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Structure and activity of a Raney copper film catalyst

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A Raney copper film obtained from a Cu–Al alloy deposited by evaporation on a steel plate was found to behave as a copper on alumina catalyst. Contrary to what is found when the Raney is prepared directly from the alloy, prereduction with CO caused an increase in the catalytic activity for CO oxidation.

Keywords: Raney copper film catalyst; Raney film catalyst; catalytic activity for CO oxidation

1. Introduction

In a previous report [1], we have discussed the possible development of an all-metallic monolith catalyst formed by coating the metal monolith starting material (e.g., the unfolded foil) with the precursor alloy of a Raney catalyst. Such a catalyst system appears to have relevant advantages with respect to the conventional ceramic supported monolith, as the latter features poorer mechanical strength, lower thermal conductivity, and thicker cross section [2,3].

Preliminary experiments [1] in which a Cu–Al alloy was deposited by evaporation over a steel plate, following extraction of aluminium from the deposited film using an alkaline solution, led to a Raney film catalyst with high surface area and activity, but about ten times thinner than conventional monolith washcoats.

In the present communication we discuss additional data showing that such a catalyst behaves as a disperse copper aluminate rather than as a conventionally prepared Raney copper.

2. Experimental

The Raney copper catalyst supported on a stainless steel plate was prepared as described in detail previously [1]. Briefly, a powdered 50-50 wt% Cu–Al alloy (almost pure crystalline Al_2Cu as XRD revealed) was evaporated and deposited on the plate (steel type 304, 1×1 $cm^2 \times 1$ mm), employing a Baltzer vacuum evaporation system. After deposition, the plate was submitted to heat treatment under an inert atmosphere. Extraction of the aluminium from the alloy to form the Raney film was carried out by immersion into a solution 2% NaOH for 15 min followed by extensive washing, and drying at 100 ° C.

Bulk composition of the film, down to about 2,000 Å depth, was obtained using a disperse X-ray analyzer of a scanning electron microscope.

Auger spectra were obtained employing an all metal system with a cylindrical mirror analyzer using 5 μA and 3 keV for the primary beam. The analyses were at glancing incidence in order to minimize the depth of beam penetration.

X-ray photoelectron spectra (XPS) were acquired with a MgKα X-ray source using the sample holder signal (Au4f) as reference and a 1 eV flood gun for minimizing charging effects. The data reported is based on 10 scans, and deconvolutions were according to a 80% Gaussian peak model.

Catalytic activity was referred to the steady state CO conversion to CO_2 after oxidation with air at 400 ° C. This was measured by employing an apparatus and procedure previously described [1]. The CO concentration employed was 10 vol% in dried air, and the total flow was 130 cm^3/min measured at ambient conditions. Catalysts were also prereduced with pure CO at 400 ° C for 3 hours before activity tests.

3. Results and discussion

3.1 STRUCTURE AND COMPOSITION OF THE PRECURSOR ALLOY FILM

Microscope examination accompanied by analysis of disperse X-rays reported previously [1] has shown that before leaching, the alloy film mainly consisted of discrete Al_2Cu grains of around 10 μm arising over an alloy groundfilm. The grains were formed probably as a result of migration and coalescence during treatment under inert atmosphere at 500 ° C, as such structure was not seen in the non heat treated alloy film. The heat treatment was found necessary in order to create proper binding between the precursor alloy film and the steel plate. Otherwise, the film detached from the plate (as very thin foil pieces) during leaching.

The average atomic bulk composition of such a film (about 2.5 μm thick), measured down to about 2,000 Å depth, was about 1.6 Al/Cu, reaching values very close to 2 in the grains.

Thicker films (> 5 μm), obtained by more extended evaporation, required a higher temperature (e.g., 600 ° C) in order to avoid detaching during leaching. It may be anticipated that the linking between the film and the steel originates from some diffusion of the film material into the metal plate and/or viceversa,

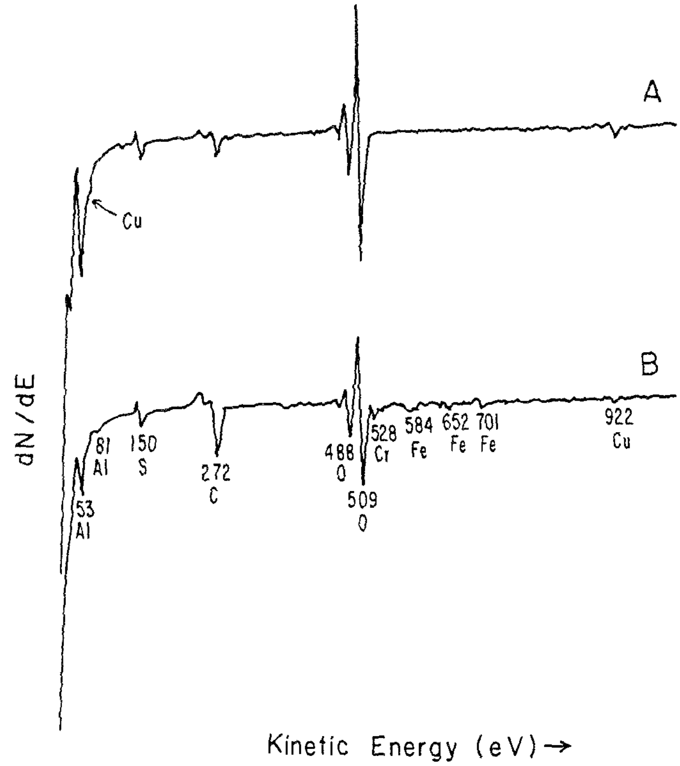

Fig. 1. Auger spectra of the alloy precursor film (thickness: 2.5 μm). Treatment temperature: A, 500 ° C; B, 600 ° C.

as a result of heat treatment. This was confirmed by the Auger spectra (fig. 1) which showed that treatment at 600 ° C, though necessary for thicker-film samples, brought into the thinnest film surface considerable amounts of the steel plate constituents: Cr and Fe, causing a decrease in the surface concentration of Al and Cu.

From fig. 1, it seems that the precursor alloy film surface is enriched with aluminium; i.e., there is a well defined Al signal at about 53 eV, whereas Cu signal appears as a shoulder at the right of that signal (fig. 1A). Such Al-rich surface is apparently oxidized because of the presence of the oxygen signals. Therefore, leaching may not completely extract such oxidized aluminium resulting, as seen below, in an Al-rich oxide surface in the Raney catalyst.

3.2 STRUCTURE AND COMPOSITION OF THE RANEY COPPER FILM

Microscope examination [1] has showed that after leaching, the grain structure remained similar, but featuring a marked roughness probably caused by development of porosity by the extraction of the aluminium. Leaching also produced a decrease of about 75% in the average atomic bulk composition Al/Cu of the film, as measured by the analysis of disperse X-rays.

XPS of the Raney film (fig. 2) shows signals corresponding to aluminium, copper and oxygen, as well as to adventitious carbon. Quantitative data derived from the spectra is shown in table 1. The Al and Cu signals suggest that these elements are not present as metals but as oxides [4,5]. Signals attributed to aluminium apparently correspond to alumina: 74.9 eV [5] and to aluminate compounds: 73.2 eV [6]. The oxygen signal at 531.5 eV suggests the element is forming alumina and/or aluminate [6] rather than copper oxide, as this latter should display an oxygen signal at lower values: 529.8–530 [7]. The oxide formation may be a result of the pyrophoric characteristics of dried Raney metals [8]; however, the oxide may be also present before drying as discussed in section 3.1.

Surface atomic concentrations (table 1) indicate a ratio O/Al very close to 2, suggesting the presence of an aluminate rather than of alumina. However, the Cu/Al ratio is much smaller than expected for bulk aluminate; thus a Cu-deficient aluminate is a possible surface species in the Raney film.

Nevertheless, another possibility that does not contradict the XPS is the presence of an oxygen capping layer covering a surface composed of alumina with copper cations occupying empty sites of the alumina matrix, like in a spinel structure.

In any case, the copper-aluminium oxide species (Al-rich) is probably covering a Cu-rich surface in the Raney porous structure, because the bulk Al/Cu average ratio (about 0.4) is significantly smaller than surface Al/Cu obtained from XPS (Al/Cu = 4.5 from table 1).

3.3 CATALYTIC ACTIVITIES

Table 2 shows CO oxidation activities of samples having different film thickness, treated at 500 or 600 °C before leaching, and with or without CO prereduction. Notice that CO conversion of the non CO pretreated sample is directly related to its absolute surface area (i.e., m^2/cm^2).

For comparative purposes, a powdered Raney copper prepared with the same starting powdered alloy and a 5 wt% Cu/Al_2O_3, are introduced in table 2. These have been employed in obtaining previously reported results on CO oxidation catalysts [9,10]. An important difference among these two catalysts, seen in table 2, is the opposed response to CO pretreatment: the activity decreases in the bulk Raney copper while it does increase in the alumina supported copper.

The activity decrease after prereducing with CO the bulk Raney copper has been attributed [9] to the presence of bulk CuO at the fresh Raney surface, which reduces to metal and sinters during CO reduction. On the other hand, the activity increase in the alumina supported copper after CO prereduction ap-

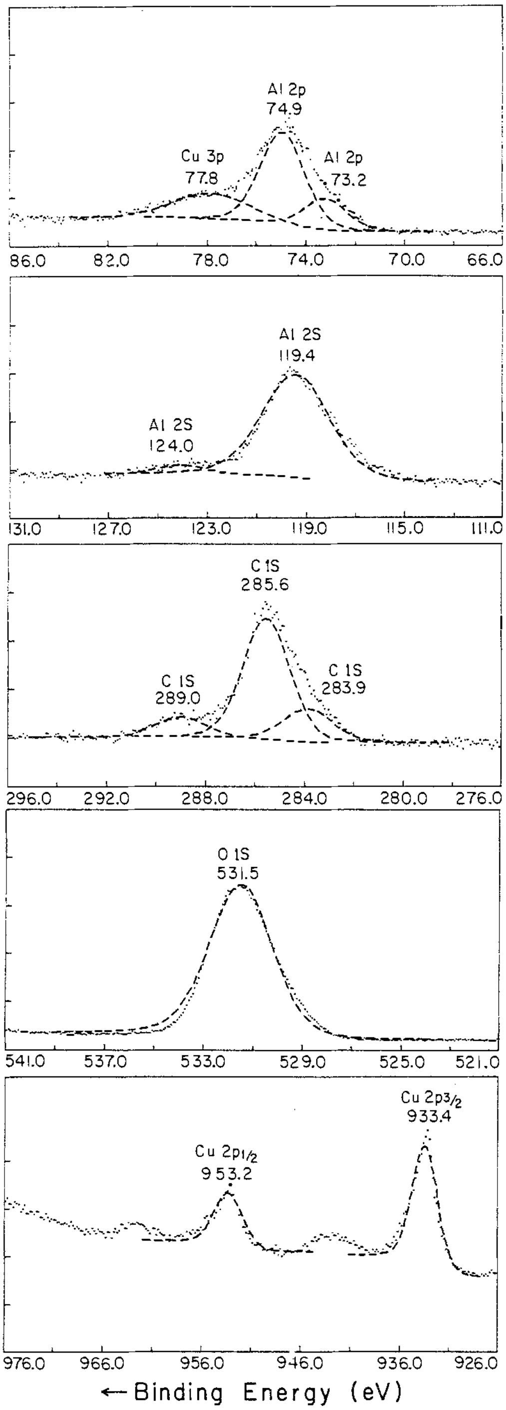

Fig. 2. XPS of the Raney film (alloy treatment at 500 °C, thickness: 2.5 μm).

Table 1
Surface composition from XPS of the Raney film (film thickness 2.5 μm, alloy treatment at 500 °C)

Element	Level	Binding energy (eV)	at%	Total at%
Al	2p	73.2	5.8	
	2p	74.9	17.7	23.5
C	1s	283.9	4.2	
	1s	285.6	14.7	
	1s	289.0	2.5	21.4
O	1s	531.5	49.9	49.9
Cu	$2p_{3/2}$	933.3	5.2	5.2

pears to be related [10,11] to the formation of active copper species at the surface, as a result of migration of copper cations from aluminate sites to the surface, where attraction forces suppress sintering. Similarly as occurring in alumina supported copper, the Raney copper film activity also increases after CO pretreatment (table 2), suggesting an increase in the exposure of active copper.

It can be derived from table 2 that the enhancement in activity brought about by CO pretreatment increases with increasing the alloy treatment temperature and with decreasing film thickness. This behavior could be the result of the presence of increasing amounts of chromium and iron at the surface, arising by diffusion from the plate during heat treating the alloy film, as the Auger spectra revealed (fig. 1).

Table 2
Catalytic activities

Catalyst	Alloy treatment temperature [a] (°C)	Film thickness [b] (μm)	B.E.T. surface area		Activity (%CO conv. at 400 °C)	
			(m^2/cm^2)	(m^2/g)	Non-pretreat.	CO pretreat.
Raney film	500	2.5	0.28	250	46	53
	600	3.4	0.17	110	28	52
	600	7.8	0.20	70	30	42
	600	13.8	0.23	30	42	50
Bulk Raney [c]	–	–	–	30	35	10
5% Cu/Al_2O_3 [d]	–	–	–	85	40	65

[a] 500 °C for 24 h or 600 °C for 1 h under inert atmosphere.

[b] Film thickness was calculated from the weight deposited assuming an alloy density of 6.5 g/cm^3.

[c] Activity was measured using 1 mg of the Raney diluted with 20 mg of inert alumina.

[d] Activity was measured using 20 mg of 5 wt% Cu/Al_2O_3 (i.e., 1 mg of Cu).

Therefore, the lower activity found in the nonprereduced 600 ° C samples can be attributed to a low exposure of copper at the surface due to the presence of inactive Cr and Fe. Indeed, in the case of copper-chromite [12], CO prereduction has been shown to produce surface enrichment with copper increasing activity for CO oxidation.

4. Conclusion

A novel Raney copper catalyst in the form of a thin film bonded to a steel surface has been prepared. Surface characterization and catalytic behavior for CO oxidation with or without CO prereduction suggested the presence of a disperse copper aluminate on the Raney film. The catalyst activity was also a function of the treatment temperature of the precursor Cu–Al alloy film and of the film thickness.

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