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Exposure of Metallic Copper Surface on $Cu-Al_2O_3$-Carbon Catalysts*

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The bifunctional nature of $Cu-Al_2O_3$-on-carbon catalysts, used in the direct catalytic conversion of ethanol to ethyl acetate, prompted an examination of the dispersion of Cu on the composite catalyst. For this, the N_2O-method of Osinga *et al.* for estimation of bare metallic copper surface on composite copper catalysts has been adapted for use on a gravimetric adsorption unit and then applied to several promoted and supported copper catalysts. For catalysts with Cu/Al atomic ratio 0.8 to 26, all reduced at 300°C, the copper surface is only 1–8% of the total surface of 500–560 m^2/g, but 50–430 m^2/g Cu. The maximum Cu dispersion is obtained for the catalyst with $Cu/Al = 6$, which is also one of the best catalysts for the esterification reaction. The Cu surface rapidly increases from 1 to 10% of the total surface as the temperature of reduction of the catalyst is raised from 100 to 400°C. On a low area (32 m^2/g) asbestos carrier, a relatively higher Cu coverage of 55% can be obtained, but the activity of this catalyst is very poor. On use in the esterification reaction, the carbon-supported catalyst gets a more reddish brown copper color, however there is no increase in the exposed copper area.

X-ray microscan studies of the catalyst prove that the copper sites on the surface (in an $1\,\mu$-thick layer) are mostly in close association with the Al sites of the alumina promoter. Results from catalyst testing show that these Cu-Al sites or junctions are necessary to catalyze the condensation to ester of the acetaldehyde formed in the primary dehydrogenation of ethanol over copper. The microscan studies on the same spot on one and the same catalyst particle indicate that the distribution of Cu and Al in the $1\,\mu$-thick layer on the catalyst surface does undergo some alterations when the catalyst is reduced at 300°C and subsequently used in the esterification reaction at 275°C. The exact nature of these alterations is still not clear.

INTRODUCTION

The direct catalytic conversion of ethanol to ethyl acetate over promoted and supported copper catalysts has been studied in detail by Dolgov and coworkers (*1*, *2*):

$$2\,C_2H_5OH = 2\,CH_3CHO + 2\,H_2 \qquad (1)$$
$$2\,CH_3CHO = CH_3COOC_2H_5 \qquad (2)$$
$$2\,C_2H_5OH = CH_3COOC_2H_5 + 2\,H_2 \qquad (3)$$

In experiments with copper-alumina catalysts supported on active carbon as carrier, we have observed (*3*, *4*) the strong bifunctional nature of this catalyst for the direct esterification: the dehydrogenation of ethanol (reaction 1) proceeds on copper, while the subsequent condensation of acetaldehyde to the ester (reaction 2) takes place only on the copper-alumina sites or junctions. Practically no ester is obtained when copper or alumina alone is used as a catalyst, or when they are used separately in two reactors connected in series, but even a mechanical mixture of copper and alumina gives a good yield of the ester. This has led us to a study of the dispersion of copper on the composite catalyst for

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which we have resorted to the N_2O-method of Osinga *et al.* (*5*) for estimation of the bare metallic copper surface. The X-ray microscan (also called electron microprobe) technique has been applied for one sample of the catalyst to follow the distribution of copper, aluminum, and carbon in an 1 μ-thick layer of the catalyst surface, and to see the changes, if any, in this distribution (in one and the same part of a single catalyst particle) during the reduction and subsequent use of the catalyst in the direct esterification of ethanol at 275°C. The results obtained from these two studies are given in this paper.

EXPERIMENTAL

Specific copper surface area measurements. The method of Osinga *et al.* (*5*) is based on the reaction of N_2O with copper at room temperature:

$$N_2O + Cu = CuO + N_2.$$

Below 100°C the reaction is confined to copper atoms at the surface, whereas above this temperature the metal is attacked in depth. The amount of nitrogen formed was determined by freezing out the excess N_2O at liquid nitrogen temperature in a cold finger for 2 hr and measuring the residual nitrogen pressure in a volumetric adsorption apparatus. In the present work this method was adapted for use on a gravimetric adsorption unit as follows: Gas from a commercial N_2O cylinder was passed through an alkaline pyrogallol bubbler to remove traces of oxygen, dried over anhydrous calcium sulfate and silica gel, and filled into evacuated 3-liter glass bulbs connected to the manifold of a McBain sorption balance. The quartz spiral of the balance could take a maximum load of 5 g and its elongation was measured with a precision cathetometer correct to 0.01 mm, corresponding to 0.25 mg. About 2 g of catalyst was taken in the basket of the sorption balance. It was evacuated at 300°C, reduced in a stream of dry oxygen-free hydrogen at 300°C for 6 hr, again evacuated at 300°C, and finally cooled to room temperature in vacuum. Then N_2O was admitted to the balance part to get a pressure of 20 cm Hg. After the catalyst had attained steady weight, it was evacuated at room temperature to remove all unreacted and physically adsorbed N_2O and the product N_2. The weight increase (Δw) of the catalyst over its weight in the reduced and evacuated state gave the oxygen uptake by the exposed bare copper surface of the composite catalyst. A sample containing alumina deposited on the carrier, but without any copper, was subjected to exactly identical treatment as for the above catalyst. After exposure to N_2O and evacuation at room temperature there was no increase in weight of the sample. This showed that the promoter alumina and the carrier carbon did not contribute anything to the weight increase Δw.

For the calculation of the specific copper surface area the value of 0.176 ml (NTP) N_2O/m^2, found by Osinga *et al.* (*5*) was used. In the gravimetric method used in the present work the final weight increase Δw is due to the oxygen uptake by the copper from its reaction with N_2O. Hence 0.176 ml of N_2O will correspond to a weight increase due to oxygen uptake of 0.126 mg, or 1 mg in the weight increase will correspond to 8 m^2 of the copper surface.

The total (BET) surface area of the catalyst samples were determined in the McBain sorption balance by benzene adsorption from a benzene-nitrogen flow system (*6*). Surface areas of active carbons determined by benzene adsorption are sufficiently reliable (*7*, *8*) and comparable (*9*) with those obtained from nitrogen adsorption in a conventional BET volumetric apparatus.* In the present work also, occasional checks with nitrogen adsorption at 77°K gave surface area values agreeing with the benzene areas within 5–10%. The catalyst samples were given the same pretreatment as for the N_2O studies, namely evacuation for 3 hr, reduction for 6 hr, and again evacuation for 3 hr, all oper-

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* However, the evaluation of BET surface area from Type I adsorption isotherms, usually obtained for activated charcoal, is controversial (cf. Chapter 4 in Ref. *12*). It can perhaps better be regarded as an apparent surface area, good enough for purposes of comparison.

ations being carried out at 300°C unless otherwise specified.

X-ray microscan studies. The X-ray microscan unit gives a local chemical analysis by making use of a finely focused electron beam to excite characteristic X-radiation from a small volume at the surface of a solid specimen. The wavelength and intensity of the characteristic X-ray lines are used to determine the elements which are present in the target and their relative mass concentrations. At the present time, analysis can be made for all elements of atomic number greater than 5 (boron). The spatial resolution of the method of analysis is about 2–3 μ, the sensitivity ranges from 1 in 10^4 to 10^3, and the relative accuracy is 1–2% if the concentration is greater than a few per cent. Details of the microscan apparatus have been given by Wittry (*10*) and the versatility of its applications has recently been reviewed by von Rosenstiel and de Lange (*11*).

The present X-ray microscan studies were made in the Department of Mechanical Engineering, Twente Technological University, Enschede, The Netherlands, on an apparatus made by Applied Research Laboratory, Palo Alto, California. The catalyst examined was Cu-20% Al_2O_3 on carbon (No. 6 of Table 1). The volume element of the catalyst surface examined was $500\,\mu \times 450\,\mu \times 1\,\mu$ depth or $15\,\mu \times 12\,\mu \times 1\,\mu$ depth, depending on magnification. The scanning was done separately for C, Al, and Cu. The scan for oxygen was too weak to photograph.

In our catalyst testing work it was repeatedly observed that the dull brown color of the reduced catalyst turned much brighter after using it in the esterification of ethanol at 250–300°C. To check if any appreciable surface migration of alumina or copper occurred during reduction or in the catalytic reaction, the microscan study was also carried out on one corner of one catalyst particle (a) unreduced, (b) after reduction in hydrogen at 300°C for 3 hr, and (c) after using (b) as catalyst for the reaction at 275°C for 3 hr. By making an orienting crossline on the aluminumdisc sample mount, it was possible to repeatedly

TABLE 1

Metallic Copper Surface Area and Total Surface Area of Catalysts

No.	Catalyst	At. ratio Cu/Al	Surface area (m²/g catalyst)	
			Copper[a]	Total
1	Carbon (carrier)		0	622
2	Cu on carbon		26	546
3	Cu-3%[b] Al_2O_3 on carbon	26	23	528
4	Cu-6% "	13	34	500
5	Cu-12% "	6	43	558
6	Cu-20% "	3.2	28	560
7	Cu-40% "	1.2	23	474
8	Cu-50% "	0.8	5	525
9	Cu-20% Al_2O_3-2% Cr_2O_3 on carbon	3.2	30	555
10	Cu-20% Al_2O_3 on carbon, vacuum impregnation	3.2	26	545
11	Cu-20% Al_2O_3 on asbestos	3.2	18	32
12	Cu-20% Al_2O_3 on carbon, reduced at	100°C	5	570
13	" "	200°	10	598
14	" "	300°	28	560
15	" "	400°	63	625

[a] Since the copper content in all the catalysts is the same and equal to 10%, multiplying the values in this column by 10 gives the specific copper surface area in m²/g Cu.

[b] Based on the weight of Cu + Al_2O_3, excluding the weight of the carrier. Thus 100 g of this catalyst on reduction at 300°C will contain 10 g Cu, 0.31 g Al_2O_3, and the rest the carrier carbon.

bring the sample to exactly identical position in the vacuum chamber of the microscan unit. Thus scanning could be done on the same small spot on one and the same catalyst particle and hence a direct comparison could be made of the microscan photographs obtained for the three cases.

Preparation of catalysts. A series of catalysts with the same copper content (10% Cu), but with varying alumina content (3–50% of the weight of $Cu + Al_2O_3$ in the final reduced catalyst), were prepared with coconut shell charcoal as carrier. The atomic ratio Cu/Al was thus varied from 26 to 0.8 for catalysts No. 3 to 8 in Table 1.

The catalysts were precipitated from a mixture of copper acetate and aluminum nitrate solutions in the presence of the carbon (2–3 mm size, kept in boiling water for 1 hr to expel all air). The precipitate was washed free of alkali and of nitrate ions and dried with constant stirring to get a uniform coating of the precipitate on the carbon particles. The separation of the catalyst ingredients from the carrier particles in the form of fines or dust in subsequent handling and experimental studies was negligible. The chemicals used in catalyst preparation were all of BDH Analar grade. The activated coconut shell charcoal used was Hycol CSG, produced and marketed by Regional Research Laboratory, Hyderabad.

RESULTS AND DISCUSSION

The results of total and specific copper surface areas are given in Table 1. The total surface areas of carbon-supported catalysts are 500–560 m^2/g while that of the support alone is 622 m^2/g. The copper surface areas for the above catalysts are all below 45 m^2/g catalyst, or 450 m^2/g Cu. Hence, the metal contributes only a small part (roughly 5–8%) of the total surface area. Prior evacuation of the carbon followed by flooding it (while still under vacuum) with a mixture of copper acetate and aluminum nitrate solutions and subsequent precipitation of the hydroxides has also been tried. The copper surface is still only 27 m^2/g catalyst, showing that the dispersion is not improved by this vacuum impregnation.

For carbon-supported catalysts with increasing promoter content (3–50% Al_2O_3) the copper surface area shows a maximum at 12% Al_2O_3. The addition of 2% Cr_2O_3 to Cu-20% Al_2O_3 does not improve the dispersion of copper to any appreciable extent. The use of asbestos, instead of carbon, as the carrier for the catalyst yields a relatively high copper surface area compared to the low total surface area of only 32 m^2/g.

Assuming that the copper is composed of cubes or spheres, all of the same size, a mean particle size (l) of copper in the catalyst can be calculated (*12*) from the copper surface area (S) values using the relation $l = 6/\rho S$, where ρ is the density of copper. For catalyst No. 5 with the maximum specific copper surface area of 430 m^2/g Cu, $l = 16$ Å, which is close to the mean pore radius (~ 15 Å) of the active carbon carrier.** Catalyst No. 8 with 50 m^2/g Cu has a value $l = 133$ Å.

Recently Erofeev *et al.* (*13*) studied the catalytic activity of copper on several oxide carriers in the dehydrogenation of cyclohexane and the ESR spectra of these catalysts. They have concluded that copper does not penetrate into deep layers of the carrier lattice, instead it concentrates at cation sites on the surface.

Testing of the catalysts in Table 1 for the direct esterification of ethanol at 275°C has shown (*3, 4*) that catalysts with 12% and 20% Al_2O_3 (No. 5 and 6) give the best yield of ester and are almost equally good, although the latter has a sustained activity over a longer period of testing. This was the reason for choosing catalyst No. 6 for the reduction experiments (No. 12–15 in Table 1) as also for study with X-ray microscan technique. The asbestos-supported catalyst was very poor in activity.

Different portions of the Cu-20% Al_2O_3 catalyst were evacuated at 300° for 3 hr,

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** The mean pore radius $\bar{r}$ was calculated from $\bar{r} = 2V/S$, where V is the volume of adsorbate at $p/p_0 = 0.98$. The adsorption of nitrogen at −196°C gave the pore volume V of 0.46 ml.

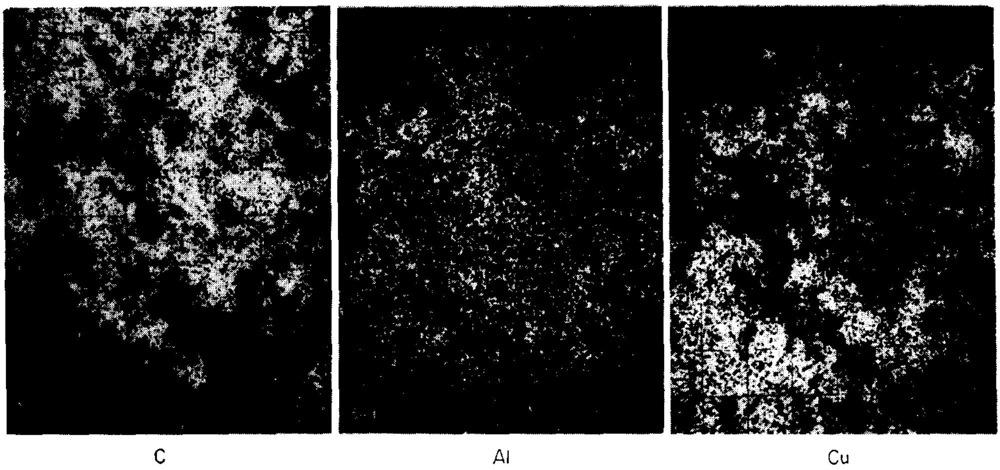

FIG. 1. X-ray microscan photographs of reduced Cu-Al_2O_3-carbon catalyst (No. 6 of Table 1). The part scanned here is 500 μ × 400 μ × 1 μ depth. There is close similarity between the Al and Cu photos, while the carbon photo is almost a negative of the Cu photo. For a magnified view see Fig. 2.

reduced at 100, 200, 300, or 400° for 6 hr, evacuated at the same temperature for a few minutes and finally at 300° for 3 hr. The copper surface areas of these samples are found to increase almost exponentially with increase in reduction temperature. Obviously, reduction at higher temperature exposes more copper surface on the catalyst. But the yield of ethyl acetate decreases if the catalyst is reduced above 300°C.

The X-ray microscan photos (of which Figs. 1 and 2 are two typical examples) show the separate pattern of distribution of the carbon of the catalyst carrier, Al of the alumina promoter and copper (both reduced and unreduced) in a 1 μ-thick layer of the catalyst surface examined at two different magnifications. A comparison of the Al and Cu photographs reveals that the Cu sites are lying mostly at/over/under the Al sites or in close proximity to them. These Al-Cu or Al_2O_3-Cu sites or contact junctions are necessary to catalyze the condensation of acetaldehyde to the ester (reaction 2), as mentioned at the beginning of this paper.

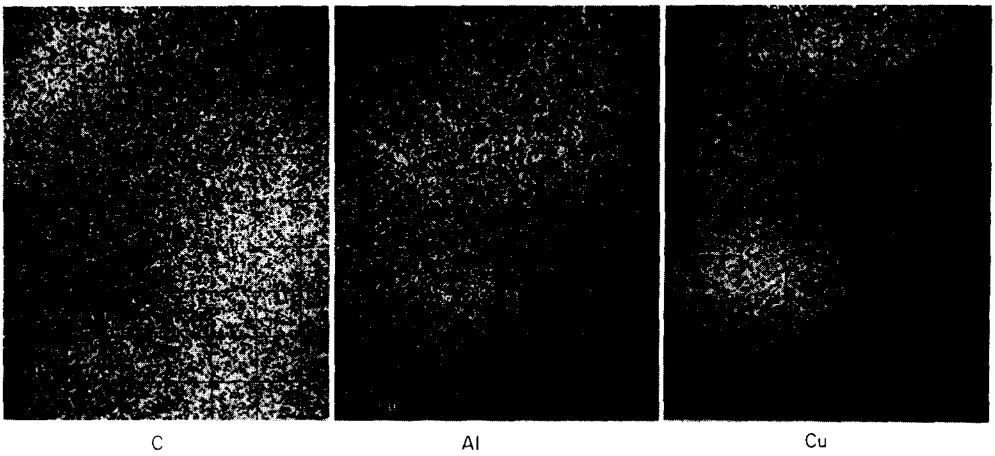

FIG. 2. X-ray microscan photographs of reduced catalyst No. 6. The part scanned here is 15 μ × 12 μ × 1 μ depth. See remarks for Fig. 1.

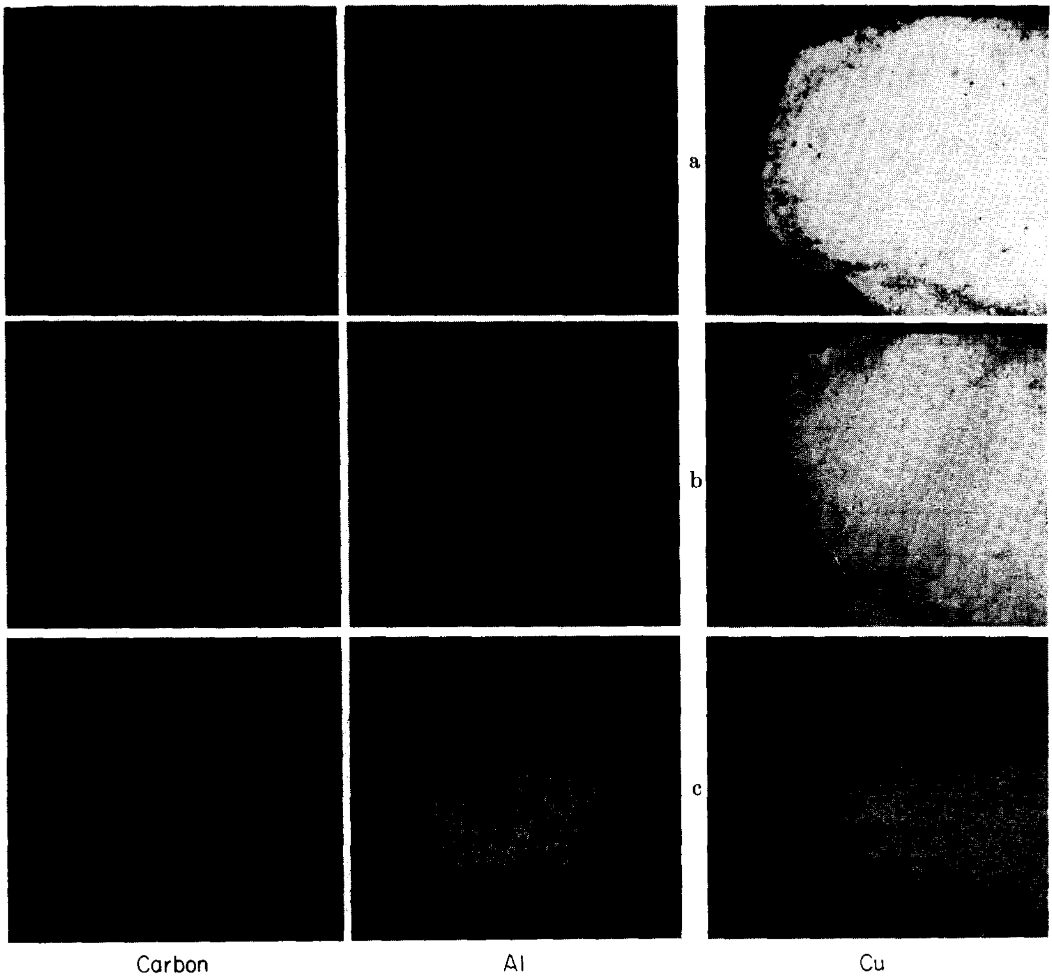

FIG. 3. X-ray microscan photographs of one corner on a single catalyst (No. 6) particle: (a) before reduction, (b) after reduction, (c) after using (b) in esterification of ethanol at 275°C. Same magnification as in Fig. 1. Change in intensity of the oscilloscope trace has caused the difference in brightness of the white patches in (a), (b), and (c). Some alterations in the locations of the white patches are still noticeable.

It is interesting that the freshly reduced catalyst is dull brown in color, while it turns into the typical bright reddish brown copper color after use in the esterification reaction. Also, the glass wall of the reactor often gets a fine copper film or mirror deposited on it. It was suspected that during the reaction either more copper diffuses to the catalyst surface from the interior, or a greater degree of reduction of CuO to Cu is caused by the nascent hydrogen formed on the surface during the dehydrogenation reaction. However, it has been repeatedly found that the specific copper surface values determined by the N$_2$O method, are the same for the catalyst before and after use in the reaction. Hence there is neither any appreciable diffusion of fresh copper to the surface nor a greater degree of reduction during the reaction. The X-ray microscan photos of a single catalyst particle (Fig. 3) shows some minor alterations in the catalyst after its reduction and after the esterification reaction over it. The exact nature of these alterations will be clear only from a more detailed study. They may perhaps be facilitated by any volatile copper-organic compound formed under reaction conditions, which may also be responsible for the copper film or mirror formed on the reactor walls.

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