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Role of the support and of the preparation method for copper-based catalysts in the 2-propanol decomposition

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Pure copper oxide and mixed CuO/ZnO catalysts with different Cu:Zn atomic ratios were tested for the 2-propanol decomposition in order to investigate the nature of the active site and the role of the ZnO support. Fresh catalysts as well as catalysts oxidized in pure oxygen did not exhibit any catalytic activity below 373 K. When reduced either in pure hydrogen or in reaction mixture (helium plus alcohol) both copper oxide and mixed two-phase catalysts showed a dehydrogenating activity in the temperature range 323–423 K . The apparent activation energy for both reduced CuO and reduced CuO/ZnO catalysts was 60 ± 8 kJ mol^{-1}. The first order rate constants were found to be a linear function of the exposed zero-valent copper area . The comparison of Cu(0) turnover frequency in unsupported Cu(0) and in Cu(0)/ZnO samples did not show any synergic effect of the support. The role of the preparation method on the Cu(0) dispersion is also discussed.

Keywords: Copper catalyst; alcohol decomposition; synergic effect

1. Introduction

The role of the individual components of copper-based catalysts on the catalytic activity and on selectivity for the low temperature synthesis of methanol and the WGS reaction, is still currently debated [1–8]. In particular, the preparation methods, the oxidation state of copper and the possible synergic effect of the oxidic component ZnO, have attracted the attention of many investigators. As a result, a great deal of effort has been given to the catalyst characterization by means of bulk and surface techniques in order to detect possible chemical and physical interactions in binary and ternary systems re-

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sponsible for the catalytic behaviour [9–17]. With similar goals in mind, we have already investigated copper-based model systems CuO/Al_2O_3 and $CuO/ZnO/Al_2O_3$ with low copper content on the 2-propanol decomposition [18,19]. The most interesting results were: (i) a linear correlation was found to exist between dehydrogenation rate constants and zero-valent copper surface areas and (ii) the presence of zinc oxide and/or zinc aluminate increased by one order of magnitude the turnover frequency of Cu(0).

In the present work unsupported Cu(0) and supported Cu(0)/ZnO samples are considered in order to investigate the possible influence of ZnO on the activity of the Cu(0)/ZnO system during 2-propanol decomposition. In addition, the role of different preparation methods for the dispersion of zero-valent copper on the catalytic activity is also investigated.

2. Experimental

2.1. CATALYSTS

The catalysts have been prepared by coprecipitation of copper–zinc nitrate solutions either at variable pH, according to the method reported by Herman et al. [20] (catalysts A), or at $pH = 8$ according to Porta et al. [21] (catalysts B).

As a standard procedure the catalyst was treated in oxygen (99.5% purity) for 1 h at 623 K and then reduced by flowing either pure hydrogen or the reaction mixture (helium plus 2-propanol) at different temperatures (373–523 K) and times (12–100 h). The reduction treatment was long enough to ensure the complete reduction of the copper in all the samples. In addition it was possible to obtain different zero-valent copper surface area values, S_0, by varying both temperature and reduction time.

The Cu(0) surface titration was usually performed after catalysis by N_2O dissociative chemisorption at room temperature according to Osinga et al. [22]. A value of 0.176 ccNTP of N_2 per square meter of Cu(0), corresponding to 1.47×10^{19} Cu(0) atoms was assumed [23]. The S_0 values were checked before and after catalysis.

The dispersion, $D_{Cu(0)}$, defined as the ratio between the surface zero-valent copper and the total zero-valent copper content, was calculated by considering a complete reduction of the copper oxide.

2.2. CATALYSIS

The catalytic experiments were carried out in the flow system previously described [24]. The sample was maintained at a given temperature in the reducing medium for a variable time until the total amount of the water produced during the reduction process ensured the copper oxide reduction being completed. The reduced catalysts were tested for 2-propanol decomposition, at temperatures lower than those used in the reduction procedure in order to avoid Cu(0) surface area variation due to the reaction.

The employed kinetic treatment assumes a first order reaction whose integral form was derived in condition of ideal displacement,

$$k = (1/\tau)\{[(2+R)a/P] \ln a/(a-x) - x/P\}, \tag{1}$$

where k is the experimental rate constant for dehydrogenation (moles/time · cat.mass · pressure); τ = contact time = w/F (cat. mass · time/feed mass); R = moles of helium in the feed/moles of alcohol in the feed; a = moles of alcohol in the feed/feed mass; x = moles of acetone/feed mass. Taking into account that the total pressure P varied slightly in different experiments (1.3–1.5 atm), the calculated value of $(2+R)a/P$ was practically constant and equal to 0.12 mol g^{-1} atm^{-1}.

3. Results

3.1. CATALYSTS

Most of the samples investigated are part of the system previously described for the propene hydrogenation and details of their characterization can be found in ref. [25]. Details of the characterization of the samples Cu : Zn 5 : 95 B and 67 : 33 B are in refs. [26,27]. Here it is sufficient to recall that the two different preparation procedures give rise to well distinct precursors whose calcination at 623 K in air produces in all cases but one (100 : 0) a biphasic system of copper oxide plus zinc oxide and that for the mixed oxides obtained from monophasic precursors (preparation A), the surface composition reflected bulk composition as monitored by XPS spectra [26–28]. The role of the precursors on the interdispersion of CuO and ZnO and on their mutual interaction, has already been discussed [28]. One of the important results is that for samples B the BET areas of the calcined samples are usually much higher and the CuO particle sizes, d_{CuO}, measured by X-ray line broadening [25,27] lower.

Table 1 summarizes some of the features of the catalysts investigated in the 2-propanol decomposition, whereas the S_0 values and the reduction conditions are reported in table 2, toghether with the $D_{\mathrm{Cu(0)}}$ values calculated as described in the experimental section. It must be noted that, after the complete reduction of a catalyst at a given temperature, its further permanence in the reducing medium always lowers the Cu(0) surface area as a result of the metallic copper sintering, whereas the S_0 values measured here before and after catalysis were identical.

Table 1
Catalysts investigated and their main features

Sample CuO/ZnO	Cu (wt%)	Zn (wt%)	d_{CuO} (nm)	d_{ZnO} (nm)	S.A. ($m^2\ g^{-1}$)	Ref.
100:0 A	79.8		80		2.4	[25]
100:0 B	79.8		105		47.8	[25]
5:95 A	3.9	74.5		20	39.2	[26]
5:95 B	3.9	74.4			73.0	[25]
30:70 A	25.9	55.9	6	13	43.5	[25]
67:33 A	51.4	24.8	45	100	7.0	[25]
67:33 B	46.5	22.7	6.5	10	74.0	[27]

3.2. CATALYSIS

3.2.1. *Pure oxides, ZnO and CuO*

Pure zinc oxide both oxidized and reduced was active only at temperatures higher than 490 K. The dehydrogenation was the unique reaction observed in

Table 2
Reduction conditions, catalytic activity at 383 K and zero-valent copper surface areas of reduced catalysts

Sample CuO/ZnO	T_{red} (K)	S_0 ($m^2\ g^{-1}$)	$k^{383} \times 10^5$ ($mol\ s^{-1}\ g^{-1}\ atm^{-1}$)	$D_{Cu(0)}$ (%)
100:0 A	alc, 423	4.1	6.2	0.8
100:0 A	H_2, 448	4.4	8.0	0.9
100:0 B	alc, 373	0.7	2.2	0.1
100:0 B	alc, 373	5.9	8.5	1.1
100:0 B	alc, 383	4.3	5.9	0.8
100:0 B	alc, 402	3.4	3.9	0.7
5:95 A	H_2, 373	1.1	1.4	4.4
5:95 B	alc, 383	1.4	2.7	5.6
5:95 B	H_2 3%, 373	8.0	12.0	32.0
5:95 B	alc, 402	2.2	4.4	8.9
5:95 B	alc, 426	2.1	4.5	8.4
30:70 A	alc, 473	9.2	11.5	5.5
67:33 A	alc, 423	4.5	6.2	1.4
67:33 B	alc, 373	19.5	31.0	6.5
67:33 B	alc, 383	15.0	22.0	5.9
67:33 B	alc, 403	12.0	17.0	4.0
67:33 B	alc, 403	16.8	23.0	5.7
67:33 B	alc, 523	10.0	11.0	3.2

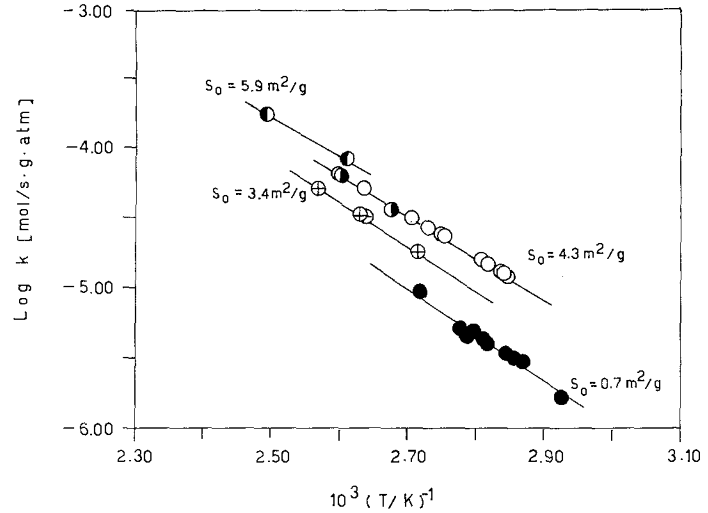

Fig. 1. Arrhenius plots for unsupported Cu(0) (from reduced CuO) with different S_0 (see table 2).

stationary conditions and the apparent activation energy, E_a, was calculated to be 126 ± 10 kJ mol^{-1} [24].

The oxidized copper oxide, by contrast, was inactive below ≈ 373 K. If, however, it was prereduced either in hydrogen or in 2-propanol medium, an appreciable dehydrogenation activity obtained, its value depending on the reduction treatment. The temperature range usually explored for catalysis was 323–423 K, i.e. much lower than that needed for monitoring 2-propanol decomposition on ZnO. Only acetone and hydrogen were found and, at a given temperature, their yield was constant for a period as long as 72 h. The results of a random investigation of the decomposition at different temperatures were exceptionally reproducible. The E_a value was definitely lower than that measured on ZnO and calculated to be 60 ± 8 kJ mol^{-1}.

The validity of the first order kinetic law assumed for the data treatment was checked by testing eq. (1) at different values of τ. For contact times lower than 280 s, i.e. for catalyst mass of 0.150–0.250 g and gas flow of 2.0–4.5 ccs^{-1}, no deviation from linearity was found. This finding, together with the large effect of the reduction on the activity points to a true chemical control of the reaction. As an example, in fig. 1 the Arrhenius plots for unsupported Cu(0) (from reduced CuO) with different zero-valent copper surface areas are reported.

3.2.2. *Mixed oxides, CuO / ZnO*

Several portions of catalysts with different Cu : Zn ratio and obtained from different precursors were investigated in the temperature range 323–423 K. As for pure copper oxide they were usually reduced at a given temperature and then subjected to catalysis at temperatures lower than that of reduction. The

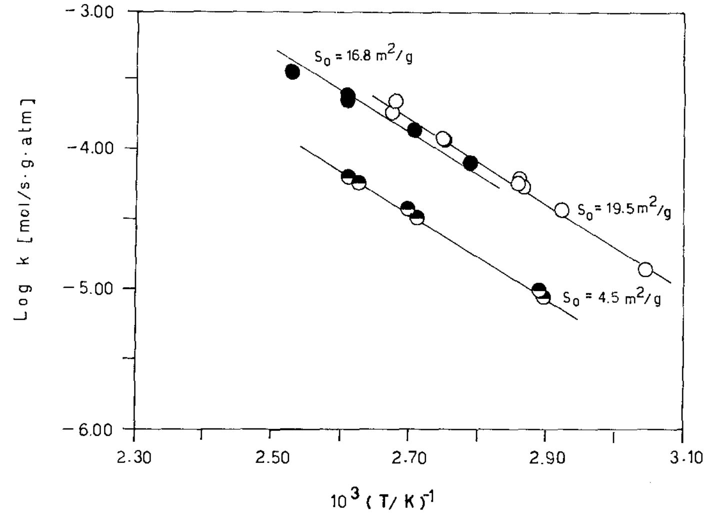

Fig. 2. Arrhenius plots for reduced 67:33 A (o) and 67:33 B (•, o) with different S_0 (see table 2).

2-propanol decomposition gave acetone and hydrogen only and the activity levels were dependent on the reduction treatment. The E_a values were all around 60 ± 8 kJ mol^{-1} as for unsupported Cu(0). As a representative example in fig. 2 the Arrhenius plots for reduced 67:33 A and 67:33 B samples are reported. For comparison, the rate constants at 383 K, k^{383}, have been assumed as a measure of the activity. In table 2 their values have been reported toghether with the S_0 values.

4. Discussion

4.1. ACTIVE SITE IN THE DEHYDROGENATION

The activities of ZnO and CuO have been widely investigated. In fact one of the factors which have an important influence upon the selectivity of metal oxides surfaces for dehydrogenation has been singled out in the collective-electron factor related to the position of the Fermi level at the surface of semiconducting metal oxide.

In the context of mechanisms where charge transfer between surface and alcohol related species may play a crucial role, semiconducting oxides as n-type ZnO and p-type CuO have been considered as classical examples [29–32]. For zinc oxide, a detailed work, mainly by TPD, has been published on the kinetic and the mechanism of secondary alcohol decomposition [33–35] and it is generally accepted that the 2-propanol decomposition is a structure-sensitive reaction [36]. It is sufficient to recall here that ZnO showed an appreciable dehydrogenation activity only at temperatures between 490 and 560 K [24]. As far as the copper oxide is concerned, there is agreement that reduced copper species are involved in the 2-propanol dehydrogenation and that the alcohol medium has a marked effect on reducing the CuO surface. However, some marked discrepancies about the nature of the active center are worthy of mention. Volta et al. [37] found that, once reduced, CuO increased its activity and suggested as a possible center for the dehydrogenation a mixed valence site. Their rate constants at 406 K, however, are two orders of magnitude lower than the present ones as a result of a possible oxidation of the surface and/or of incomplete precursor decomposition. Cunningham et al. [38] found that the 2-propanol decomposition obeyed a first order kinetic law after an induction period on oxidized CuO. After that, the activities of initially oxidized CuO and prereduced CuO were coincident. From their data a turnover frequency of 0.2 molecules per site per second was calculated at 475 K whereas we found a value of 0.8 at 383 K on our Cu(0). The discrepancy may be attributed to the higher temperature range explored by Cunningham, while the possibility of surface poisoning by products of side reaction cannot be ruled out. In fact, a large burst of acetone is reported to occur in that range of temperature [39]. In a subsequent work [40] they claimed to have found a synergic effect between metallic copper and copper oxides and identified the active center in the couple Cu(0)–CuO, acting with a long range mechanism. They based their model on experiments of 2-propanol decomposition on a physical mixture of Cu(0) and CuO. However, their results might be explained just as well as being due to the reduction by 2-propanol of CuO to Cu(0), this last species acting as dehydrogenation center. In addition, from their dependence of log conv% versus $1/T$, an E_a of about 50 kJ mol^{-1} can be calculated for CuO prereduced in H_2 at 673 K; such a value, taking into account the different data treatment , is not too different from the present value of 60 kJ mol^{-1}.

In the present work CuO has been completely reduced and separate experiments in our lab [41] have demonstrated that a time of 1 h was sufficient to reduce completely CuO to zero-valent copper at 473 K. Of course we are well aware that traces of oxygen are always present. The nature of the Cu–O site formed on oxygen adsorption and its role in the dehydrogenation activity has been discussed in depth by Chinchen et al. [42] and by Bowker and Pudney [43]. The former concluded that the compound formed by adsorption of oxygen on copper metal for $\theta_{\mathrm{O_{ads}}} < 0.5$ is some 110 kJ mol^{-1} more stable than cuprous oxide. The latter showed that oxygen predosed on Cu(110) face is able to increase the sticking coefficient of 2-propanol and, hence, the amount of alkoxy species formed on the surface. In any case the copper involved in the Cu–O sites, apart from its oxidation state, seems to partecipate only in the oxidative dehydrogenation, when water is produced.

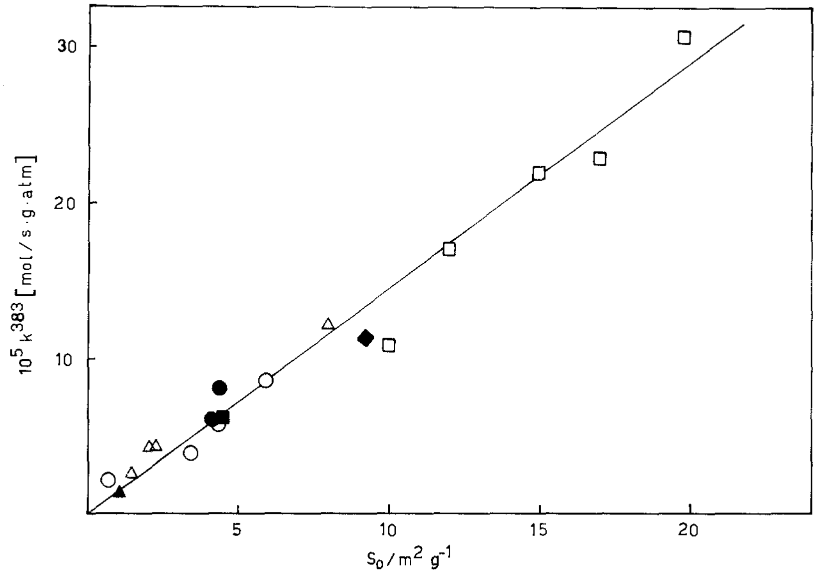

Fig. 3. Activity of unsupported Cu(0) and of supported Cu(0)/ZnO catalysts as a function of S_0, at 383 K: (●) 100:0 A; (○) 100:0 B; (▲) 5:95 A; (△) 5:95 B; (◆) 30:70 A; (■) 67:33 A; (□) 67:33 B.

In the present experiments water was found only during the reduction treatments, acetone and hydrogen being the sole products in sustained catalysis conditions. In addition, the agreement in S_0 values as measured before and after catalysis makes us confident that the oxygen coverage is quite negligible. We conclude that the uncertainty about the zero-valent copper surface areas in most of the experiments quoted in literature does not allow the identification of the active site. Here, by contrast, because the constancy of E_a places any observed difference in activity on the preexponential factor only, it is possible to identify the active centres as the Cu(0) species. In fact

$$k = (n_s K_A / L)\nu \exp(-\Delta H^*/RT) \exp(\Delta S^*/R), \tag{2}$$

where k is the rate constant per gram of calalyst, n_s is the number of active centres on the surface per gram of catalyst, K_A is the adsorption constant of 2-propanol, L the Avogadro number, T the absolute temperature, ν is the vibrational frequency of the activated complex responsible for products formation, ΔH^* and ΔS^* are the differences in enthalpy and in entropy repectively between the activated complex and the reactant. Hence k is directly proportional to n_s only. From table 2 and fig. 3, the ratio k^{383}/S_0 is satisfactorily constant with the possible exception for the sample having the lowest S_0 value (0.7 m^2 g^{-1}, prereduced in alcohol at 373 K for 120 h) where, however, a large error in the measure may exist.

Finally, it should be mentioned that the kinetic law here observed is in agreement with the finding of Bowker and Madix [44] who proposed the αC–H bond breakage of the adsorbed alkoxy species as the rds of the dehydrogenation.

4.2. ACTIVITY OF CuO/ZnO SAMPLES: ROLE OF ZnO

Several roles have been proposed in literature for ZnO in hydrogenation–dehydrogenation reactions [45–49]. These can be summarized as

(i) stabilization of copper(I) by solid solution;

(ii) different reaction mechanism operating on unsupported Cu(0) and ZnO supported Cu(0);

(iii) creation of sites at the border line Cu(0)–ZnO;

(iv) junction effect responsible of a drastic increase in the number of the oxide defects;

(v) stabilization of high index crystallographic planes of Cu(0) by ZnO.

The presence of Cu(I) in ZnO is still matter of debate [10,11,45,46]. We have proved on reduced CuO/Al_2O_3 samples that the Cu(I) does not participate in the 2-propanol decomposition [18].

With respect to a difference in the reaction mechanism operating on pure Cu(0) and ZnO supported Cu(0), it appears that the reaction pathway on copper alone is similar to that on zinc oxide, E_a being lower [24,35,40].

The creation of new sites at the region contact between Cu(0) and ZnO (synergic effect), has been disregarded by Bowker et al. [47] in methanol synthesis. De Rossi and Ferraris, instead, on the samples presently investigated, found a synergic effect in propene hydrogenation [25]. However, this effect was monitored only on severe dehydration of the oxide component at 723 K, whereas, when the samples were dehydrated at 473 K, a linear dependence between rate constants and S_0 was obtained. The junction effect, even found an attractive theory well accounting for the activity of systems like copper/thoria in the methanol synthesis, unfortunately cannot be considered as an unifying theory as proposed by Frost [48], and it is probably operative only when the energies involved in the reaction on the separate components are similar.

The stabilization of high index crystallographic planes brought about by ZnO with respect to Cu(0) [16], is controversial when chemical reactions are considered, because of the reconstruction of the surface in reaction medium.

Finally, the hypothesis that the O^{2-} anions of the oxidic component would provide a better stabilization of the surface population of alkoxy species as proposed by Chan and Griffin for methanol decomposition on Cu/ZnO oriented thin films [49], seems not to be valid in, the present case; this may be due to the lower gas phase acidity of methanol in comparison with that of 2-propanol [50]. As a result, the present investigation shows that for the supported Cu(0)/ZnO system the activity is proportional to S_0 (table 2). Hence the only active species for the dehydrogenation is still the surface zero-valent copper. In addition, from fig. 3 clearly appears that unsupported Cu(0) and Cu(0)/ZnO samples have the same dependence of k^{383} versus S_0. It is concluded that the ZnO support does not play any role on the catalytic activity of Cu(0) for the reasons outlined above. Moreover, either the preparation method or the dispersion are not affecting the activity at the Cu(0) site.

However, the possibility of having high Cu(0) surface areas in the 67:33 B sample in comparison with unsupported Cu(0), points out to a structural promotion effect of ZnO, i.e. the effect to increase or to maintain the number of active sites without any influence on their individual activity. In fact ZnO would be responsible of a better dispersion and of smaller dimensions of Cu(0) particles.

In conclusion, we have shown that:

(i) Reduced copper oxide and reduced copper oxide supported on ZnO have the same turnover frequency in the 2- propanol dehydrogenation.

(ii) The active species has been identified in Cu(0) species with no effect of oxidized forms of copper.

(iii) The unique role of the support is that of providing a better dispersion of the active sites, without any interference either in the activity at the Cu(0) site or in the reaction mechanism.

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