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Catalytic Behavior and Surface Chemistry of Copper/ZnO/Al_2O_3 Catalysts for the Decomposition of 2-Propanol

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$CuO/ZnO/Al_2O_3$ samples (1 and 4 Cu atoms and 1, 5, 15, and 30 Zn atoms per 100 Al atoms, respectively) have been tested as catalysts for the decomposition of 2-propanol. The samples were pretreated in a controlled way in hydrogen or in the reaction medium in order to have a known surface content of Cu(0). Below 440 K the samples showed only dehydrogenating activity. A linear relationship was found between the rate constant and the surface area of zero-valent copper. It is hence proposed that surface Cu(0) species are responsible for the dehydrogenation. The higher values of turnover frequency for the present system in comparison with the values previously found on CuO/Al_2O_3 enable a proposal to be made for the role of the zinc in the activity of the Cu(0) species. The beneficial effect of the zinc on the reducibility of Cu^{2+} ions and a reduction mechanism are also discussed.

INTRODUCTION

A class of catalysts interesting for their hydrogenating–dehydrogenating activity are the copper-based systems, the study of which has been boosted recently by their activity and selectivity in methanol synthesis and in the water gas shift reaction. There is much debate on the role of the oxidic components and on that of the oxidation state of the copper. Reference can be made to the reviews published by Chinchen *et al.* (*1*), Bart and Sneeden (*2*), and Ghiotti and Boccuzzi (*3*).

With the aim of obtaining a better understanding of the possible correlation between the catalytic activity, the selectivity, the oxidation state, and the stability of copper species and of the role of the oxidic components, γ-Al_2O_3 and ZnO, the surface chemistry of the systems CuO/ZnO, CuO/Al_2O_3, and $CuO/ZnO/Al_2O_3$ (*4–7*) and the catalytic behavior of the systems CuO/Al_2O_3, ZnO/Al_2O_3, and $CuO/ZnO/Al_2O_3$ (*8–11*) have already been investigated. In particular the H_2–D_2 equilibration on pure γ-Al_2O_3, ZnO/Al_2O_3, and $CuO/ZnO/Al_2O_3$ was found to be positively influenced by the presence of zinc ions on alumina (*10*); similarly in propene hydrogenation (*11*) the presence of zinc was shown to have a very marked influence on the activity, irrespective, however, of the zinc content. In addition the rate constant was a linear function of the Cu(0) surface content.

In the present work we have investigated the 2-propanol dehydrogenation on the ternary system $CuO/ZnO/Al_2O_3$ with the aim to investigate the nature of the surface active species and the role of zinc in the oxidic component on both the catalytic behavior and the reducibility of Cu^{2+} ions.

EXPERIMENTAL

1. Preparation, Characterization, Conditioning, and Surface Content of Samples

The samples $CuO/ZnO/Al_2O_3$ are designed AZCux:y, where x = 1, 5, 15, 30 indicates the number of zinc atoms and y = 1, 4 indicates the number of copper atoms per 100 atoms of aluminum, respectively.

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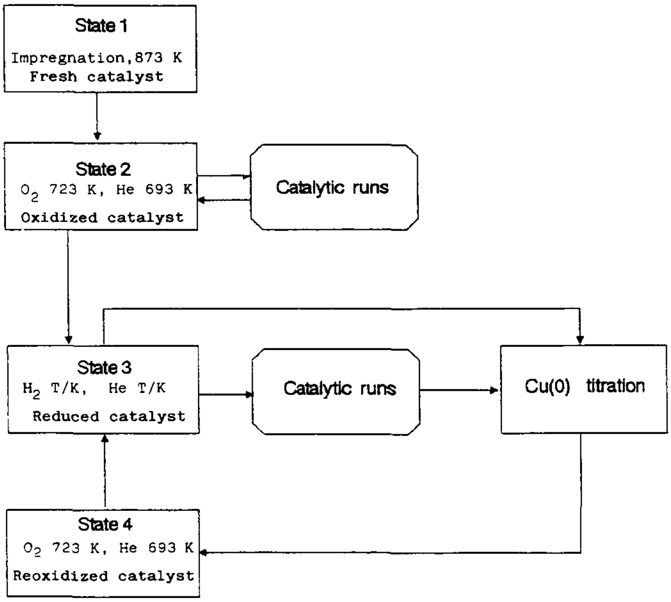

FIG. 1. Scheme of the pretreatments, the catalytic sequence, and determination of the exposed Cu(0) surface area.

They were obtained by impregnating ZnO/Al_2O_3 samples, AZ*x*, prepared as described previously (*9*), with a copper nitrate solution, followed by drying at 393 K and subsequent calcination in air at 873 K for 24 h. All chemicals were C. Erba reagent grade. The catalysts were analyzed by atomic absorption for zinc and copper loading.

X-ray analysis, both with a Debye–Scherrer camera and with a counter diffractometer (Cu$K\alpha$ radiation, $\lambda = 1.54178$ Å, Ni filtered), and diffuse reflectance spectroscopy with a Beckman DK-1A spectrometer (wavelength range 250–2500 nm, MgO as reference) were used for characterization. The surface areas were measured with a conventional BET apparatus (N_2 as adsorbate, $\sigma = 16.27$ Å^2, $T = 77$ K).

Both the metallic copper content and the Cu(0) surface area can be varied depending on redox treatments and on the history of the sample. It is therefore necessary to define the state of the catalyst. Figure 1 represents the various conditioning treatments in a schematic way. State 1 represents the "as-prepared" catalyst. The conditioning given thereafter always includes an oxidation in flowing oxygen (99.5% purity) overnight at 723 K, followed by a flushing in high-purity helium (H_2O and O_2 less than 1 ppm). The "oxidized" catalysts (state 2) could be directly tested in a catalytic experiment. Alternatively, the oxidized specimen was reduced at a different temperature and time by flowing pure hydrogen (T range 443–693 K; flow rate = 20–60 cm^3 min^{-1}; pressure = 1.5–2.5 atm).

The "reduced" catalyst (state 3) could be tested for catalysis and/or submitted to N_2O titration for estimation of the Cu(0) surface area. Some titration experiments were performed both before and after catalysis in order to check possible differences in Cu(0) surface area due to a reduction during catalysis. In fact, as shown below in the catalysis section, an oxidized specimen could be reduced directly during the catalytic decomposition. Then, as a necessary procedure, the catalyst was always reduced at temperatures higher than those of catalysis.

The reduced catalyst, after catalysis and/or Cu(0) titration, was reconditioned overnight in oxygen at 723 K. Due to the redox treatments, reoxidized catalysts 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 reduced again and then subjected to catalysis or directly tested as reoxidized.

The Cu(0) titration was performed by N_2O dissociative chemisorption at room temperature. The N_2O, doubly distilled, was circulated over the catalyst for 30 min at room temperature. The N_2 resulting from the decomposition was measured after freezing the undecomposed N_2O at 77 K. A value of 0.176 cm^3 NTP per m^2 of Cu(0), corresponding to 1.35×10^{19} Cu(0) atoms, was assumed following Osinga *et al.* (*12*).

The mean Cu(0) crystallite diameter was calculated according to the following expression and assuming that all the copper has been reduced to Cu(0):

$$D = 6000\, g/dS_0, \qquad (1)$$

where D is the mean diameter in nanometers assuming spherical crystallites, g the copper mass per gram of catalyst, d the copper density (g cm^{-3}), and S_0 the Cu(0) surface area per gram of catalyst (m^2 g^{-1}).

2. *Catalysis: Method and Data Treatment*

The catalytic experiments were carried out in a flow system. A stream of helium (10–60 cm^3 min^{-1}) was used as carrier for the 2-propanol (Fluka reagent, water content <0.1%), which was contained in a bubbler maintained at different temperatures in order to vary the alcohol partial pressure (15–40 Torr; 1 Torr = 133.3 N m^{-2}). The carrier gas was passed through a purifier (Matheson 6406) to remove traces of oxygen. The catalyst (0.150–0.600 g) was contained in a silica reactor vertically positioned in an electric heater, the temperature of which was controlled to ±1 K. At selected time intervals, a known volume (1 cm^3) of the reacted mixture was sampled and analyzed with a dual column gas chromatograph (Carbopack B 80/120 mesh plus Carbowax 20 M at 395 K, He carrier flow of 20 cm^3 min^{-1}, thermal conductivity detector at 473 K and 150 mA). The areas of GC peaks were determined with a Shimadtzu C-R1 B integrator.

The kinetic treatment used assumes a first-order reaction whose integral form derived under conditions of ideal displacement is

$$\ln \frac{1}{1-x} = k\frac{V}{\phi}, \qquad (2)$$

where x is the degree of conversion, k the rate constant, V the volume of catalyst (cm^3), and ϕ the flow rate of the reactant (cm^3 s^{-1}). In Eq. (2) the volume variation of the gas mixture due to the reaction is neglected because the partial pressure of both reactant and products is always less than one-tenth that of the carrier.

RESULTS

1. *Catalyst Characterization*

The XRD investigation has been performed on both the supports AZ*x* before impregnation and on samples AZCu*x*:*y*. Diffractometer analysis showed that:

(i) for all the AZ*x* supports the presence of γ-Al_2O_3 and the zinc aluminate phase was detected. The peaks at $2\theta = 34.5°$ and 47.6°, characteristic of ZnO phase, were never detected;

(ii) the addition of copper to the AZ*x* supports increases the peaks at $2\theta = 31.3°$, 36.9°, 59.4°, and 65.3°, characteristic of a spinel phase (ASTM No. 5-0669), as shown in Fig. 2 for the most concentrated samples.

With the Debye–Scherrer photographic method (8 h exposure) the AZ30 support showed peaks at $2\theta = 34.5°$ and 47.6°. Before impregnation, this was the only support where some ZnO was detected by XRD. By contrast, the films of the series AZCu30:*y* confirmed the findings of the counter diffractometer analysis, i.e., the absence of ZnO

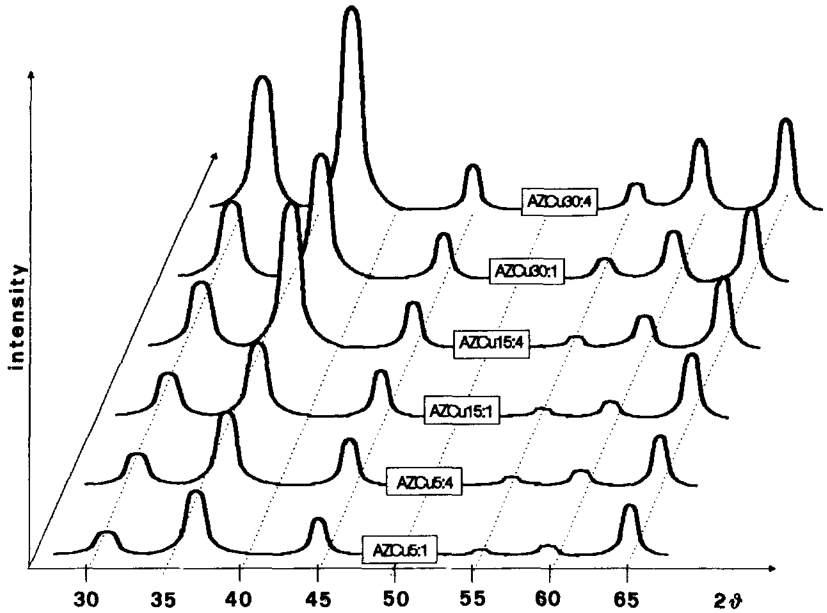

FIG. 2. X-ray diffractograms for AZCux : y samples.

phase as a result of the additional thermal treatment (873 K for 24 h) with respect to the parent AZ30. Such a treatment has allowed further diffusion of zinc ions into the γ-Al_2O_3 defective structure.

When reflectance spectra are considered, an absorption edge at ca. 390 nm (attributable to the transition valence–conduction band of ZnO, $E_g \approx 3.2$ eV) is present in the AZCu30 : 4 sample only. All the copper-containing samples showed a typical absorption band due to Cu^{2+} ions in octahedral symmetry centered at about 750 nm. The band, related to the spin-allowed transition $^2E_g \rightarrow {}^2T_{2g}$, is very intense, mainly for AZCux : 4 samples. Because the band due to Cu^{2+} ions in tetrahedral symmetry is located in the 1400- to 1600-nm region and its extinction coefficient is about 10–100 larger than that for the octahedral band (5), it can be inferred that almost all of the cupric ions are located in the octahedral sites of the surface spinel. The absorption peaks observed in the wavelength region 1500 to 2000 nm are due to surface hydroxyls. Table 1 summarizes the most outstanding sample features detected by the above techniques together with the surface area values.

The results of the surface investigation in terms of Cu(0) content are listed in Table 2 where reduction conditions, flushing treatments, and metallic copper surface areas, S_0, are reported, with the results obtained

TABLE 1

Phases Detected and Specific Surfaces Areas of AZCux : y Samples

Sample	Surface area ($m^2\ g^{-1}$)	Phases detected by XRD
AZCu1 : 1	166	A, MeA_2
AZCu1 : 4	150	A, MeA_2
AZCu5 : 1	144	A, MeA_2
AZCu5 : 4	138	A, MeA_2
AZCu15 : 1	144	A, MeA_2
AZCu15 : 4	106	A, MeA_2
AZCu30 : 1	127	A, MeA_2
AZCu30 : 4	94	A, MeA_2, ZO(r)

Note. A, γ-alumina; MeA_2, $Cu_xZn_{1-x}Al_2O_4$, surface spinel; ZO, zinc oxide. r, as detected by reflectance spectra.

TABLE 2

Reduction Conditions, Flushing Treatments, and Metallic Copper Surface Area for ACu*y* and AZCu*x* : *y*

Experiment	Sample	H_2		He		S_0 ($m^2\ g^{-1}$)
		T(K)	*t*(min)	*T*(K)	*t*(min)	
1	ACu3	443	30	693	60	0.62
2		473	30	693	60	1.0
3		693	30	693	60	3.3
4		693	120	693	60	3.1
5	ACu4	425	30	693	60	1.8
6		693	30	693	60	3.8
7	AZCu1 : 4	473	30	473	30	5.1
8		693	30	298	60	1.5
9	AZCu5 : 4	473	30	693	30	1.0
10		473	60	693	60	1.2
11		473	100	573	30	6.2
12		473	30	573	30	5.5
13		473	30	473	30	5.4
14		473	30	573	60	4.8
15	AZCu30 : 4	473	15	693	30	0.7
16		473	30	693	30	1.0
17		473	100	573	30	2.2
18		573	30	573	30	5.1
19		473	100	573	30	4.5

Note. Experiments 1 and 17 were carried out on "oxidized" samples. All other experiments were carried out on "reoxidized" samples.

on the CuO/Al_2O_3 samples, ACu, previously investigated (*8*). Inspection of Table 2 shows that:

(i) oxidized AZCu30 : 4 (experiment 17) is less reducible than reoxidized AZCu30 : 4 (experiment 19) as a result of the presence of a more superficial copper spinel in the reoxidized sample with respect to the oxidized one.

(ii) An increase in reduction temperature of ACu3 increases S_0 (experiment 2 vs 3). Inspection of the behavior of ACu4 (experiment 5 and 6) confirms the trend. It can be inferred that temperatures as low as 473 K (experiment 2) or 425 K (experiment 5) are able to reduce the ACu system to a limited extent. Because a prolonged reduction time (experiment 3 vs 4) is responsible for a very small variation in Cu(0) surface areas, the low value of S_0 for ACu3 and ACu4 for reduction at $T \leq 473$ K is not due to the successive flushing in helium at 693 K, but it is a true result of a limited reduction by hydrogen.

(iii) High-temperature treatment in helium after reduction has a dramatic effect in reducing the surface area of the metallic copper in the case of the AZCu samples. Thus, for reduction at 473 K, AZCu5 : 4 shows a very different S_0 depending on the subsequent He treatment temperature (experiment 9 vs 12, 13, 14). The same behavior is shown by AZCu30 : 4 (experiment 16 vs 18).

(iv) No appreciable role of the zinc content is envisaged by considering AZCu1 : 4 (experiment 7) vs AZCu5 : 4 (experiment 13) and AZCu5 : 4 (experiment 14) vs AZCu30 : 4 (experiment 19).

A few experiments on different samples showed that S_o was the same before and after the catalytic runs on reduced catalysts (state 3, Fig. 1). Because the catalysis was investigated at temperatures lower than the reduction temperatures, the titration of Cu(0) *after catalysis* has been adopted as a standard method (Fig. 1).

Finally, the zinc and copper contents of all the samples AZ*x* and AZCu*x*:*y* determined by atomic absorption were satisfactorily in agreement with the theoretical ones.

2. *Catalysis*

The AZ*x* supports exhibited both dehydrating and dehydrogenating activity in the temperature range 450–540 K. The apparent activation energies for dehydration and dehydrogenation were 170 ± 10 kJ/mol and 126 ± 10 kJ/mol, respectively, and it was found that the activities were due to the γ-Al$_2$O$_3$ and to the ZnO phases (*9*).

In the present work the *T* range investigated was 350–440 K although the upper limit of this range was seldom reached. The copper-containing samples below 440 K exhibited dehydrogenating activity only. The constancy of the dehydrogenating activity for times as long as 48 h suggests that the presence of water in the 2-propanol feed did not have a poisoning effect on dehydrogenation.

The validity of the first-order kinetic law assumed for the data treatment was checked by testing Eq. (2) at different values of contact time for the series AZCu*x* : 4. For contact times <0.2 s, no deviation from linearity was observed. The same results holds for different 2-propanol pressures. This finding, together with the very large effects of the reduction extent of the catalyst on the activity, points to a true chemical control of the reaction.

The results expressed as rate constants normalized per gram of catalyst, k_o, as a function of temperature, have shown that the activities of all the oxidized catalysts (state 2 of Fig. 1) in the *T* range 343–414 K were negligible for times as long as 48 h. However, when the reaction was investigated at 413 K on a reoxidized AZCu30 : 4, the catalyst developed a well-defined dehydrogenating activity that was then a function of the time on stream, t.o.s., and of the number of redox treatments. The phenomenon has already been observed on a reoxidized ACu4 and it was attributed to the formation of a more superficial spinel phase during the reoxidation treatment.

When a reduction treatment in hydrogen is adopted (see Table 2) at temperatures higher than 443 K the catalysts exhibited dehydrogenating activity depending on the degree of reduction. The Arrhenius plots for the series AZCu*x* : 4 with a given S_o, included catalysts reduced both in hydrogen and in alcohol. The agreement of the results in spite of the different reduction procedures indicates that the most important parameter governing the activity is the S_o. The apparent activation energies, E_a, were all around 67 ± 10 kJ/mol. Finally, the presence in the feed of 20–40 ppm of oxygen (2.4–4.8 μmol h^{-1} of O$_2$ with a flow of 0.83 scc s^{-1}), after a reducing treatment, lowered the activity with respect to the level shown in absence of oxygen.

DISCUSSION

1. *Active Site in the Dehydrogenation*

The activity of the matrices AZ*x* was studied previously (*9*) and it is sufficient to recall that they showed both dehydrogenating and dehydrating activity in the temperature range 450–540 K. The dehydrogenation activity was found to be a complex function of zinc content and calcination temperature. As an example, the AZ30 matrix at 483 K showed a selectivity toward dehydrogenation of 0.9 when calcined at 773 K for 3 h, and of 0.1 when calcined at 873 K for 24 h. Oxidizing and reducing treatments did not cause variations in either activities or E_a values in steady-state conditions. Hence, the selectivities remained unchanged also.

Water poisoning was found to be effective on the dehydrating activity only and acetone preadsorption gave a transitory poisoning effect on dehydrogenating activity, which was, however, restored to the standard level during t.o.s.

When copper is added, the dehydrogenation reaction is so improved that it is the only observable reaction at 350–440 K, which is a considerably lower range of temperature than that investigated for the dehydrogenation on AZ*x* matrices. In addition, the E_a values were strongly diminished to 67 ± 10 kJ/mol.

The results also show that oxidizing and reducing treatments have a marked influence on the dehydrogenating activity. The increase in dehydrogenating activity brought about by reducing treatments either in hydrogen or in reaction mixture was found to depend on the Cu(0) content. By contrast, the decrease in activity when oxygen is added should reflect the oxidation of some Cu(0).

The arguments previously discussed on the possible role of Cu^+ species for the system CuO/Al_2O_3 (*8*), allow us to deduce that the metallic copper sites only are responsible for the large differences in activity observed after the reducing pretreatments in the AZCu*x* : 4 systems irrespective of the zinc content. In fact, the relationship shown in Fig. 3 stresses that for each system a linear dependence of k_0 vs S_0 is observed. However, there are two important differences between AZCu and ACu:

(i) the slope of the linear dependence is larger for AZCu and the turnover frequency, TOF, at 383 K is 3×10^{-2} molecules per second per site with AZCu compared with 3×10^{-3} with ACu;

(ii) there is easier reducibility of AZCu both in hydrogen and in alcohol medium with respect to ACu.

The former point is considered after the suggestion of a possible reduction mechanism of the AZCu samples.

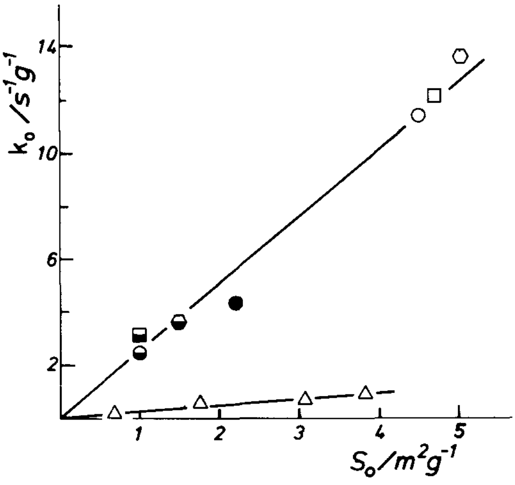

FIG. 3. Relationship between rate constant and Cu(0) surface area at 383 K. , AZCu1 : 4 (S_0 = 5.1 m^2 g^{-1}); □, AZCu5 : 4 (S_0 = 4.8 m^2 g^{-1}); ○, AZCu30 : 4 (S_0 = 4.5 m^2 g^{-1}); ○, AZCu30 : 4 (S_0 = 1.0 m^2 g^{-1}); , AZCu1 : 4 (S_0 = 1.5 m^2 g^{-1}); □, AZCu5 : 4 (S_0 = 1.0 m^2 g^{-1}); ●, AZCu30 : 4 (S_0 = 2.2 m^2 g^{-1}); △, ACu reduced samples (see Ref. (*8*)).

2. *Reduction Mechanism*

(*a*) *Reduction in hydrogen.* When H_2 is admitted in the pretreatment of AZCu samples, it is activated as $H^+ \cdots H^-$ pairs via a reverse spillover and then transferred from the oxidic components to the surface $Cu^{2+} \cdots O^{2-}$ pairs (*13*).

Recent work on H_2–D_2 equilibration on γ-Al_2O_3 and on ZnO/Al_2O_3 has shown that the presence of Zn^{2+} on the alumina, mainly as a defective surface zinc aluminate, is able to increase the equilibration velocity by at least one order of magnitude (*10*). In addition, the activity of pure ZnO and of ZnO/Al_2O_3 was quite similar; the same result was found comparing an AZ5 and an AZCu5 : 4, thus pointing out the inactivity of the reduced copper in the equilibration. These findings strongly suggested that , in addition to the heterolytic splitting of dihydrogen on ZnO via the complex ZnH ··· OH (*14*), other $Zn^{2+} \cdots O^{2-}$ containing arrays as existing in the defective zinc aluminate are also able to activate molecular hydrogen if the appropriate *cus* requisites are created. It turns out that a ZnO/Al_2O_3 surface, at a given temperature, is more populated by $H^+ \cdots H^-$ pairs than an alumina surface and, as a consequence, the H^- ions should be able to reduce Cu^{2+} to Cu(0) to a larger extent when $Zn^{2+} \cdots O^{2-}$ arrays are present on γ-Al_2O_3.

As a result, AZCu samples are reduced at temperatures as low as 473 K where ACu samples of comparable S_o needed temperatures somewhat higher (see Table 2). The possibility that, once some Cu(0) crystallites are nucleated, the reduction process might proceed also by hydrogen activation on Cu(0) cannot be completely ruled out. The published data on dihydrogen adsorption and dissociation on polycrystalline copper are often inconclusive and contradictory as a result of different experimental conditions. Mikovsky *et al.* (*15*) observed appreciable H_2–D_2 exchange at $T \gtrsim 590$ K, while Pritchard *et al.* (*16, 17*) claimed that even at room temperature dissociative hydrogen chemisorption appears to be clearly established and the low heat of adsorption might account for the contradictory reports on the behavior of copper in hydrogen chemisorption.

(*b*) *Reduction in alcohol.* When the reducing effect of the alcohol medium is being considered, it should be mentioned that a freshly prepared AZCu*x* : 4 was inactive in dehydrogenation in the temperature range 343–413 K. However, if the reaction temperature was raised to 433 K, the fresh sample progressively showed an increasing activity as a result of a reduction caused by the alcohol and a time of 100 min was necessary to reach the highest and most stable activity level. The investigation at lower temperatures allowed an activity level and an E_a value to be calculated, the latter coincident with all the other values found in different reduction conditions and the former in fairly good agreement with the measured S_o value. Recalling that a fresh ACu4 was not reduced in alcohol medium for time as long as 48 h at 434 K, the different behavior of the AZCu's would imply the presence of $Zn^{2+} \cdots O^{2-}$ pairs. In fact $Zn^{2+} \cdots O^{2-}$ pairs, at least in the zinc oxide phase, are able to adsorb dissociatively the 2-propanol giving stable surface isopropoxy species (*18, 19*). The stability and the evolution of this species depend on the crystallographic planes considered. The reaction sequence proposed was:

$$C_3H_7OH(g) \rightleftharpoons C_3H_7OH(ads) \rightleftharpoons C_3H_7O(ads) + H(ads) \quad (3)$$

$$C_3H_7O(ads) \rightarrow C_3H_6O(ads) + H(ads) \quad (4)$$

$$2H(ads) \rightleftharpoons H_2(g). \quad (5)$$

Because free zinc oxide was found only on the AZCu30 : 4 sample, the reducibility shown in alcohol medium by all the samples AZCu*x*:4 strongly suggests that the presence of $Zn^{2+} \cdots O^{2-}$ sites is sufficient for the hydrogen extraction. The recombination of hydrogen adatoms in reaction (5) would be responsible for the H_2 main desorption peak at 441 K on ZnO, but the t.p.d. experiments by Chadwick and O'Malley (*18*) clearly showed that H_2 started to desorb at $T \approx 400$ K. It seems reasonable to infer that the reduction of copper(II) may be realized both by migration of a form of hydride ions suggested in the H eliminations by Chadwick and O'Malley (*18*) and Waugh *et al.* (*20*) and by readsorption of the H_2 evolved in the *T* range 400–500 K. The latter hypothesis might explain why, at temperature lower than 413 K, no reduction was observed. Once Cu(0) is formed, the further reduction may proceed by the hydrogen formed in the alcohol dehydrogenation. In fact temperature-programmed reaction spectra for the adsorption of 2-propanol on Cu(110) have shown that H_2 and acetone start to desorb at 335 K (*21*). Then the Cu(0) formed can sustain the catalysis with contemporary reduction of copper sites by the H_2 produced in the reaction. The present results confirm that the decomposition of 2-propanol on Cu(0) can be effective at temperatures as low as 350 K.

In summary, the copper reduction either in H_2 or in alcohol needs to be started via H_2 activation by the zinc-containing oxidic component and then might continue via the formed Cu(0) sites (*21, 22*). However, the S_0 values, as outlined in Table 2, also depend on the history of the sample and the flushing procedure. As a result the AZCu samples are easy to reduce and there is more sintering of metallic copper at 693 K than with ACu. In fact, the flushing at 693 K in He tends to smooth out differences in S_0 for AZCu samples. These findings must be ascribed to a role of the different supports and the presence of a surface defective zinc aluminate in all the AZCu samples which favors the observed greater sintering of the metallic copper.

3. *Activity of Zero-Valent Copper in ACu and AZCu Systems*

The constancy of the E_a values found on ACu (*8*) and the present values of E_a for AZCu places, for each system, any observed difference in activity on the preexponential factor. Accordingly,

$$k_0 = n_s K_A (kT/V) \nu \{\exp(-\Delta H^*/RT) \exp(\Delta S^*/R)\}, \quad (6)$$

where k_0 is the rate constant per gram of catalyst, n_s is the number of Cu(0) atoms on the surface per gram of catalyst, K_A is the adsorption constant of 2-propanol, k the Boltzmann constant, T the absolute temperature, V the reactor volume, ν is the vibrational frequency of the activated complex responsible for product formation, ΔS^* and ΔH^* are the differences in entropy and enthalpy, respectively, between the activated complex and the reactants.

The observed higher activity per Cu(0) atom in AZCu with respect to ACu would imply a higher value of ΔS^* and/or a higher value of n_s for the AZCu. In the present reaction two Cu(0) sites are to be involved in the alkoxy decomposition leading to an adsorbed acetone and an adsorbed atomic hydrogen (possibly as H^-). If we assume that the alkoxy decomposition is the rate-limiting step (*18, 21*), the acetone and the dihydrogen desorption being fast, the population of the alkoxy species on Cu(0) sites would depend on the number of available sites and on the stability of the surface complex. Now the Cu(0) sites occupied by the hydrogen and acetone produced in the alkoxy decomposition may act as active sites if they are able to desorb acetone and molecular hydrogen quickly. It is likely that the presence of $Zn^{2+} \cdots O^{2-}$ arrays and/or of ZnO helps the hydrogen desorption just as a reverse reaction of the hydrogen adsorption and splitting. Additionally, the presence of the zinc-containing oxidic component might favor special surface unsaturation and/or specific crystal plane exposure of the Cu(0) crystallites (*23*); it is known that adsorption by single crystals has a pronounced crystal face dependence due to coordinative unsaturation and ensemble size of the adsorbing site (*24*). This might imply a lesser stability of the alkoxy-surface complex with a consequent higher activity of AZCu. However, the constancy of the TOF value for each system together with the variation of the crystallite dimension (D = 5–49 nm) would support the hypothesis that the 2-propanol decomposition would be a structure-insensitive reaction in the D range presently investigated.

Finally, the close parallel between propene hydrogenation (*11*) and the reaction investigated here must be stressed. In both cases, the presence of zinc in AZCu is responsible for a higher activity than with ACu, irrespective of the zinc content, and the velocity depends linearly on S_0. These findings confirm a role of the zinc in governing the adsorption–desorption equilibrium of molecular hydrogen in both reactions.

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