JOURNAL OF CATALYSIS **102**, 160–171 (1986)

Surface Synergisms between Copper and Its Oxides

I. Isopropanol Dehydrogenation over Unsupported CuO, Cu_2O, and Cu Metal

J. CUNNINGHAM, G. H. AL-SAYYED, J. A. CRONIN, J. L. G. FIERRO,[1] C. HEALY,
W. HIRSCHWALD,[2] M. ILYAS, AND J. P. TOBIN†

Department of Chemistry, University College, Cork, Ireland

Received February 11, 1985; revised December 16, 1985

Selective dehydrogenation of isopropanol, $(-H_2)$, has been utilised over unsupported powdered samples of high purity $Cu^{II}O$, Cu^{I}_2O, and Cu^0-metal in efforts to clarify the relative importance of these three valence states in the catalysis of hydrogen-handling reactions by copper catalysts. Comparisons are made of high exposure activity profiles, delineating the approach to pseudo-stationary-state levels of conversion to acetone, attained from CuO, Cu_2O, and Cu-metal starting materials under a continuous flow of isopropanol vapour at temperatures from 423 to 523 K. Highest activity and lowest lead-in time to attainment of the "working state" was observed with a physical mixture of CuO with prereduced Cu-metal. "Initial state" activities are compared using low exposure activity profiles, obtained by admission and detailed product analysis for each of a series of micropulses of isopropanol at 473 K. These low exposure activity profiles for CuO, Cu_2O, and Cu-metal, and their modification by mild surface prereduction, confirmed that significant ongoing $(-H_2)$ activity only developed when "oxidised" and metallic copper locations were present simultaneously.

INTRODUCTION

The activity and selectivity of some copper-containing solids (*1–4*) and enzymes (*5*) as catalysts for hydrogenation $(+H_2)$ and dehydrogenation $(-H_2)$ processes at moderate temperatures is well established. The copper-containing solids employed in industry for the heterogeneous catalysis of gas-phase hydrogenations, such as methanol synthesis by hydrogenation of carbon oxides, commonly feature one or more host oxides, e.g., Cu/ZnO or $Cu/ZnO/Al_2O_3$. However, in respect of these rather complex catalysts considerable disagreement has developed in the literature on the following central points: (i) the valence state(s) of copper in the sites possessing the requisite activity and selectivity for $(+H_2)$ and/or $(-H_2)$; (ii) the extent to which the oxide support plays a direct or indirect role in the functioning of the catalyst. The broad range of current disagreement may be appreciated from the following contrasting views: those of research groups at ICI (*6, 7*), who argue for a central role of metallic Cu^0 sites in activating hydrogen, plus a role of oxidised surface in adsorption and activation of carbon dioxide; and those of Klier and co-workers (*8a,b*), who have argued for a central role of Cu^+ ions, dispersed in the zinc oxide phase, in the adsorption and activation of carbon monoxide.

Our intention in undertaking the work reported here and in subsequent papers (*9*) was to concentrate attention upon point (i) above, by making detailed comparisons of the relative activities of powered samples of high purity $Cu^{II}O$, Cu^{I}_2O, or Cu^0-metal for the catalysis of model $(+H_2)$ and $(-H_2)$ processes at moderate temperatures. Results reported here concerning isopropanol dehydrogenation $(-H_2)$ over unsupported CuO, Cu_2O, and Cu-metal will be followed by studies on acetone hydrogenation over

---

† Deceased.

[1] Instituto de Catalisis y Petroleoquimica, CSIC, Madrid, Spain.

[2] Institut für Physikalische Chemie, Freie Universität, Berlin, F.R.G.

0021-9517/86 $3.00

TABLE 1

Ratios between Yields of Various Products Measured at Indicated Pulse Numbers during Low Exposure Activity Profiles for Isopropanol Dehydrogenation over CuO, Cu_2O, and Cu Metal at 473 K

Pulse	Material	$\frac{H_2}{\text{Acetone}}$	$\frac{H_2}{H_2O}$	$\frac{H_2O}{\text{Acetone}}$	$\frac{(H_2 + H_2O)}{\text{Acetone}}$
4	Cu^0-metal ($0.16\ m^2\ g^{-1}$)	1.08	—	—	1.08
10	($0.16\ m^2\ g^{-1}$)	0.99	—	—	0.99
15	($0.16\ m^2\ g^{-1}$)	0.94	—	—	0.95
18	($0.16\ m^2\ g^{-1}$)	0.92	—	—	0.93
5	Cu_2O ($0.2\ m^2\ g^{-1}$)	0.31	0.44	0.70	1.01
15	($0.2\ m^2\ g^{-1}$)	0.24	0.30	0.79	1.03
30	($0.2\ m^2\ g^{-1}$)	0.20	0.27	0.77	0.97
60	($0.2\ m^2\ g^{-1}$)	0.22	0.30	0.73	0.95
80	($0.2\ m^2\ g^{-1}$)	0.24	0.30	0.80	1.04
110	CuO ($1.2\ m^2\ g^{-1}$)	0.30	0.40	0.76	1.06
160	($1.2\ m^2\ g^{-1}$)	0.32	0.45	0.73	1.05
210	($1.2\ m^2\ g^{-1}$)	0.35	0.48	0.72	1.06
260	($1.2\ m^2\ g^{-1}$)	0.36	0.49	0.74	1.11

the same materials (*9*). The somewhat unconventional use of the pure powdered materials, without any foreign support oxide, is an integral part of the strategy, since point (ii) should thereby be avoided. Avoidance of the complications which could attach to the presence of ZnO as another oxidic support seemed particularly desirable in view of our choice of the interconversions

$$(CH_3)_2CHOH \underset{(+H_2)}{\overset{(-H_2)}{\rightleftharpoons}} (CH_3)_2CO$$

as model reactions for testing catalytic activity. Thus our published survey of the activities of the oxides of 3*d*-transition metals towards isopropanol vapour at 473 K (*10*) had demonstrated that, whereas CuO was highly active and 99% selective for dehydrogenation, ZnO was much less active and selective. In common with many other workers (*11*) we found ZnO to exhibit significant undesirable dehydration activity at 473 K. However, the subsequent literature contains an interesting and relevant report (*12*) that deposition of Cu^0 in monolayer amount onto the $(10\bar{1}0)$ face of a single crystal of zinc oxide eliminated the dehydration activity, thus leaving the surface selective for alcohol dehydrogenation.

EXPERIMENTAL

Gas chromatographic procedures. Details have been given elsewhere (*10*) of appropriate flow paths of reactant(s) through the microcatalytic reactor, gas-sampling valve and gas chromatograph (Pye 104) for measurements of conversion in the continuous reactant flow (c.r.f.) mode and in the pulsed reactant flow (p.r.f.) mode. Activity profiles obtained in these two modes are denoted, respectively, as high exposure activity profiles (h.e.a.p.) and low exposure activity profiles (l.e.a.p.).

Materials. Powdered samples of high purity (+99.99%) copper metal, cuprous oxide and cupric oxide (spectroscopically pure materials from Spex Industries), served as starting materials. Surface areas and other data are summarised in Table 1. Prior to use they were subjected, *in situ* in the quartz microcatalytic reactor, to various pretreatments (see below), some of which were selected to be analogous to those of published XPS and XAES studies on these materials which had been shown to yield clean surfaces dominated respectively by Cu^0, Cu^I, or Cu^{II} (*13*). "Analar" grade isopropanol (i.p.) was introduced as the pure deoxygenated liquid into saturators packed with deoxygenated Molecular Sieve (Linde 3A) and maintained at constant temperature. These served to supply the pure vapour at constant pressure into the flow of carrier gas prior to entry into the microcatalytic reactor.

Pretreatment. Temperatures during various pretreatments are indicated in the text or on the legends. In view of the known ease of oxidation of copper metal (*14, 15*), pretreatments (except preoxidation) were made with flowing gases in which oxygen content had been diminished to low levels. Thus prereductions were made with chemically pure H_2, or 3% H_2 in N_2, which were additionally purified by flowing over copper turnings at 573 K and subsequent drying. Sample-outgassings aimed at removal of water or other adsorbed impurities were made in argon with especially low levels of oxygen impurity (BOC "zero-grade"), since other workers had reported that maintaining clean copper surface for 7 h at 1173 K in a flow of C.P. argon had resulted in a surface layer of Cu_2O (*14*). Argon with especially low residual O_2 was likewise utilised as carrier-gas for experiments involving copper metal. Despite these precautions to minimise oxygen impurity levels, it is only realistic to recognise that surfaces of copper metal samples thus pretreated were unlikely to be completely oxygen-free, since even 1 ppm of residual oxygen would add up to an exposure of 2.7 Torr during a 1-h continuous flow. For pretreatment of CuO or Cu_2O samples, which already possessed a high content of lattice oxygen, C.P. grade argon, H_2 or 3% H_2 in N_2 were used "as received."

RESULTS

A. Profiles en Route to Pseudo-Stationary-State (p.s.s.) Activity in Continuous Flow Conditions

$Cu^{II}O$. Gravimetric measurements of weight loss from the CuO material on a vacuum microbalance demonstrated progressively more severe loss of lattice oxygen when maintained in vacuo for 1 h at temperatures of 423–590 K. The weight loss after heating for 1 h at 423 K was equivalent to a fraction of a monolayer, whereas that after 590 K was equivalent to several monolayers. Comparable levels of deoxygenation were to be expected upon heating CuO to these temperatures in a flow of C.P. argon, and the $(-H_2)$ activity of CuO towards i.p. vapour was first examined in conditions where the rate of deoxygenation of CuO in the argon flow itself would be minimal, i.e., at 423 K. The data on plot (i) of Fig. 1, which were obtained at 423 K over a CuO sample previously well oxidised for 13 h in O_2 at 673 K, demonstrate that no significant activity for conversion to acetone developed during 2 h contact with isopropanol flow at 423 K for CuO under those conditions. However, the data on plot (ii) of Fig. 1, which were obtained subsequent to some deoxygenation of the CuO sample by maintaining it for 13 h in a flow of argon at 673 K, demonstrate a rapidly rising activity profile at 423 K for the CuO sample thus prereduced. A marked shortening of the induction period (required prior to rapid growth of $(-H_2)$ activity over well-preoxidised CuO) was apparent (*10*) when the reaction temperature in the i.p. flow was 473 K.

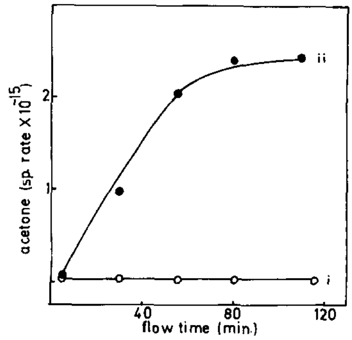

FIG. 1. Data illustrating marked difference between: (i) insignificant growth of $(-H_2)$ activity towards isopropanol vapour at 423 K over well preoxidised cupric oxide surfaces (open circles, data obtained after preoxidation in flow of O_2 for 13 h at 673 K); and (ii) rapid growth in $(-H_2)$ activity over deoxygenated CuO surfaces (obtained by 13 h in flow of pure argon at 673 K) under similar flow conditions (filled circles).

Photoemission (XPS) results presented elsewhere in full (*13*) provided direct evidence for enhanced surface reduction of the CuO powder when heated above 250 K in the presence of adsorbed alcohol. Powder X-ray diffraction (XRD) measurements were made in the present study on the CuO before, and after long (40 h), exposure to a flow of i.p. vapour at 473 K, or to argon at 673 K. The starting material gave only XRD lines characteristic of the CuO lattice, whereas lines characteristic of copper metal dominated the XRD pattern after the

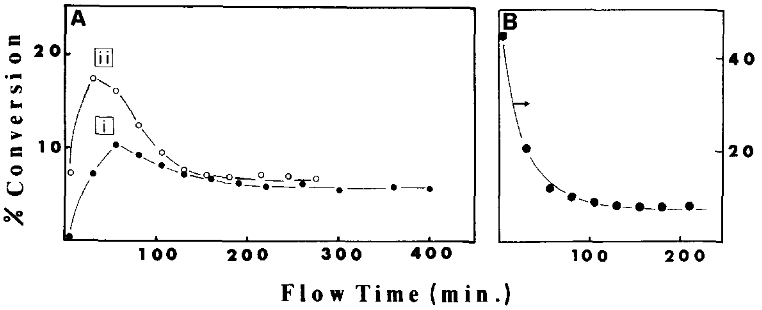

FIG. 2. Illustrations of the effect of sample reduction in H_2 at 423 K upon h.e.a.p. plots of the dehydrogenation activity of cuprous oxide at 473 K. (A) (i) Sample only flushed in argon flow at 423 K for 13 h; (ii) as for (i) but prereduced by H_2 at 423 K for 1 h. (B) Sample as used in A (i), but subsequently kept in argon 16 h at 300 K and then reduced by H_2 at 423 K for 1 h.

indicated pretreatments. High probability for the development of small metal particles upon CuO during reduction at 473 K could be inferred from these observations (cf. Ref. (*13*) and Section B below). It seemed probable that such copper metal product upon CuO contributed to the rapidly rising activity profiles and to the initial plateau reached in the p.s.s. $(-H_2)$ activity of $[(CH_3)_2CHOH + Ar]_{(g)}/CuO_{(s)}$ interfaces at 473 K (*10*).

Cu$_2$O. Just as the foregoing results for CuO provided evidence for an important role of prereduction of the oxide for the development of significant on-going $(-H_2)$ activity, so also were surface-redox effects found in the $(-H_2)$ activity of cuprous oxide. Thus Fig. 2A compares a $(-H_2)$ activity profile at 473 K for a sample of Cu_2O when it had been flushed only in argon for 13 h at 423 K (lower plot) with another h.e.a.p. taken when the sample had been prereduced in a flow of H_2 for 1 h at 423 K (upper plot). Both plots show an initial growth of the conversion to acetone leading to a maximum value after ca. 50 min contact with i.p. at 473 K, followed by subsequent decline to a lower p.s.s. level. The maximum conversion attained over the prereduced sample was almost double that over the argon-treated sample, but this difference was not maintained. Rather, the $(-H_2)$ activity over $(CH_3)_2CHOH/Cu_2O$ interfaces declined to low p.s.s. levels. This marked difference from much higher p.s.s. activity at $(CH_3)_2CHOH/CuO$ interfaces could be understood on the basis of reports of greater resistance of Cu_2O than CuO to reduction by alcohol vapour (*13*) or argon bombardment (*14*). Data in Fig. 2B demonstrate, however, that a temporary enhancement of $(-H_2)$ activity could again be achieved after the p.s.s. condition, by switching to a flow of argon and again prereducing the sample in H_2 at 423 K for 1 h. The subsequent profile of $(-H_2)$ activity shown in Fig. 2B show that the initial enhancement achieved by this second reducing treatment in H_2 was greater than the first and that subsequent decline in this $(-H_2)$ activity in the flow of i.p. vapour at 473 K was more abrupt. These results show that initial $(-H_2)$ activity achieved by prior H_2 reduction of Cu_2O surfaces was rapidly deactivated in a flow of i.p. vapour.

Cu^0 metal. Profiles featuring a steep decline in $(-H_2)$ activity from an initially high value were likewise obtained in a flow of i.p. vapour for samples of powdered copper metal which had been carefully prereduced *in situ* in prepurified H_2 and then maintained in a flow of high purity argon before admixing i.p. vapour therein. For example, the bottom plot of Fig. 3A corresponds to a h.e.a.p. plot obtained for a copper metal powder sample which had been prereduced overnight in prepurified H_2 at 573 K, and then cooled to 463 K in argon before a con-

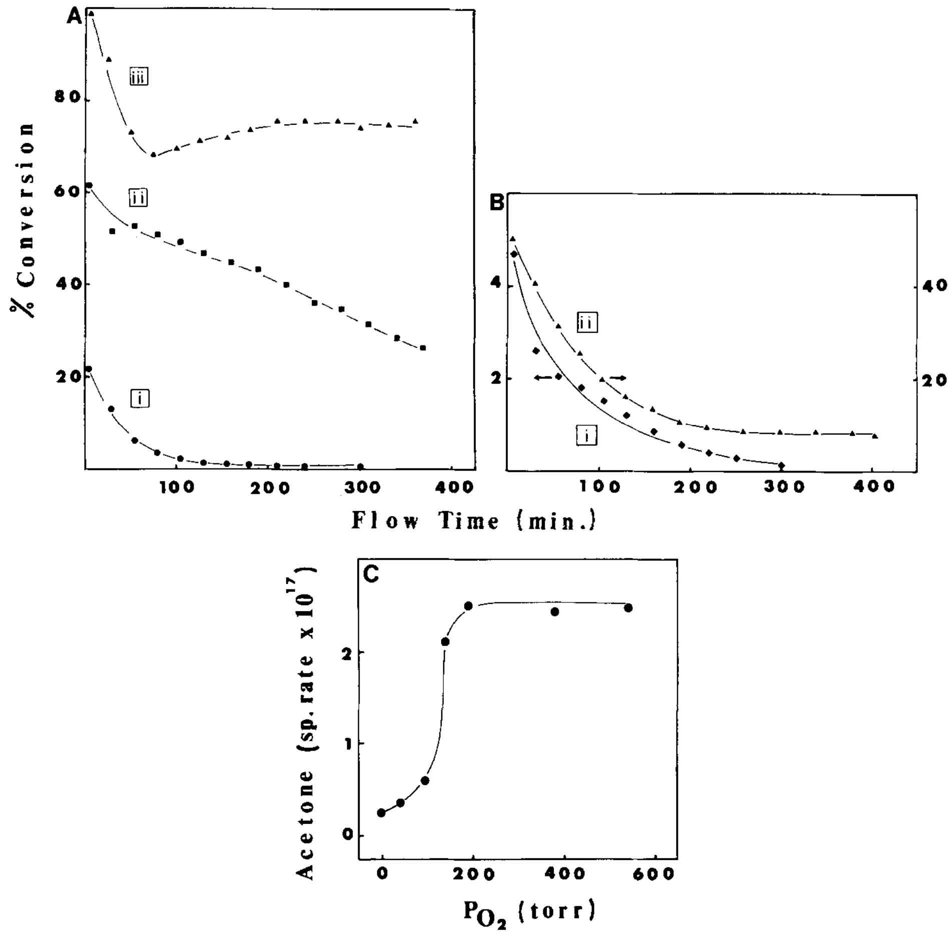

FIG. 3. High exposure activity profiles for dehydrogenation of isopropanol to acetone, measured at 473 or 423 K over high-purity powdered copper metal. (A) H.e.a.p. over samples: (i) prereduced in H_2 at 573 K for 14 h; (ii) as in (i) but preoxidised in a flow of O_2 at 473 K for 2 h; (iii) as for (i) followed by reoxidation in O_2 at 673 K for 11 h. (B) H.e.a.p. plots at reaction temperatures 423 K (plot (i)) and 523 K (plot (ii)) after prereduction 16 h in H_2 flow at 573 K. (C) Dependence of level of pseudo-steady-state activity at 473 K over a prereduced sample upon partial pressure of gaseous oxygen admixed with isopropanol reactant after attainment of p.s.s.

tinuous flow of i.p. was established. Although a 23% conversion was first measured on the exit gases after an alcohol exposure of ca. 144,000 Torr s, the ($-H_2$) activity declined to an insignificant level after 5 h on-stream in i.p. vapour at 473 K. Furthermore, it could be concluded from similar h.e.a.p. plots obtained at reaction temperatures of 423 and 523 K (c.f. plots (i) and (ii) of Fig. 3B) that the ($-H_2$) activities of metallic copper samples, which had received comparable prereductions: (a) were initially greatest for reaction temperature 523 K and least for 423 K (when compared at equal net exposure to i.p. vapour), and (b) declined at each temperature with increasing alcohol exposure, thereby establishing the deactivation of copper metal in i.p. vapour across this temperature range.

Plots (ii) and (iii) of Fig. 3A facilitate comparison of the ($-H_2$) activity profiles at 473 K of reoxidised copper metal surfaces with that for the carefully prereduced copper metal sample at the same temperature.

The central h.e.a.p. (plot (ii) of Fig. 3A) was obtained with a copper metal powder whose surface had been mildly preoxidised after an earlier reduction. Comparison with plot (i) for the prereduced sample makes it clear that preoxidation enhanced the $(-H_2)$ activity and capacity of the copper metal powder. This trend is further confirmed by plot (iii), the topmost h.e.a.p. plot of Fig. 3A. This was obtained with a sample of copper metal powder which had been more strongly preoxidised (in a flow of O_2 for 11 h at 673 K) before contact with deoxygenated i.p. vapour at 473 K. Other workers had reported (*15*) that oxidation of copper metal surfaces to cupric oxide could occur in those conditions. Thus it appeared possible that the enhancing effect of prior reoxidation of the copper metal powder could have its origins in the development of a sample in which Cu^0 and CuO coexisted.

An experiment was carried out to examine the possibility that the rapid decline in $(-H_2)$ activity of the carefully prereduced copper metal powder, when maintained in the flow of i.p. vapour (cf. plot (i) of Fig. 3A), could have arisen from the reducing effect of i.p. vapour and from the resultant removal of essential "oxidised" surface locations which had developed during the exposure to argon flow at 473 K. The experiment was based on the argument that, if such were the case, subsequent introduction of oxygen at partial pressures similar to those of the i.p. vapour should partially reverse the reducing action of the alcohol and so restore $(-H_2)$ activity by generating oxidised surface locations. Positive results of this experiment are summarised in Fig. 3B which shows the level to which p.s.s. $(-H_2)$ activity was restored whenever the indicated partial pressures of oxygen were admixed with i.p. vapour over a copper–metal sample which had first been taken through an activity decline of the type in plot (i) of Fig. 3A.

A working hypothesis consistent with the foregoing results was that high on-going $(-H_2)$ activity required the simultaneous presence of exposed Cu^0-metal locations and "oxidised-copper" locations. A further experimental test of this hypothesis was to check whether or not some admixture of metallic copper powder as a "physical mixture" into $Cu^{II}O$ would have the effects of promoting $(-H_2)$ activity and diminishing the period of initial growth which characterised CuO alone. For a meaningful test, it was arranged that the aliquot of copper metal intended for use in the physical mixture should first have had its surfaces adequately prereduced by hydrogen *in situ* in the reactor in the absence of CuO lest hydrogen-spillover from the metal to the oxide occur during prereduction.[3] Following *in situ* admixture with CuO in an argon flow, and agitation to promote physical mixing, the system was heated to 473 K in argon for 2 h. Within 5 min of establishing a flow of i.p. reactant at 473 K, the first sample of exit gas was withdrawn for analysis. The observed conversion to acetone was 96.5%. This high level of conversion experienced only a minor decline to 81% whilst 12 samples were taken over a period of 5 h on-stream. These results demonstrated that the physical mixture of metallic Cu^0 and $Cu^{II}O$ exhibited a h.e.a.p. plot for $(-H_2)$ which was markedly enhanced relative to that for either Cu^0 metal alone or $Cu^{II}O$ sample alone. In view of this evidence for synergisms between different valence states of copper in the "working state," and of consequent difficulties in distinguishing their individual contributions to steady-state $(-H_2)$ activity, "initial" activities of surfaces strongly dominated by Cu_2O, CuO, or Cu-metal were also studied.

Initial Valence States on CuO, Cu_2O, and Cu^0-Metal Surfaces and Their Activities in Isopropanol Dehydrogenation

Identification of the copper valence state(s) present in surface regions of appropriately pretreated samples of the pow-

---

[3] *Note added in proof.* Temperature programmed reduction upon physical mixtures of Cu^0 and CuO yielded evidence of hydrogen spillover.

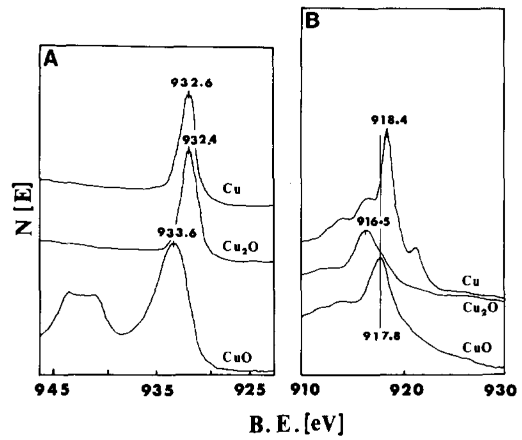

FIG. 4. X-Ray photoelectron spectra (XPS) and X-ray-induced Auger electron spectra (XAES): (A) Room-temperature XPS spectra measured in the Cu $2p_{3/2}$ energy region under UHV conditions from powdered samples of high purity: (i) copper metal, Cu^0, after prereduction in oxygen-free H_2 at 575 K; (ii) cupric oxide, $\mathrm{Cu^{II}O}$, after oxidation in O_2 at 675 K and subsequent evacuation at 425 K; (iii) cuprous oxide, $\mathrm{Cu^{I}_2O}$ after heating to 423 K in UHV. (B) Room-temperature XAES spectra from powdered copper and its oxides obtained from samples treated as per (i), (ii), and (iii) above.

dered CuO, Cu_2O, and Cu-metal materials before exposure to isopropanol vapour was achieved by a combination of XPS and XAES (cf. Fig. 4). Information on the initial activity of samples in those well-defined states was then sought through admission of isopropanol vapour as a sequence of micropulses (cf. the low exposure activity profiles in Figs. 5, 6, and 7). The XPS and XAES results in Figs. 4A and B serve to establish the following features for surface regions of samples pretreated in the manner indicated on the legends of those figures: (i) that surfaces were effectively free of carbon or other impurities; (ii) that $\mathrm{Cu^{II}}$ strongly predominated in the surface region of CuO (witness in Fig. 4A not only the existence of the shake-up satellite (at 940–945 V) uniquely characteristic of the $\mathrm{Cu^{II}}$ valence state, but also an appropriate ratio of its intensity to that of the main $2p_{3/2}$ XPS peak at 933.6 V); (iii) that $\mathrm{Cu^{I}}$ was the predominant valence state in the surface regions of Cu_2O (witness the absence of any significant shake-up satellite in the XPS features in Fig. 4A, whereas the XAES features from this sample, as shown in Fig. 4B, shows a feature at 916.5 V characteristic of $\mathrm{Cu^{I}}$, and furthermore, the fact that there was no indication of the significant XAES feature expected at 918.4 V, if Cu^0 existed as metallic copper in significant amount in surface regions of the CuO or Cu_2O sample); (iv) that features in the XAES spectra of copper metal powder correspond well to those reported by other workers (*14*, *15*). Analogous pretreatments were then given to samples of the same CuO, Cu_2O, and Cu-metal materials, now located in the quartz microcatalytic reactor. Measurement of their ability to dehydrogenate isopropanol in the p.r.f. mode yielded the results shown in Figs. 5, 6, and 7. These represent l.e.a.p. obtained by plotting the extent of non-steady-state conversion to acetone, as evaluated for each of a series of pulses of i.p. delivered to the initially $\mathrm{Cu^{II}O}$, $\mathrm{Cu^{I}_2O}$, or Cu^0-dominated surfaces.

CuO. Plot a of Fig. 5 demonstrates that significant conversion to acetone only became detectable over the $\mathrm{Cu^{II}O}$ samples af-

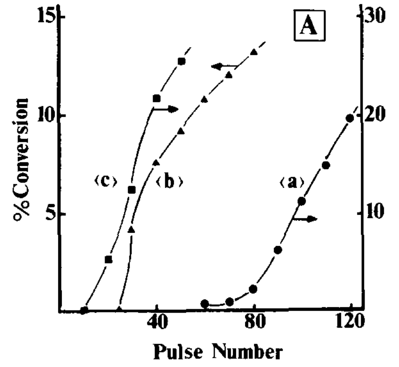

FIG. 5. Low exposure activity profiles for isopropanol dehydrogenation measured in the pulsed mode at 475 K over cupric oxide, CuO, pretreated in analogous manner to Fig. 4A (ii), viz: (a) preoxidised in O_2 + Ar (1 : 1) for 1 h, at 773 K and flushed just 5 min in argon at 473 K; (b) preoxidised in O_2 + Ar (1 : 1) for 3 h at 673 K and flushed 0.5 h at 473 K in argon; (C) preoxidised in O_2 + Ar (1 : 1) for 19 h and flushed 3 h in argon at 473 K.

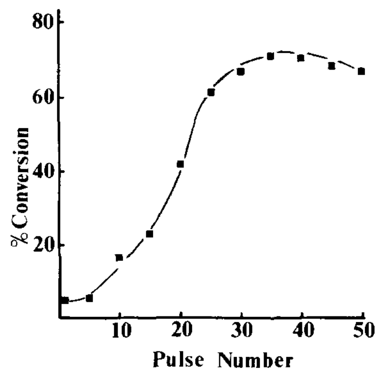

FIG. 6. L.e.a.p. for ($-H_2$) at 473 K over copper metal prereduced at 723 K in a flow of "oxygen-free" 3% H_2 in N_2 for 16 h and flushed 0.5 h in argon at 473 K.

ter the passage of at least 60 pulses. This result confirms that activity for dehydrogenation of isopropanol, ($-H_2$), was not an intrinsic property of surfaces predominated by $Cu^{II}O$. It is also clear from Fig. 5 that ($-H_2$) activity did eventually develop for the preoxidised surface at high pulse numbers (cf. plot a). Plots b and c of Fig. 5 show activity developing at lower pulse numbers if the sample surfaces were pretreated in a manner which, according to results described earlier, would have caused some deoxygenation of the surface. In our view these observed up-turns in activity signify the beginnings of a move away from the initially well-defined $Cu^{II}O$ surface condition towards a "working" surface featuring a mixture of valence states of copper.

Cu^0 metal. Figure 6 illustrates the type of l.e.a.p. plot obtained by the p.r.f. procedure upon passing a train of pulses of i.p. at 473 K over a prereduced sample of finely divided copper metal powder with a quoted purity of 99.999%. The rather low conversions shown to result from contact of the first pulses with metallic copper powder, after pretreatments designed to yield minimal oxygen content in its surface, indicated rather low initial conversion (ca. 3%) to acetone over surfaces dominated by Cu^0 at 473 K. Neither the origin of the surprisingly low initial activity of the copper metal sample, nor the reasons for the steep rise in activity at higher pulse numbers are immediately apparent from the data in Fig. 6. Significantly, however, l.e.a.p. plots with a gradual build-up in activity of the type shown were only obtained when the indicated precautions were taken to minimise possibilities for residual oxygen content within, or on the surfaces of, the copper metal powder. With less rigorous deoxygenation the number of pulses required for attainment of high conversion was diminished. Thus the pattern of our l.e.a.p. observations, showing greater ease of development of ($-H_2$) activity for less rigorous deoxygenation of the copper metal sample, was qualitatively similar to that for our h.e.a.p. observations (cf. Fig. 3).

Cu_2O. In Fig. 7 the l.e.a.p. plot representative of Cu_2O, pretreated so as to yield a surface strongly predominated by Cu^{I}_2O, is labelled a. Although this shows some increase in ($-H_2$) activity at pulse numbers 8–20, the maximum conversion reached was only 1.6%, and these results point to low initial ($-H_2$) activity of Cu^{I}_2O. At higher pulse numbers conversion declined in a manner qualitatively similar to h.e.a.p. observations upon the ($-H_2$) activity (cf. Fig. 2). Plots b and c of Fig. 7, which were ob-

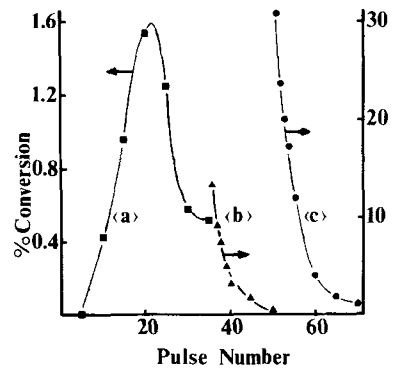

FIG. 7. L.e.a.p. for isopropanol dehydrogenation measured in the pulsed mode at 475 K over cuprous oxide pretreated in analogous manner to Fig. 4A (iii) above, viz: (a) flushed 3 h in pure argon at 423 K; (b) as for (a) but prereduced in H_2 at 423 K for 1 h and flushed 10 min at 423 K in argon; (c) as for (b) but prereduced for 3 h at 423 K in H_2.

tained with Cu_2O whose surfaces had been prereduced in H_2 prior to admitting the first pulse of i.p. vapour, show that the maximum conversion reached in the "spike" of $(-H_2)$ activity at pulse numbers 35 ± 15 was much enhanced by such prereduction in hydrogen, and would be consistent with a promoting effect of Cu^0-metal product. The decline in activity at higher pulse numbers indicates, however, that such promoting effect was transitory for the Cu_2O sample at 475 K.

Mass balance in dehydrogenation of micropulses of isopropanol. Test injections onto a column packed with a 50/50 mixture of Poropak Q and R established acceptable sensitivities with a katherometer detector and also demonstrated that this column yielded adequate separation between various possible products such as acetone, acetaldehyde, lower alcohols, CO, H_2, CO_2, and H_2O. Data suitable for testing mass balance, and degree of agreement of product distribution with Eqs. (1), (2), or (3), could thus be obtained. Equation (1) represents simple dehydrogenation $(-H_2)_s$, whereas (2) and (3) represent oxidative dehydrogenation accompanied by reduction of the oxide surface $(-H_2)_{ox}$.

$$(CH_3)_2CHOH_{(g)} \rightarrow (CH_3)_2CO_{(g)} + H_{2(g)} \quad (1)$$

$$Cu^{II}O_{(s)} + (CH_3)_2CHOH_{(g)} \rightarrow (CH_3)_2CO_{(g)} + H_2O + Cu^0_{(s)} \quad (2)$$

$$Cu^I_2O_{(s)} + (CH_3)_2CHOH_{(g)} \rightarrow (CH_3)_2CO_{(g)} + H_2O_{(g)} + 2Cu^0_{(s)} \quad (3)$$

Table 1 lists such data for pulse numbers at which activity had developed to a significant level. Data obtained over the copper metal powder agreed well with the requirements of Eq. (1), since the ratio (yield of H_2)/(yield of acetone), was unity within experimental error. The absence of any significant yield of H_2O (or propene) provided further evidence that the dominant conversion initiated on the Cu^0-dominated samples was $(-H_2)_s$. Table 1 also lists ratios of product yields observed over $Cu^{II}O$ or Cu^I_2O-dominated samples at low i.p. exposures. These confirm that the ratio (yield of acetone)/(net yields of (H_2 + H_2O)) remained effectively at unity, as required for any combination of (1) with (2) or (3). However, the ratio (yield of H_2)/(yield of acetone) fell short to unity with values of 0.2 to 0.36. Taken together with the substantial values observed for the ratios H_2O/acetone and H_2/H_2O, the data indicate that, in association with the observed up-turns in total $(-H_2)$ activity over the copper oxides, at least one $(-H_2)_{ox}$-type process took place in parallel with a $(-H_2)_s$ process. Indications of a time lag between early onset of trace H_2O product levels and eventual onset of acetone production were obtained over CuO. Summation of these early H_2O yields were made to arrive at a value for "Total number of oxygen atoms accumulated as H_2O molecules." Comparison of this value with the "Total number of oxide ions in the surface monolayer" of CuO showed them to be within a factor of 2. These observations would be consistent with an autocatalytic process featuring: (i) an initial $(-H_2)_{ox}$ process leading to nucleation and growth of Cu^0 particles on the CuO substrate whenever θ_{Cu^0} approached unity, and (ii) the progressive acceleration of a $(-H_2)_s$ process as the number and size of Cu^0 metallic particles increased.

DISCUSSION

Explanations of the foregoing observations, which showed mutual enhancement of dehydrogenation activity by "oxidised-copper" and metallic-copper locations, may be sought on the basis of "short-range" or "long-range" interactions. The former term, and the general symbol S, will here be applied to interactions between oxidised-copper and metallic-copper locations lying within ca. 0.5 nm of one another, and possessing thereby the requisite geometry for synchronous, two-centre attack upon alcohol-related adsorbate. Situations already identified in the literature as having the potential for favouring such short-range interactions include: S(O_{ads}), metallic copper surfaces partly covered by chemisorbed oxygen (*15, 16*); or S(Cu^x-Cu^y), "mixed-valence" pairs (*10*) at surface locations where the electron density of proximate copper species are differently affected by nonuniform oxygen incorporation (*15*) and/or lattice defects (*17*) in the surface layers. However, the level of oxygen preexposure ($\sim 10^{12}$ Langmuir) required to enhance the ($-H_2$) activity of copper metal in the present study (cf. Fig. 3A), or the pressures of oxygen (~50–300 Torr) required to reverse deactivation (cf. Fig. 3C), were orders of magnitude greater than values of 10^2–2×10^{-3} Langmuir associated in the literature with oxygen chemisorption on copper. In literature reports of S(O_{ads})-type effects upon alcohols on slightly oxygenated copper metal surfaces (*16*), the role assigned to individual O_{ads} is that of a base, serving to abstract the hydroxylic hydrogen from adsorbed alcohol, and thereby to yield an alkoxy surface intermediate bonded to Cu^0. Serious objection against this as the direct and dominant mechanism responsible for results reported here exists on the basis of the large discrepancy just noted between the requisite oxygen exposures/pressures. Such objection would have only slightly less force in respect of an S(Cu^x-Cu^y) mechanism involving "mixed-valence" pairs brought about by nonuniform incorporation of oxygen into subsurface layers, since oxygen exposures of 10^2–10^7 Langmuirs have been reported (*15*) as sufficient to produce oxygen incorporation into subsurface layers of copper. A further difficulty with direct action of either of these short-range models in respect of present results is their apparent inability to account for the enhanced ($-H_2$) activity here noted for the "physical" mixture of CuO and Cu-metal. That observation points, instead, towards a "long-range" interaction.

The term "long-range" and the general symbol L, will here be applied to situations in which "oxidised-copper" has its origin at locations far distant (e.g., >100 nm) from metallic-copper locations. Since synchronous, two-centre attack would be precluded in such L-type situations, possibilities for synergistic effects would be restricted to long-range transfer events, such as charge transfer (L(±)) and transfer of reactant or reaction intermediate(s) (L(reac)), between the oxidised-copper and metallic-copper locations. Spillover of alcohol or hydrogen or oxygen between metallic and oxidised locations would be of this type. (It may be noted, however, that in the limit of low dynamic θ_0 upon "distant" metallic copper locations by diffused oxygen (as $O_{(ads)}$ or as $O_{(inc)}$), some convergence becomes possible between experimentally observable effects caused by oxygen originating in that manner and oxygen-induced effects of type S(O_{ads}) and S(Cu^x–Cu^y). In other words, an L(O_{diff})-type process may produce effects qualitatively indistinguishable from the latter, except in relation to its dependence upon level of oxygen preexposure.)

In efforts to assess the importance of L(reac) type effects, insight into the adsorption/desorption behaviour of isopropanol vapour at metallic locations and at oxidised locations was sought from adsorption isotherms, measured respectively on Cu-metal powder and CuO. These were obtained using a microbalance technique, and 473 K was selected as a representative reaction temperature. On preoxidised CuO surfaces the equilibrium coverages attained at 5, 10, and 20 torr corresponded, respectively, to 0.09, 0.12, and 0.16 monolayer, thereby indicating that the average surface condition of isopropanol adsorbate on oxidised CuO locations at 473 K was as an isolated entity. However, over the same range of isopropanol pressures the metallic copper powder exhibited an S-shaped isotherm characteristic of adsorbate condensation in multilayers. The conclusion that metallic-Cu locations represented regions with higher $\theta_{i.p.}$ than on oxidised CuO locations gained further support from comparative adsorption studies made at room temperature upon preoxidised and prereduced CuO samples. After varying extents of prereduction *in vacuo,* the total and the irreversibly adsorbed amounts of isopropanol were found to have increased with the percentage of surface prereduction. It may be inferred from these results that, in two-phase systems featuring metallic-Cu locations and oxidised CuO locations, surface concentration gradients for adsorbed isopropanol should favour migration from metallic to oxidised locations. However, in view of kinetic observations with the vacuum microbalance, showing very rapid equilibration between gas-phase and adsorbed isopropanol at 473 K, it appeared probable that these latter equilibria, rather than surface diffusion, would control $\theta_{i.p.}$. For example, for Cu-metal powder at 473 K, under isopropanol pressures of 4×10^{-1}, 8×10^{-2}, and 8×10^{-3} Torr (selected to limit $\theta_{i.p.}$ to monolayer amounts), adsorption was very fast and reached a maximum in ca. 2 s.

A converse situation should apply to local concentration gradients in surface oxygen concentrations, θ_O, high values being expected at oxidised CuO locations and negligible values on "clean" metallic locations. Furthermore, in the absence of significant gas-phase oxygen, the possible influences of such concentration gradients upon $(-H_2)_{i.p.}$ would not be circumvented by oxygen adsorption/desorption equilibria. Oxygen-spillover as well as hydrogen-spillover thus merits further study as long-range processes making possible the synergisms between copper and its oxides here reported in respect of dehydrogenation of isopropanol. Results are in preparation from further examinations of the involvement of these and other long-range processes in the hydrogenation of acetone and the dehydrogenation of methanol over copper and its oxides (*9*).

ACKNOWLEDGMENTS

Financial support from the Department of Education of the Irish Government (J.A.C. and C.H.), from the Deutsche Akademische Austauschdienst of the German Government (J.P.T.), and from University College Cork (M.I. and G.A.S.) is gratefully acknowledged. The availability of machine-time for ESCA measurements at the Free University of Berlin and for vacuum microbalance measurements at C.S.I.C. Madrid, is also gratefully acknowledged.

REFERENCES

1. (a) Natta, G., "Catalysis" (P. H. Emmett, Ed.), Vol. 3. Reinhold, New York, 1955; (b) Kung, H. H., *Catal. Rev. Sci. Eng.* **22,** 235 (1980).

2. (a) Roberts, D. L., and Griffin, G. L., *Appl. Surf. Sci.* **19,** 298 (1984); (b) Dupriz, D., Barbier, J., Ferhat-Hamida, Z., and H. Bettaher, *Appl. Catal.* **12,** 219 (1984).

3. (a) Delk, F. S., II, and Wavere, A., *J. Catal.* **85,** 380 (1984); (b) Ai, M., *Appl. Catal.* **11,** 259 (1984).

4. (a) Cant, N. W., Tonner, S. P., Trimm, D. L., and Wainwright, M. S., *J. Catal.* **91,** 197 (1985); (b) Tonner, S. P., Wainwright, M. S., and Trimm, D. L., *Appl. Catal.* **11,** 93 (1984).

5. Williams, R. J. P., *Inorg. Chim. Acta.* **5,** 137 (1971).

6. (a) Bowker, M., Hyland, J. N. K., and Waugh, K. C., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. II, p. 37. Verlag Chemie, Weinheim, 1984; (b) Bowker, M., Houghton, H., and Waugh, K. C., *J. Chem. Soc. Faraday Trans. 1* **77,** 3023 (1981).

7. Chinchen, G. C., Waugh, K. C., and Whan, D. A., *Appl. Catal.* **25,** 101 (1986).

8. (a) Herman, R. G., Klier, K., Simmons, G. W., Finn, B. P., and Bulko, H. B., *J. Catal.* **56,** 407 (1978); (b) Klier, K., "Advances in Catalysis," Vol. 31, p. 243. Academic Press, New York, 1982; (c) Klier, K., *Appl. Surf. Sci.* **19,** 267 (1984).

9. Cunningham, J., Sayyed, G. Al, Fierro, J. L. G., and McNamara, D., *J. Catal.*, in press.

10. Cunningham, J., Hodnett, B. K., Ilyas, I., Tobin, J. P., and Leahy, E. L., *Faraday Discuss. Chem. Soc.* **72,** 283, 305 (1981).

11. (a) Bowker, M., Houghton, H., and Waugh, K. C., *J. Chem. Soc. Faraday Trans. 1* **79** (1983); (b) Hirschwald, W., and Hoffmann, D., *Surf. Sci.* **140,** 415 (1984); (c) Bowker, M., Petts, R. W., and Waugh, K. C., *Appl. Catal.* **25,** 121 (1986); (d) Jacobs, H., Mokwa, W., Kohl, D., and Heiland, G., *Surf. Sci.* **126,** 368 (1983); (e) Jacobs, H., Mokwa, W., Kohl, D., and Heiland, G., *Surf. Sci.* **126,** 368 (1983).

12. Mokwa, W., Kohl, D., and Heiland, G., *Fresenius Z. Anal. Chem.*, 314, 315 (1983).

13. (a) Tobin, J. P., Hirschwald, W., and Cunningham, J., *Appl. Surf. Sci.* **16,** 441 (1983); (b) *Spectrochim. Acta. Part B* **40,** 725 (1985).

14. Panzner, G., Egert, B., and Schmidt, *Surf. Sci.* **151,** 400 (1985).

15. (a) Benndorf, C., Egert, B., Keller, G., Seidel, H., and Thieme, F., *Surf. Sci.* **74,** 635 (1978); (b) Benndorf, C., Caus, H., Egert, B., Seidel, H., and Thieme, F., *J. Electron Spectrosc. Relat. Phenom.* **19,** 77 (1980).

16. (a) Madix, R. J., and Bowker, M., *Surf. Sci.* **116,** 549 (1982); (b) Bowker, M., and Madix, R. J., *Surf. Sci.* **95,** 190 (1980).

17. (a) Jennings, T. J., and Stone, F. S., "Advances in Catalysis," Vol. 9, p. 441. Academic Press, New York, 1957; (b) McKee, C. S., Renny, L. V., and Roberts, M. W., *Surf. Sci.* **75,** 92 (1978).