the thermally activated composite Cu(II)/SnO_2 catalyst, which is indicative of some synergism between the two components. Similar strong synergistic effects have been observed in mixed Fe_2O_3/SnO_2[29] and Mn_2O_3/SnO_2[29] as well as Cu/CeO_2[30] catalysts. Both Cu(II)/SnO_2 and Cu(II)/CeO_2[19] catalysts function efficently at very low temperatures, where no significant copper reduction occurs as previously observed for both unsupported

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[28] Santilli, C. V.; Pulcinelli, S. H.; Brito, G. E. S.; Briois, V. *J. Phys. Chem. B* **1999**, *103*, 2660.

[29] Kulshreshtha, S. K.; Gadgil, M. M.; Sasikaia, R. *Catal. Lett.* **1996**, *37*, 181.

[30] Martinez-Arias, A.; Fernandez-Garcia, M.; Soria, J.; Conesa, J. C. *J. Catal.* **1999**, *182*, 367.

copper(II) oxide[31] and other supported copper(II) catalysts such as Cu(II)/Al$_2$O$_3$.[32–34] Hence, it may be concluded that both components are important for the high catalytic activity observed in the present case, which raises the question of how the synergism operates.

Our earlier infrared studies demonstrated that unidentate and bidentate carbonate and a carboxylate species are formed by adsorption from CO/O$_2$ mixtures onto the surface of tin(IV) oxide alone.[5,6] From these observations, we proposed that the catalytic oxidation of carbon monoxide over tin(IV) oxide proceeded via initial adsorption of CO at a surface oxygen forming a surface carbonato species, followed by desorption of carbon dioxide leaving a surface vacancy. The latter was restored by dissociative chemisorption of dioxygen.[3–6] Additional surface species are also formed on copper(II)-modified tin(IV) oxide, including what appeared to be a surface Cu–CO carbonyl species.[7,8] The adsorption of CO on this Cu(II)/SnO$_2$ catalyst material is substantial (81.3 μmol g^{-1} catalyst at an applied pressure of 1.33 kN m^{-2} CO), and is also reversible.[8] The implication of these infrared data is that the role of copper is to provide a facile adsorption site for CO, catalytic conversion proceeding via spillover onto tin(IV) oxide and the mechanism being similar to that proposed for tin(IV) oxide alone.

The EPR data, however, suggest a somewhat different role for the copper. It is apparent that only surface copper(II) is reactive in a catalytic sense with CO, since bulk copper(II) only reacts with CO under relatively extreme conditions. At ambient temperature surface copper(II) species are reduced quite slowly to copper(I) on exposure to CO. Dioxygen appears to adsorb on the surface of tin(IV) oxide at ambient temperature to form $O_2^-{}_{ads}$ even in the presence of CO. Facile reduction of surface copper(II) occurs on heating to ≥373 K, but concomitantly the $O_2^-{}_{ads}$ is consumed. When all the copper(II) is reduced and the $O_2^-{}_{ads}$ is exhausted, the CO starts to reduce surface Sn(IV) to Sn(III) species. The material could be restored to its fully oxidized form by exposure to dioxygen at elevated temperature.

Thus, the mode of action of these catalyst materials appears to be via the reduction of a surface metal cation, either copper(II) at low temperatures (373 K) or tin(IV) at elevated temperatures (673 K) by CO. These reduction processes most probably occur by the abstraction of a surface oxygen by gas-phase CO-forming carbon dioxide which desorbs leaving a surface vacancy together with two negative charges. The role of the copper(II) is to scavenge the negative charge and be reduced to copper(I). In the absence of copper(II), this function is carried out by surface tin(IV) cation, but only at a greatly elevated temperature. Surface carbonates are probably formed by the readsorption of carbon dioxide on the surface. Dissociative chemisorption of dioxygen replenishes the surface vacancies and reoxidizes copper(I) to copper(II).

The catalyst can be deactivated reversibly by exposure to highly reducing atmospheres such as high concentrations of carbon monoxide, or irreversibly by thermal treatment at very high temperatures. Reversible deactivation occurs by the depletion of surface oxygen, but this may be restored by treatment with molecular oxygen which restores the levels of active surface oxygen species necessary for the adsorption of CO. The irreversible deactivation can be attributed to two processes which occur at temperatures ≥873 K, the phase separation of copper(II) oxide particles and rapid particle size growth which severely reduces the specific surface area. The onset of rapid particle size growth occurs at temperatures ~873K. Thermal processing at this temperature produces particles ~2–3 times this size after processing at 673 K, and much larger particles are produced at higher temperatures (Table 2). Crystalline copper(II) oxide is observed in all but the lowest copper loadings after processing at 1273 K, and has been characterized by EXAFS in the Cu(II)/SnO$_2$ (Cu:Sn 0.21) catalyst material prepared by impregnation after processing at 873 K.

The expression in eq 2 shows that the surface concentration of copper atoms increases with increasing copper loading and also with particle size. Thus as the particles become larger with increase in temperature (Table 2 and Figure 4) so the surface will become richer in copper. However, for crystallites of copper(II) oxide to form, the surface concentration of copper has to exceed that required for crystalline copper(II) oxide[21] (16.7 Cu atoms nm^{-2}). Hence, depending on the copper loading, there will be a critical particle size at which this surface concentration of copper atoms is exceeded thus allowing unit cells of crystalline CuO to be formed. For Cu:Sn loadings of 0.2–0.3, this critical particle size will be in the range ~20–13 nm. Since particles of this size are not produced during thermal processing until >873 K, it is not surprising that crystalline copper(II) oxide is not observed at lower thermal treatment temperatures. That copper(II) oxide is discernible by EXAFS for the Cu(II)/SnO$_2$ (Cu:Sn 0.21) catalyst material prepared by impregnation after processing at 873 K where the particle size is 13.2 nm, but not for other compositions and synthetic routes processed at this temperatures where the particle size is significantly lower lends credence to this argument. For crystallites of ~200 nm in size produced after thermal treatment at 1273 K, the calculated surface concentration of copper atoms for a copper loading of 0.2 corresponds to a copper(II) oxide layer ~10 units cells thick, i.e., after high-temperature thermal processing substantial amounts of copper(II) oxide are to be expected. Indeed, after treatment at 1273 K crystallites of copper(II) oxide are discernible in the X-ray diffractograms at these loadings. Consistent with this hypothesis are the catalytic data for CO oxidation for the Cu(II)/SnO$_2$ catalyst thermally processed at 1273 K and neat copper(II) oxide which exhibit very similar light-off temperatures.

Thus the major factor affecting nature of the Cu(II)/SnO$_2$ catalyst materials is the temperature of the pretreatment activation processing. The preparative route and the level of copper loading have a lesser effect. A summary relating the CO activity properties and catalyst deactivation with the constitution of the materials at various processing temperatures is shown in Table 6.

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(31) Jernigan, G. G.; Somorjai, G. A. *J. Catal.* **1994**, *147*, 567.

(32) Severino, F.; Brito, J.; Carias, O.; Laine, J. *J. Catal.* **1986**, *102*, 172.

(33) Choi, K. I.; Vannice, M. A. *J. Catal.* **1991**, *131*, 22.

(34) Park, P. W.; Ledford, J. S. *Appl. Catal. B, Environ.* **1998**, *15*, 221.

Table 6. Summary of the Nature of Cu(II)SnO$_2$ Catalyst Materials after Various pretreatment temperatures

pretreatment temperature	nature of catalyst material	activity toward CO oxidation	comments
333 K	Copper present largely as $\{Cu(H_2O)_6\}^{2+}$ ions adsorbed on the surface on tin(IV) oxide nanocystallites (average particle size 1.8−2.5 nm), with no lattice incorporation of copper except in the coprecipitation route where a low level (*ca.*∼5% of the total copper loading) occurs	Exhibits greater activity than either CuO or SnO$_2$ alone, but not as high as after thermal processing at 573−673 K.	
573−673 K	Comprises small (3−5 nm) SnO$_2$ particles with a superficial amorphous oxide layer which has a disordered structure containing both tin(IV) and copper(II) ions. No phase separation of CuO crystallites has yet occurred, and the copper(II) ions are dispersed in the superficial oxide layer.	Exhibits the highest activity for CO oxidation, with light-off at ca. ∼300 K and complete conversion at ca. ∼355 K.	Catalyst is deactivated by running under highly reducing conditions, but activity is restored by thermal processing in a stream of air at 573 K.
873 K	The onset of rapid particle size growth. SnO$_2$ particle sizes in the range 6.7−13.2 nm. CuO is observed by EXAFS in the Cu(II)/SnO$_2$ (Cu:Sn 0.21) catalyst material prepared by impregnation after processing.	Complete CO conversion not achieved until 487 K, but activity still better than either CuO or SnO$_2$ alone.	
1273 K	SnO$_2$ particle sizes in the range 170−207 nm. Crystalline CuO (average particle size 14 nm) observed in all but the lowest copper loadings.	Activity poor with light-off temperature similar to that of CuO. Complete conversion not achieved until ca. ∼727 K.	Loss of activity irreversible.

Conclusions

Cu(II)/SnO$_2$ catalyst materials can be prepared by three methods: (i) coprecipitation from aqueous solutions containing Cu^{2+} and Sn^{4+} ions, (ii) sorption of Cu^{2+} ions on to preformed tin(IV) oxide gel, and (iii) destabilization of choline-stabilized tin(IV) oxide colloidal sols by the addition of aqueous copper(II) nitrate solution.

Both impregnation of preformed tin(IV) oxide gel using aqueous copper(II) nitrate solution and coprecipitation afford essentially the same material, which comprise small (∼2 nm) particles of tin(IV) oxide on which are sorbed hexaaqua $\{Cu(H_2O)_6\}^{2+}$ ions. Only in the case of the coprecipitation route does a small (up to 1%) level of Cu(II) incorporation into the tin(IV) oxide lattice takes place.

The most active catalyst material is formed by thermal processing at ∼673 K producing a material comprising small (4−5 nm) particles of tin(IV) oxide on the surface of which is dispersed copper(II) amorphously.

In catalysts calcined at high temperatures (1273 K), the copper is segregated as copper(II) oxide crystallites and the particles of tin(IV) oxide are very large (∼180−200 nm). These materials are relatively inactive.

Promotion of tin(IV) oxide with copper(II) enhances the activity toward the oxidation of carbon monoxide dramatically, the highest activity for the Cu:Sn 0.30 catalyst being obtained when the catalyst is precalcined at 673K. A 100% conversion occurs at 353 K even for high CO concentrations and stoichiometric CO/O$_2$ compositions.

Only surface copper(II) is reactive in a catalytic sense with CO, since bulk copper(II) only reacts with CO under relatively extreme conditions. At ambient temperature surface copper(II) species are reduced quite slowly to copper(I) on exposure to CO, but facile reduction of surface copper(II) occurs on heating to ≥373 K.

Dioxygen appears to adsorb on the surface of tin(IV) oxide at ambient temperature to form $O_2^-{}_{ads}$ *even in the presence of CO*. When all the copper(II) is reduced and the $O_2^-{}_{ads}$ is exhausted, CO reduces surface Sn(IV) to Sn(III) species.

The mode of action of these catalyst materials appears to be via the reduction of a surface metal cation, either copper(II) at low temperatures (373 K) or tin(IV) at elevated temperatures (673 K) by CO. Dissociative chemisorption of dioxygen replenishes the surface vacancies and reoxidizes copper(I) to copper(II). The role of the copper(II) is to scavenge the negative charge formed when CO abstracts surface oxygen and is thereby reduced to copper(I). The significant enhancement of catalytic activity is due in large part to the efficiency of the Cu(II)/Cu(I) couple in this process.

Catalyst deactivation at low temperatures under reducing conditions is due to depletion of the catalyst surface of active oxygen. The catalytic activity is restored by treatment in air at moderate temperatures. Deactivation at high temperatures is irreversible and is due to the phase separation of copper(II) oxide coupled with a dramatic increase in particle size.

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