

## Catalytic Behavior and Surface Chemistry of Copper/Alumina Catalysts for Isopropanol Decomposition

F. PEPE,<sup>1</sup> C. ANGELETTI, S. DE ROSSI, AND M. LO JACONO

*Centro di Studio del CNR su "Struttura ed Attività Catalitica di Sistemi di Ossidi," Dipartimento di Chimica dell'Università di Roma, Rome, Italy*

Received January 3, 1984; revised May 15, 1984

Supported copper on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (1, 3, and 4 Cu atoms per 100 Al atoms) have been pretreated in a controlled way in oxygen and in hydrogen in order to have a known surface concentration of Cu(II), Cu(I), and Cu(0). These samples were tested as catalysts for the decomposition of 2-propanol. Below 443 K the samples showed only dehydrogenating activity which increased with the extent of catalyst reduction. A linear relationship was found between the kinetic constant and the surface area of copper metal. It is hence proposed that surface Cu(0) species are responsible for the dehydrogenation. The effect of the copper concentration on the sample stability under reaction conditions is also discussed. © 1985 Academic Press, Inc.

### INTRODUCTION

In recent years copper-based catalysts have attracted considerable interest because of their selective properties in reactions involving hydrogen. Copper is present in the catalysts used for the synthesis of methanol (1-3) and for the water gas shift reaction (4), and various studies have been devoted to the elucidation of the role of copper in the catalysis of reactions such as partial and stereoselective hydrogenation of alkynes (5), selective hydrogenation of carbonyl groups in unsaturated aldehydes and ketones (6, 7), and hydrogen transfer to ketones over hydroxyapatites (8). It is also of interest that hydrogenolysis reactions are practically absent during hydrogenation over copper-based catalysts. However, some aspects of the catalytic behavior of copper-containing catalysts are not completely understood. In particular, some doubts still exist concerning the nature of the active species.

With the aim of understanding better the correlation between catalytic properties and oxidation states of copper, a study has been undertaken in this laboratory on the

structural properties, surface chemistry and catalytic behavior of the supported system CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The investigation included surface redox cycles (9), catalytic hydrogenation (10), and dehydrogenation on systems with a well-defined surface concentration of the different oxidation states of copper. The present paper reports on the decomposition of 2-propanol over this system.

The 2-propanol decomposition has often been chosen in the past for correlating selectivity with physicochemical properties of the solid (11-13). In the present case, the study of the 2-propanol decomposition was used as a means for investigating the activity and selectivity toward dehydrogenation as a function of the copper concentration and oxidation state. The results throw some light on the nature of the active surface species and also on the stability of the copper oxidation states under reaction conditions as a function of copper concentration.

### EXPERIMENTAL

#### *Catalyst Preparation, Conditioning, and Surface Composition*

The copper on alumina samples are des-

<sup>1</sup> To whom correspondence should be addressed.

ignated as  $A\gamma\text{Cu}1$ ,  $A\gamma\text{Cu}3$ , and  $A\gamma\text{Cu}4$ , where the figure indicates the nominal number of copper atoms per 100 atoms of aluminum. Details of the preparation (impregnation technique) and of the subsequent operation are reported elsewhere (9, 14). The final calcination temperature in air was 873 K. The surface area values (BET,  $\text{N}_2$  adsorption) were in the range  $170\text{--}180\text{ m}^2\text{g}^{-1}$ .

The surface composition in terms of  $\text{Cu(II)}$ ,  $\text{Cu(I)}$ , and  $\text{Cu(0)}$  molar fraction can be varied depending on the treatment. It is therefore important to distinguish the *state* of the catalyst, and, to this end, Fig. 1 represents the various conditioning treatments in a schematic way. The freshly prepared catalyst calcined in air is denoted as state 1. The conditioning thereafter given always included an oxidation in flowing oxygen (99.5% purity) overnight at 723 K, followed by a flushing in high-purity helium ( $\text{H}_2\text{O}$  and  $\text{O}_2$ , about 1 ppm) for 1 h at 693 K. These samples are referred to as "oxidized" (state 2). The oxidized catalysts could be directly tested in a catalysis experiment.

Alternatively, the specimen was preliminarily reduced at different temperatures by flowing high-purity hydrogen ( $\text{H}_2\text{O}$  and  $\text{O}_2$ , about 1 ppm) at a given temperature (693, 473, 443, 425, 333 K) for 0.5 or 2 h. The reduction step was then followed by a flushing in helium for 0.25 h at the reduction temperature and by a conditioning at 693 K for 1 h in helium flow, finally obtaining a catalyst in a reduced state, designated as state 3. After a catalytic set of experiments on a catalyst with a given degree of reduction to restore the standard condition, the same conditioning in oxygen at 723 K overnight described above was adopted. Due to the history of the treatments (reduction-oxidation) catalysts so obtained may be different from those in the initial oxidized state 2, and they are designated in state 4 as "reoxidized." The reoxidized catalysts could be tested for catalysis or could be reduced again (state 5). The catalysts, both reduced and reoxidized, were used repeatedly with reproducible catalytic results.

The measure of the degrees of reduction was pursued, after catalysis, by placing the catalysts in a circulation system. A reoxidation at 723 K overnight in oxygen was performed and, after evacuation of the remaining oxygen, hydrogen was admitted as a flow at atmospheric pressure at the same temperature and time as for the catalytic test. After a standard evacuation at 693 K for 1 h, a given amount of oxygen was admitted at 723 K and allowed to circulate on the sample for 1 h. The decrease in oxygen pressure and then the amount of oxygen adsorbed by the sample enabled us to calculate the  $e/\text{Cu}$  ratio, i.e., the ratio between the number of oxygen equivalents consumed for the oxidation and the number of moles of copper in the sample. The  $\text{Cu}(n)$  mole fraction could then be evaluated using the  $\text{Cu}(n)$  vs  $e/\text{Cu}$  operational diagram described previously (9).

In addition, the exposed  $\text{Cu(0)}$  surface areas were independently measured by  $\text{N}_2\text{O}$  dissociative adsorption at room temperature.

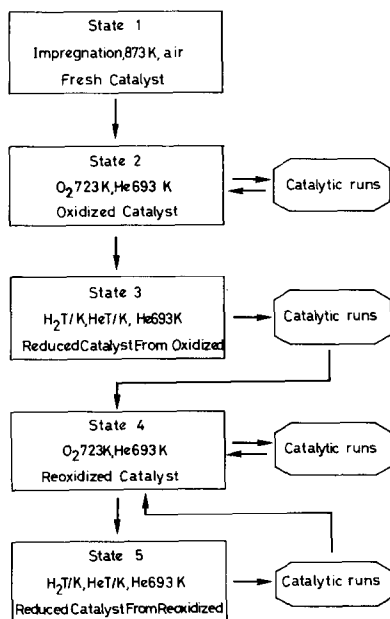


FIG. 1. Scheme of the pretreatments and catalytic sequence.

### Apparatus

The catalytic experiments were carried out in a flow system. A stream of helium (10–50 cm<sup>3</sup>/min) was used as carrier for the 2-propanol (Fluka, water content 0.1%) contained in a bubbler at room temperature. Before entering the bubbler, the carrier gas was usually passed through a trap containing copper turnings heated at 693 K in order to remove traces of oxygen. The catalyst (0.2–0.4 g) was contained in a Pyrex reactor vertically positioned in an electrical heater whose temperature was controlled to  $\pm 1$  K. At selected intervals, a known volume of the reacted mixture was sampled and analyzed with a dual-column gas chromatograph (C. Erba Fractovap G). Porapak R (80–100 mesh) and temperature program (333 to 403 K) were used for the analysis. The thermoconductivity detector was operated at 423 K and 150 mA. The areas of the GC peaks were determined with an integrator (H.P. 3370A).

## RESULTS

### Surface Composition

The system CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has been extensively studied and it is sufficient to recall that the copper ions, Cu<sup>2+</sup>, in the present concentration range, are present as a surface spinel (14).

The results of the surface investigation are listed in Table 1 where reduction condi-

tions, e/Cu ratios, the amounts of the Cu(*n*) species, the metallic copper surface area, and the dispersion [Cu(0)<sub>surf</sub>/Cu(0)], *D*, are reported. Note that each catalyst quoted has been reduced at different temperatures in the order listed in the table. For A<sub>γ</sub>Cu<sub>3</sub> two different portions were examined.

The Cu(*n*) atomic contents refer to the total amounts present both on the surface and in the bulk; only for the metallic copper was a direct and independent titration of the exposed surface made by dissociative adsorption of N<sub>2</sub>O at room temperature. The method, originally proposed by Osinga *et al.* (15), has been recently reviewed by Evans *et al.* (16), who pointed out the role of the temperature and of the components of the catalyst on the selectivity of the method. Iglesia and Boudart (17) also found that the N<sub>2</sub>O titration of Cu(0) metal surface both as powder and supported on alumina gives results in qualitative agreement with XRD line broadening. In our laboratory it was found that for low-temperature reduction of dilute CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, where an almost complete dispersion of Cu(0) is expected, the measure of the Cu(0)<sub>surf</sub> both by the water released during the reduction (9) and by the N<sub>2</sub>O dissociative adsorption was in good agreement.

Several tests of reproducibility and accuracy performed in our laboratory on different apparatus and by different operators re-

TABLE I  
Surface Composition of Reduced Catalysts

Expt	Catalyst	<i>T</i> <sub>red</sub> (K)	Time (h)	e/Cu	Cu(II) (at · g <sup>-1</sup> 10 <sup>20</sup> )	Cu(I) (at · g <sup>-1</sup> 10 <sup>20</sup> )	Cu(0) (at · g <sup>-1</sup> 10 <sup>20</sup> )	Cu(0) <sub>surf</sub> <sup>a</sup> (at · g <sup>-1</sup> 10 <sup>20</sup> )	<i>D</i>
1	A $\gamma$ Cu1	693	0.5	1.30	0.00	0.90	0.39	0.10	0.33
2	A $\gamma$ Cu1	423	0.5	0.00	1.29	0.00	0.00	0.00	—
1	A $\gamma$ Cu3	693	0.5	1.45	0.00	2.12	1.65	0.48	0.29
2	A $\gamma$ Cu3	443	0.5	0.20	3.06	0.49	0.12	0.09	0.75
3	A $\gamma$ Cu3	473	0.5					0.15	
1b	A $\gamma$ Cu3	693	2.0	1.94	0.00	0.18	3.49	0.45	0.13
1	A $\gamma$ Cu4	693	0.5	1.43	0.00	2.73	2.06	0.56	0.27
2	A $\gamma$ Cu4	425	0.5	0.97	0.72	3.40	0.62	0.26	0.41
3	A $\gamma$ Cu4	333	0.5	0.15	4.20	0.53	0.10		

<sup>a</sup> The experimental error on these figures is about  $\pm 0.04$  at · g<sup>-1</sup> 10<sup>20</sup>.

sulted in an upper limit error of  $\pm 0.3 \text{ m}^2$  on Cu(0) surface area, as a result of a careful analysis of the experimental parameters as amount of catalyst, reduction extent and  $\text{N}_2$  pressure after  $\text{N}_2\text{O}$  decomposition.

Inspection of the table shows that the  $\text{A}\gamma\text{Cu}_3$  and  $\text{A}\gamma\text{Cu}_4$  catalysts, after the catalysis cycles, behave similarly with respect to the reduction at 693 K. In fact their e/Cu ratios are identical. The value of 1.30 found on  $\text{A}\gamma\text{Cu}_1$  points to a different reducibility of the less concentrated samples.

The difference in reducibility for reoxidized samples as a function of the concentration becomes evident when lower reduction temperatures are adopted. In fact, values of 0, 0.2, and 0.97 were found on increasing copper content, when the samples were reduced at 425 and 443 K. Under these conditions a difference also between  $\text{A}\gamma\text{Cu}_3$  and  $\text{A}\gamma\text{Cu}_4$  can be envisaged. As a consequence  $\text{A}\gamma\text{Cu}_4$  reduced at 425 K has a Cu(0) concentration 5 times larger than the sample  $\text{A}\gamma\text{Cu}_3$  reduced at 443 K.

A larger Cu(0) content can also be obtained by increasing the reduction time. This is the case for  $\text{A}\gamma\text{Cu}_3$  in Expt 1b compared with Expt 1 (see Table 1). In fact, the e/Cu value rises to 1.94 when the reduction is performed for 2 h. However, in spite of the different e/Cu values (1.94 and 1.45) for which different values of  $\text{Cu}(0)_{\text{surf}}$  would be expected (10), in the present case the surface area of copper metal does not increase with the extent of reduction due to the effect of metal sintering. As a consequence different copper metal dispersion and different average particle sizes are obtained. Indeed, the  $D$  values embody the effect of temperature and time of reduction as well as the effect of the conditioning treatment at 693 K *in vacuo*, which tends to smooth out larger effects of copper loading. They range from 0.13 to 0.75 and the corresponding average particle dimensions are 79 and 13 Å, respectively, on the assumptions of a surface density of  $1.46 \times 10^{19}$  atoms/ $\text{m}^2$  and a density of  $8.96 \text{ g/cm}^3$  of the metallic copper.

### Catalysis

The  $\gamma\text{-Al}_2\text{O}_3$  used as support exhibited only dehydrating activity in the temperature range 443–523 K. Conversion was 100% at about 500 K. Different precatalytic treatments (oxidizing or reducing) did not modify the activity levels. The activation energy was  $172 \pm 10 \text{ kJ mol}^{-1}$ .

The copper-containing samples, by contrast, exhibited dehydrogenating activity below 443 K, and dehydrogenating plus dehydrating activity above this temperature. The experimental results obtained mainly refer to the lower temperature range 333–433 K, where the dehydrogenating properties of the copper were not obscured by the side reaction (dehydration). It must be noted that the constancy of the dehydrogenating activity for times as long as 48 h and the presence of water (0.1%) in the 2-propanol feed, indicates the absence of a poisoning effect by water at these concentrations. By contrast, traces of oxygen were able to reduce the activity (see below).

The dehydrogenation can be described by a first-order kinetic equation, whose integral form, derived in conditions of ideal displacement, is (18)

$$\ln \frac{1}{1-x} = k \frac{V}{\phi} \quad (1)$$

where  $x$  is the degree of conversion (upper limit about 50%),  $k$  the experimental kinetic constant,  $V$  the volume of the catalyst ( $\text{cm}^3$ ), and  $\phi$  the flow velocity of the reactant ( $\text{cm}^3 \text{ s}^{-1}$ ). In Eq. (1) the volume variation of the gas mixture due to the reaction is neglected because the partial pressure of both reactant and products is less than one-tenth with respect to that of the carrier. Equation (1) was tested for  $\text{A}\gamma\text{Cu}_3$  and  $\text{A}\gamma\text{Cu}_4$  samples by plotting  $\ln(1/(1-x))$  vs  $V/\phi$  in the range 423–453 K. Good straight lines were obtained.

No deviation from linearity was observed at low flow rate and at different isopropanol pressures. This result, together with the

very large effects of the reduction extent of the catalysts on the activity, points to a true chemical control of the reaction, with little influence of diffusion.

The only products of the reaction were acetone and hydrogen (mass balance  $100 \pm 5\%$ ). A good reproducibility of the activity levels at the steady state was observed both on different portions of the same catalysts and on the same portion aged differently, when the same pretreatment conditions were used.

The activation energies were constant for all the  $A\gamma\text{Cu}_x$  samples with a value of  $70 \pm 8 \text{ kJ mol}^{-1}$ .

### Oxidized and Reoxidized States

The results, expressed as kinetic constants normalized per catalyst surface area,  $k_{sp}$ , as a function of the temperature, show that for all the oxidized catalysts (state 2 of Fig. 1) the activity levels at 434 K were very low and tended to decay slowly during times on stream (t.o.s.) as long as 48–72 h. In Fig. 2 the  $\log k_{sp}$  values are reported as a function of copper content and of t.o.s.

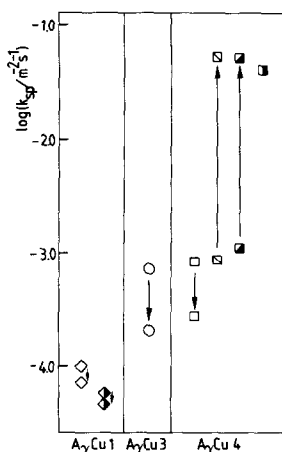


FIG. 2. Activity of oxidized, reoxidized, and low-temperature reduced samples as a function of time on stream (t.o.s.) and copper content at 434 K.  $\diamond$ ,  $A\gamma\text{Cu}1$  oxidized, t.o.s. 25  $\rightarrow$  48 h;  $\blacklozenge$ ,  $A\gamma\text{Cu}1$  reduced at 423 K, t.o.s. 0.5  $\rightarrow$  16 h;  $\circ$ ,  $A\gamma\text{Cu}3$  oxidized, t.o.s. 0.3  $\rightarrow$  48 h;  $\square$ ,  $A\gamma\text{Cu}4$  oxidized, t.o.s. 0.2  $\rightarrow$  72 h;  $\boxminus$ ,  $A\gamma\text{Cu}4$  reoxidized, t.o.s. 0.5  $\rightarrow$  24 h;  $\blacksquare$ ,  $A\gamma\text{Cu}4$  reduced at 333 K, t.o.s. 1.0  $\rightarrow$  68 h;  $\blacksquare$ ,  $A\gamma\text{Cu}4$  reduced at 425 K.

Here, the activity changes, which occur in the interval of t.o.s. specified in the figure, are indicated by the arrows; empty symbols are used for the catalysts coming from state 2 (oxidized catalysts).

For  $A\gamma\text{Cu}1$  it must be noted that also the reduction at 423 K (state 3) is unable to increase the activity to levels higher than those presented by the oxidized one (see Fig. 2). It can be deduced that the reoxidized sample  $A\gamma\text{Cu}1$  (state 4) has a very low activity level, while the most concentrated sample,  $A\gamma\text{Cu}4$ , reoxidized, is able to undergo reduction by the reaction feed *in situ*.

### Reduced State

The reduced state of a catalyst can be obtained in two ways, namely from the oxidized sample (state 3) or from the reoxidized sample (state 5). The distinction is very important because the history of the catalyst is crucial in determining its catalytic behaviour.

All the samples reduced at 423 K and coming from the oxidized state (state 3) had a very poor activity. In fact, their activity values were very close to the values of oxidized samples. It can be deduced that the reducing treatment at 423 K does not affect the activity levels, due to the difficulty in reducing the surface. If, on the other hand, we consider the samples reduced at 423 K from the reoxidized state (state 5), namely after several redox cycles, two different behaviors dependent on the copper content can be distinguished. In fact, for  $A\gamma\text{Cu}1$  the  $\log k_{sp}$  at 434 K has the same value as found before. The indication is that the redox cycles do not prevent the surface from being restored and from having a similar catalytic behavior irrespective of the preceding redox cycles; in addition, the coincidence between the activity of the oxidized and the 423 K reduced sample means that the surface strongly resists the reduction at 423 K. By contrast, the samples  $A\gamma\text{Cu}3$  and  $A\gamma\text{Cu}4$  are several orders of magnitude

more active with respect to the oxidized samples.

In Fig. 3 the Arrhenius plots are reported for samples coming from state 4 and subjected to reduction at 423 K and other temperatures. It may be seen that the reduction at 425, 443, 473, and 693 K progressively increases the activity,  $E_a$  being constant ( $70 \text{ kJ mol}^{-1}$ ). In addition the reoxidized  $A\gamma\text{Cu}4$ , when reduced at 333 K, showed an activity level increasing with t.o.s. For clarity the situation is shown in Fig. 2 where it can be seen that the final level at 434 K reaction temperature is identical to that shown by the same sample reoxidized and to that presented by the same sample reduced in hydrogen at 425 K. It is deduced that the reaction mixture was able to reduce both reoxidized and low-temperature-reduced (333 K)  $A\gamma\text{Cu}4$ . The sample  $A\gamma\text{Cu}3$  reduced at 373 K is less sensitive to the reaction feed and a possible increase in activity with time is barely visible.

Finally, the addition of oxygen in small amounts (20–40 ppm) in the helium flow after the reducing treatment at 693 K produces an initial activity of  $A\gamma\text{Cu}4$  well be-

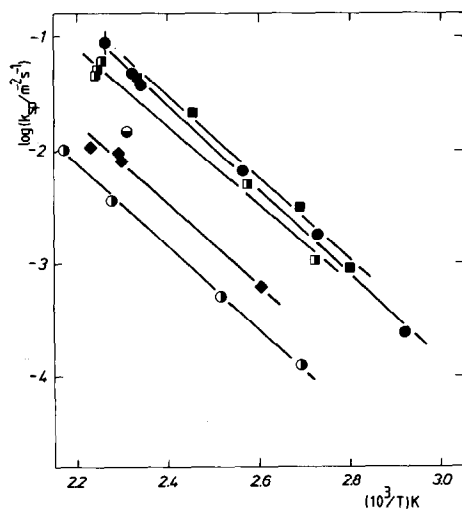


Fig. 3. Arrhenius plot for reduced samples.  $\blacklozenge$ ,  $A\gamma\text{Cu}1$  reduced at 693 K;  $\bullet$ ,  $A\gamma\text{Cu}3$  reduced at 443 K;  $\ominus$ ,  $A\gamma\text{Cu}3$  reduced at 473 K;  $\bullet$ ,  $A\gamma\text{Cu}3$  reduced at 693 K;  $\blacksquare$ ,  $A\gamma\text{Cu}4$  reduced at 425 K;  $\blacksquare$ ,  $A\gamma\text{Cu}4$  reduced at 693 K;  $\bullet$ ,  $A\gamma\text{Cu}3$  reduced at 693 K, 2 h.

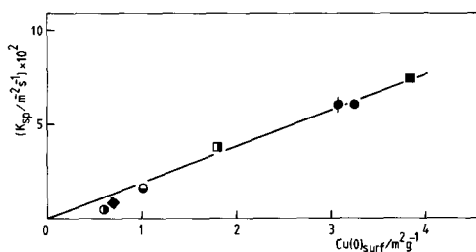


Fig. 4. Relationship between activity and  $\text{Cu}(0)$  surface area at 434 K. For symbols see Fig. 3.

low that of the same sample in the absence of oxygen. The pseudoequilibrium activity is still depressed with respect to the initial one, but higher than that of the oxidized sample.

## DISCUSSION

The dehydrating activity of  $\gamma\text{-Al}_2\text{O}_3$  is well known (19, 20). In the present investigation it was confirmed that oxidizing and reducing treatments do not produce variations in either activity levels or selectivity.

When copper is added, a dehydrogenating activity arises. This activity is shown to depend on the copper content. In fact, the activity ratio between the most concentrated sample  $A\gamma\text{Cu}4$  and the diluted one (both oxidized) is in good agreement with the copper concentration ratio.

The results also show that reducing treatments provoke an increase in the dehydrogenation activity. The increase was found to depend on both copper concentration and the history of the sample. It can be inferred that  $\text{Cu}(0)$  and/or  $\text{Cu}(I)$  species must be responsible for the large difference in activity between oxidized and reduced samples. The constancy of  $E_a$  places all the observed differences in activity on the preexponential factor. Hence, on the reasonable assumption that the reaction mechanism and the entropic part of the preexponential term are constant, the activity levels depend only on the number of the active sites present on the surface, their nature being constant. In Fig. 4 a plot of  $k_{sp}$  vs  $\text{Cu}(0)$  surface area is reported for the reaction temperature 434 K. A linear de-

pendence is observed. It can be noted that specimens having a different  $D$  value fall on the line, only the surface area value being determinant. We conclude that the 2-propanol dehydrogenation activity is not size dependent, at least in the limited particle size range examined.

We can now turn to the role of Cu(II) and Cu(I). As far as the former quantity is concerned, it has been proved that fully oxidized samples are inactive, thus excluding a role of Cu(II) in the decomposition. For the latter, it is assumed that the Cu(I) surface content parallels the variation in the total Cu(I) content. Hence a relationship between activity and Cu(I) on the surface can be excluded by comparing the Cu(I) total content and the  $k_{sp}$  values. Indeed in Table 2, for catalysts reduced at 693 K (lines 1 and 2) a comparable amount of Cu(0) on the surface and of Cu(II) is found, but the large increase in the Cu(I) content does not cause any increase in activity. In addition, comparison between catalysts reduced at 425 and 693 K (lines 4 and 3) points out that the increase of  $k_{sp}$  parallels the increase in Cu(0)<sub>surf</sub> content, whereas the Cu(I) content decreases.

As far the oxidized samples are concerned, the hypothesis that their activities are due to the presence of a small concentration of Cu(0)<sub>surf</sub> can be proposed. It can be noted that: (i) there is an increase in activity under reaction conditions of the reoxidized  $A\gamma Cu_4$ ; (ii) oxygen exerts a poisoning effect; (iii) the values of  $E_a$  for oxidized and reduced samples are comparable.

In conclusion, it is inferred that the Cu(0) species is the only one responsible for the

dehydrogenation. This conclusion is consistent with the results of Echevin and Teichner (21) on the decomposition of 2-butanol on CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, although their findings could not exclude a role for Cu(I). The results by Volta *et al.* (22) on pure CuO also agree with the present conclusion as far as the nature of the active species is concerned.

The reducing effect of 2-propanol during the reaction should also be emphasized (data for  $A\gamma Cu_4$ ). Volta *et al.* (22) noted a similar effect with pure CuO.

It should be mentioned that in a study of 2-propanol decomposition over a series of oxides, Cunningham *et al.* (23) proposed a mixed-valence model for the active site on CuO. These sites would involve the contemporary presence of Cu(II) and Cu(I). At variance with this hypothesis the present results suggest the Cu(0) species as the necessary component of the active site. The results given by Cunningham *et al.*, based on the similarity in the behavior of oxidized and reduced CuO, can be interpreted as well by assigning to Cu(0) the role of the active species, the reduced copper being generated *in situ* by reduction by 2-propanol. This alternative explanation finds support in the results of Volta *et al.* (22) on the conditioning effect of the reaction medium.

The instability in reaction conditions of  $A\gamma Cu_4$  reoxidized may be tentatively explained by considering that a surface spinel is formed at temperatures as low as 600 K (24, 25). It may be proposed, then, that in our temperature and time conditions (723 K overnight in oxygen), reoxidation of the samples produces surface CuAl<sub>2</sub>O<sub>4</sub>, but the thickness of the CuAl<sub>2</sub>O<sub>4</sub> patches is limited to a few layers. Hence, a more superficial spinel is formed, as opposed to the bulk spinel detectable by X rays which was formed during catalyst preparation when higher oxidation temperature is used (873 K, 24 h). The phenomenon is clearly dependent on the copper loading and it is then reasonable to argue that a different behav-

TABLE 2  
Comparison of Activity of Cu( $n$ ) Species

$T_{red}$ (K)	Cu(0) <sub>surf</sub> (at · g <sup>-1</sup> 10 <sup>20</sup> )	Cu(I) (at · g <sup>-1</sup> 10 <sup>20</sup> )	Cu(II) (at · g <sup>-1</sup> 10 <sup>20</sup> )	$k_{sp}$ at 434 K (m <sup>-2</sup> s <sup>-1</sup> )
693	0.45	0.18	0.0	$6.0 \times 10^{-2}$
693	0.48	2.12	0.0	$6.0 \times 10^{-2}$
693	0.56	2.73	0.0	$7.2 \times 10^{-2}$
425	0.26	3.40	0.72	$3.6 \times 10^{-2}$

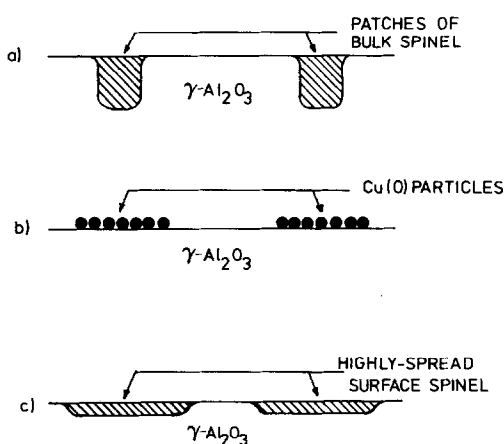


FIG. 5. Spinel and Cu(0) formation on conditioning treatments (see Fig. 1): (a) state 2, oxidized sample; (b) state 3, reduced sample; (c) state 4, reoxidized sample.

ior is found with respect to the reduction of the reoxidized and oxidized samples (Fig. 5). In fact, when hydrogen is admitted in the pretreatment, it would be activated on a  $\text{cus Al}^{3+}$  site on  $\text{Al}_2\text{O}_3$  as  $\text{H}^-\text{H}^+$  pairs, via a reverse spillover (26), and then transferred to the neighborhood of  $\text{Cu}^{2+}\text{O}^{2-}$  pairs or  $\text{Cu}^{2+}\text{O}^{2-}\text{Cu}^{2+}\text{O}^{2-}$  groups. It is understandable that the reduction can be less hindered when there is more copper, since the transfer distance is smaller. If, however, the reaction feed is thought to play a role in the reduction, it is reasonable to suggest that also the 2-propanol may be able to reduce reoxidized  $\text{A}\gamma\text{Cu4}$  considerably.

Finally, the role of the oxygen in the reaction feed can be rationalized by recalling that the oxidation of Cu atoms may occur under very low oxygen pressure. Several authors have quoted thermodynamic values of about  $10^{-37}$  atm of oxygen at 400 K for oxidizing Cu(0) metal particles to  $\text{Cu}_2\text{O}$  (27, 28). Thus the oxidation of a few isolated copper metal crystallites by water and/or by the oxygen controlled by the Cu trap is possible, but it is not reflected in a decay in activity because the amount of oxygen flowed on the catalyst, during the time on stream, is negligible. On the contrary, when 20–40 ppm of oxygen are present in the helium flow, a thorough oxidation takes

place during the flushing at 693 K, with a consequent decrease in activity. The situation reflects the oxidation of a certain number of active sites, while the  $E_a$  remains constant. The further permanence in the flow of alcohol containing the traces of oxygen provokes a further decay in activity. The final level is, however, higher with respect to that of the oxidized sample as a result of the opposing actions of the oxygen and of the alcohol.

In conclusion, it turns out that the  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  system shows well-defined activities in the 2-propanol decomposition in the range 333–434 K when reduced in hydrogen at different extents. Thanks to the reproducibility and the knowledge of the surface Cu(0) content formed in the reduction step, the Cu(0) species has been identified as the active one.

#### ACKNOWLEDGMENTS

The authors thank Professor A. Cimino for valuable discussions and for critical reading of the manuscript. This work was supported by the Project "Chimica Fine e Secondaria" of CNR (Rome).

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