

Methanol Synthesis over Raney Copper-Zinc Catalysts

II. Activities and Surface Properties of a Partially Leached Alloy

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Catalysts prepared by the caustic leaching of an alloy containing 36 wt% Cu, 15 wt% Zn, and 49 wt% Al for various periods of time have been shown to have high activities for methanol synthesis. The activity passes through a maximum with time of leaching and is related to both increased surface area and concentration of zinc oxide on the catalyst surface. It has been established that the presence of zinc oxide increases the activity of Raney copper for the methanol synthesis reaction.

INTRODUCTION

The preceding paper (1) provides information on the activity of fully extracted Al-Cu-Zn alloys of differing Cu/Zn ratios for the methanol synthesis reaction, and the associated physical and chemical properties of the resultant catalysts. The most active catalyst was produced by extracting an alloy of composition 50 wt% aluminium, 30-36 wt% copper, and 14-20 wt% zinc with aqueous sodium hydroxide at 50°C. The active component for these Raney catalysts for the synthesis of methanol from carbon monoxide and hydrogen was shown to be copper. The residual zinc in the Raney catalyst was found not only to increase the catalytic activity but also to extend catalyst life. Modern low-pressure methanol synthesis catalysts based on Cu-ZnO/Cr₂O₃ or Cu-ZnO/Al₂O₃ compositions have in their formulations more zinc than the fully extracted Raney catalysts. It therefore seems appropriate to prepare Raney catalysts with increased zinc content in their formulation in order to obtain a more active catalyst. Simply increasing the alloy zinc content does not achieve this end as almost all the zinc is in an Al-Zn solid solution which leaches completely to leave void space. The alloy phase which leaches to yield Raney metal is Cu(Zn)Al₂. This phase

becomes saturated with zinc at low alloy zinc contents as the Cu(Zn)Al₂ phase can dissolve only 3 wt% zinc (2).

A recent study on the leaching morphology and leaching kinetics (3, 4) of Al-Cu-Zn alloys or similar compositions has shown that zinc and aluminum concentrations varied across the reacted layer. The zinc and aluminum were shown to be in greatest concentration near the leach reaction front. This work has also shown that there is a higher zinc concentration in the porous copper grain near the reaction interface than would be expected by leaching the alloy Cu(Zn)Al₂ grain even on the supposition that all of the Al was dissolved but none of the Zn. This work suggests that by controlling the leaching time, the level and distribution of zinc within the resultant catalyst may also be controlled and as a result the catalytic activity of these Raney catalysts may be improved.

Recent studies by Herman and Klier and co-workers (5-8) have made a great contribution to the characterisation of the physical and chemical properties of conventional low-temperature methanol synthesis catalysts. Their work has led to a greater understanding of the roles that the individual components play in determining the activity and life of these catalysts. This paper reports the properties of Raney methanol

synthesis catalysts prepared by partially leaching an alloy that was shown to have high activity when fully leached (1). The influence of physical and chemical properties of these catalysts on the methanol synthesis reaction are discussed.

EXPERIMENTAL

The Raney catalysts used in this study were prepared from 500 to 700- μm alloy pieces with a nominal alloy composition of 50 wt% aluminium, 35 wt% copper, and 15 wt% zinc. The alloy was leached with 20 wt% aqueous sodium hydroxide at 50°C. Extraction times used in the preparation of the catalysts were 0.75, 1.0, 1.5, 2.0, 2.75, 3.5, and 4.5 h. The methods of catalyst preparation, catalytic activity, and adsorption studies are fully described in the preceding paper (1). Catalysts were characterised by X-ray line broadening for particle size, by optical microscopy for morphology, and by atomic absorption spectroscopy and electron probe microanalysis for composition. Experimental details are given elsewhere (3). A conventional low-temperature methanol synthesis catalyst, designated C79-4, obtained from United Catalysts Inc., Kentucky, was also studied.

RESULTS

A micrograph showing a section of a partially leached particle is presented in Fig. 1, where it is seen that there is a reacted rim of porous Raney metal and a core of as-yet unreacted alloy. The thickness of the catalyst rims formed after various leaching times are listed in Table 1. For reaction times up to 1.0 h the reacted rim consisted of two layers, the outer one being essentially grains of Raney copper and the inner one grains of unreacted $\text{Cu}(\text{Zn})\text{Al}_2$. At longer extraction times a single layer of Raney copper was found to exist, the reaction then being liquid-phase diffusion controlled (4).

The catalyst rim could not easily be separated from the alloy core and so chemical analysis of the whole assemblage was per-

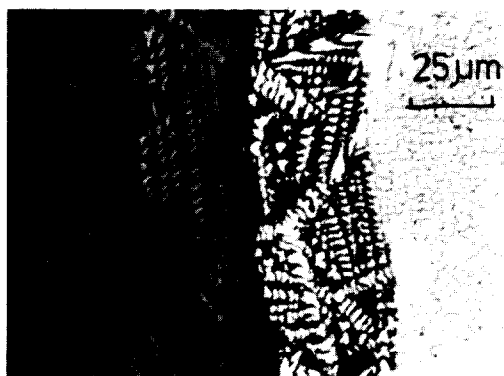


FIG. 1. Micrograph of section through a partially leached 500- to 700- μm Al-36Cu-15Zn alloy at an extraction time of 1.0 h showing unaffected alloy at right and two zones of reacted solid in the rim. The outer zone is Raney Cu and the intermediate zone is $\text{Cu}(\text{Zn})\text{Al}_2$.

formed by atomic absorption spectroscopy analysis of acid-digested samples. These results are presented in Table 1. For leaching times of 1.5 h or longer the results indicated there was no oxide present. The mass balances for the 0.75- and 1.0-h leached samples were found to total 92% and these values have not been normalised. Table 1 compares hydrogen evolution data measured by a wet gas meter in the leaching experiments, and the calculated amount of hydrogen evolved as determined from a knowledge of the original alloy and final catalyst compositions together with the stoichiometry of the leaching reaction (1).

Average chemical compositions for the reacted rims were calculated from a knowledge of the starting alloy composition and density, the thickness of the reacted rim and the initial particle size, the weight loss for the various extraction times, and the overall chemical analysis. The results of this calculation are also shown in Table 1.

Nitrogen isotherms for the partially leached samples presented in Fig. 2 are smoothed curves obtained from the experimental data. The pore size distributions for all extraction times are plotted in Figs. 3 and 4. The pore size distributions were determined by the procedure described in the

TABLE I
Composition of Partially Leached Raney Catalysts

Sample	Extraction time (h)	Bulk composition (wt%)			Distance leached into alloy core (μm)	Thickness of unetched Cu(Zn)Al ₂ layer (μm)	Average composition of reacted rim (wt%)			Hydrogen evolution (litres)	
		Cu	Zn	Al			Cu	Zn ^a	Al ^a	Calculated from AAS	Experimental measurement
Alloy		36.3	15.4	48.6							
Catalyst	0.75	57.2	17.2	25.6	105	5	66.4	17.7	7.7	9.1	9.3
Catalyst	1.0	62.8	16.9	20.5	135	10	68.2	16.7	7.0	10.4	10.9
Catalyst	1.5	76.4	14.6	10.0	180	—	81 \pm 9	14.5	5.2	12.5	12.5
Catalyst	2.0	77.7	13.9	7.0	210	—	79 \pm 6	13.8	4.9	13.0	13.2
Catalyst	2.75	86.4	10.4	4.8	255	—	86 \pm 3	10.4	4.6	13.5	13.8
Catalyst	3.5	94.5	5.0	2.6	290	—	94 \pm 0.5	5.0	2.6	13.9	14.1
Catalyst	4.5	95.5	3.3	1.9	290	—	95 \pm 0.5	3.3	1.9	14.0	14.2
Industrial ^b		70.9	21.9	6.1							

^a Error in calculated compositions for Zn and Al estimated as less than 1%.

^b Reduced (493 K, 101.3 kPa, 24 h under CO/CO₂/H₂ = 19.5/5.5/75 vol%).

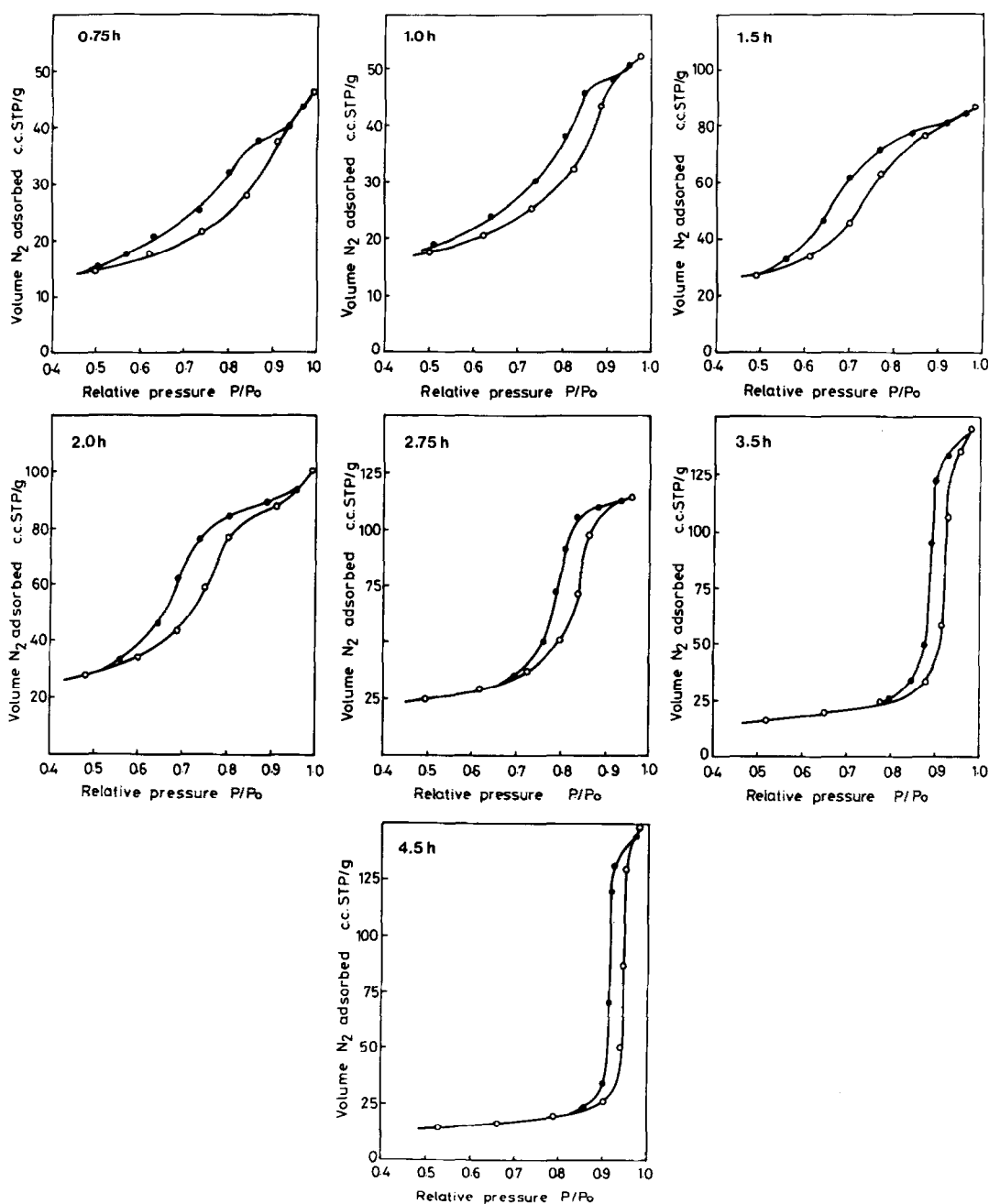


FIG. 2. Nitrogen isotherms for partially leached Raney catalysts at 77.5 K.

previous paper (1). Data derived from the physical adsorption isotherms are given in Tables 2 and 3. The surface area, S_{BET} , was calculated from the BET equation and is presented in Table 2. As the unreacted alloy core contributes nothing to the surface

area, the value of this quantity has been calculated per unit mass of catalyst rim. The pore volume, v_p , is the cumulative volume calculated from the pore size distribution procedure and then converted to liquid volume. It is shown in Table 2 on the basis

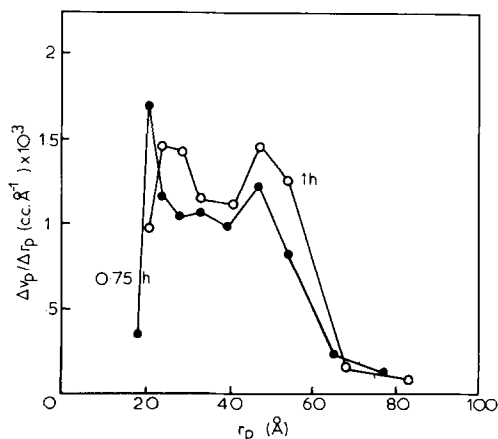


FIG. 3. Pore size distributions for extraction times of 0.75 and 1.0 h from the nitrogen isotherms at 77.5 K.

of the alloy-catalyst system mass and the mass of the catalyst rim. In the case where unleached grains of $\text{Cu}(\text{Zn})\text{Al}_2$ are present as a sublayer of the rim this phase has been assumed to possess a negligible surface area.

Pore radii, r_p and r_a , are presented in Table 3. The values of r_p correspond to the maximum in the $\Delta v_p/\Delta r_p$ plots (Figs. 3 and 4). The "average" pore radius, r_a , is the radius of an equivalent uniform cylinder

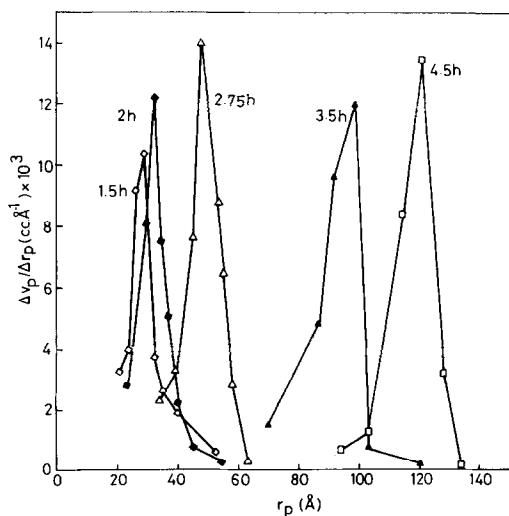


FIG. 4. Pore size distributions for extraction times of 1.5 to 4.5 h from the nitrogen isotherms at 77.5 K.

TABLE 2

Surface Areas and Pore Volumes of Raney Catalysts

Extraction time (h)	Surface area ($\text{m}^2 \text{g}^{-1}$)		Pore volume ($\text{cm}^3 \text{g}^{-1}$)	
	Composite particle	Active material	Composite particle	Active material
0.75	37.4	65.4	0.069	0.121
1.0	43.0	62.8	0.074	0.108
1.5	66.3	74.6	0.143	0.161
2.0	68.6	72.0	0.166	0.174
2.75	62.1	62.4	0.183	0.184
3.5	40.0	40.0	0.235	0.235
4.5	32.7	32.7	0.260	0.260
Industrial ^a		73.3		0.366

^a Reduced (493 K, 101.3 kPa, 24 h under $\text{CO}/\text{CO}_2/\text{H}_2 = 19.5/5.5/75$ vol%).

having the volume $v_{0.95}$, calculated as normal liquid at a relative pressure of 0.95, and is given by: $r_a = 2v_{0.95}/S_{\text{BET}}$ (9). Interpore distances were calculated from the pore data based on nonintersecting cylinders hexagonally arrayed and are shown in Table 3. Interpore distances were compared with copper crystallite diameters. The copper crystallite diameters for the partially leached catalysts shown in Table 3 were determined from X-ray diffraction line broad-

TABLE 3

Pore Radii and Crystallite Diameter of Raney Catalysts

Extraction time (h)	Pore radius (\AA)		Interpore distance (\AA)	Copper crystallite diameter (\AA)
	r_p	r_a		
0.75	21-47	35	51	76
1.0	24-50	37	54	76
1.5	29	39	50	84
2.0	32	42	51	90
2.75	48	57	67	101
3.5	95	105	110	121
4.5	120	135	130	121
Industrial ^a	42-70	72		84

^a Reduced (493 K, 101.3 kPa, 24 h under $\text{CO}/\text{CO}_2/\text{H}_2 = 19.5/5.5/75$ vol%).

ening. It can be seen from these data that as the leaching time increases both the pore radius and the interpore distance increase.

The activities of the partially leached catalysts were determined at a reaction pressure of 3450 kPa, a temperature of 513 K, and a gaseous hourly space velocity (GHSV) of 12000 h⁻¹ (calculated at STP). The feed gas had a composition of CO/CO₂/H₂ = 19.5/5.5/75 vol%. The activities of the Raney catalysts are shown in Table 4. The activities are based on the mass of alloy catalyst composite and have also been normalised to surface area. Since the activity of the catalyst is due to the reacted Raney rim, the activities have been recalculated on the basis of active catalyst material. These results are also presented in Table 4. It can be seen that these partially leached Raney catalysts are more active than the fully leached sample, reported here as the 4.5-h leached sample. The activities of the Raney catalysts are also compared with that of the industrial methanol synthesis catalyst. It can be seen from Table 4 that the Raney catalyst prepared by leaching the alloy for 2.75 h is more active than the industrial methanol synthesis catalyst measured under these conditions.

Carbon monoxide and hydrogen chemisorption on the partially leached catalysts were measured at 77.5 K by the procedure described in the preceding paper (1). The

types of isotherms obtained are illustrated by the 2.75-h leached sample shown in Fig. 5 and the volumes of carbon monoxide chemisorbed are given in Table 5. The chemisorption data have also been normalised to the same surface area by dividing the amounts chemisorbed by the monolayer value, V_m , calculated from the N₂ isotherm. All catalysts showed negligible hydrogen chemisorption measured at 77.5 K. Carbon monoxide and hydrogen adsorption were also measured on the 2.75- and 4.5-h leached samples at 473 K and pressures in the range 1–26 kPa. These results are reported in Table 6 where, for comparison, data for Raney copper, Raney zinc, and the industrial catalyst are also included.

The zinc and aluminum concentration levels in the copper phase of the reacted rim were measured by microprobe analysis for samples that had been leached from 1.0 to 3.5 h. Figure 6 shows the concentration profiles of zinc and aluminum where the position coordinate has been normalised with respect to layer thickness. The application of the normal correction procedures to microprobe data for the copper phase in the reacted rim led to apparent analyses totaling substantially less than 100%. Such results are common for porous materials and, in the absence of an appropriate correction procedure, they have been scaled to 100%. Thus it has been assumed that the

TABLE 4
Activity Data of Raney Catalysts

Extraction time (h)	Rate (mol/g composite/h)	Rate (mol/g active mat./h)	Rate (mol/m ² /h)
0.75	9.31×10^{-3}	1.63×10^{-2}	2.49×10^{-4}
1.0	$(9.47 \pm 1) \times 10^{-3}$	1.37×10^{-2}	2.18×10^{-4}
1.5	1.84×10^{-2}	2.07×10^{-2}	2.78×10^{-4}
2.0	$(2.30 \pm 0.25) \times 10^{-2}$	2.42×10^{-2}	3.35×10^{-4}
2.75	3.10×10^{-2}	3.12×10^{-2}	4.99×10^{-4}
3.5	$(1.8 \pm 0.2) \times 10^{-2}$	1.8×10^{-2}	4.50×10^{-4}
4.5	7.61×10^{-3}	7.61×10^{-3}	2.32×10^{-4}
Industrial ^a		$(2.38 \pm 0.2) \times 10^{-2}$	3.25×10^{-4}

^a Reduced (493 K, 101.3 kPa, 24 h under CO/CO₂/H₂ = 19.5/5.5/75 vol%).

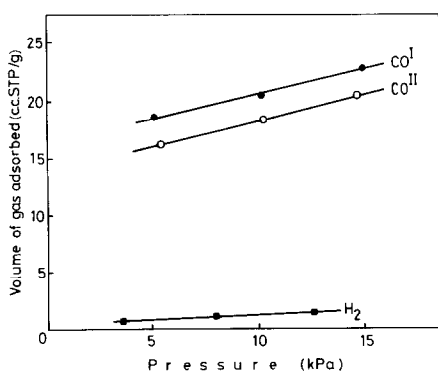


FIG 5. Adsorption of CO and H₂ on 2.75-h-extracted Al-36Cu-15Zn alloy at 77.5 K: ●, CO on catalyst evacuated at 423 K, CO^I; ○, CO on previous sample after evacuation at 203 K, CO^{II}; ■, H₂ on catalyst evacuated at 423 K.

effect of porosity on the generation and emergence of X rays is independent of the nature of the element.

DISCUSSION

Development of Catalyst Structure

Average chemical analyses and the distance the leaching reaction has progressed, shown in Table 1, indicate that the leaching proceeds in three stages. In the first stage

(times of 0.75 and 1 h) the aluminium content drops rapidly from its initial value whilst the zinc content is slightly increased. This stage corresponds to the formation of a reacted rim in which all the intergranular aluminium-zinc solid has been leached but only a proportion of the Cu(Zn)Al₂ grains has been attacked. The measured changes in elemental concentrations within the rim are consistent with the observed morphology only if there is a net transfer of zinc from the leaching Al-Zn solid solution to the Cu(Zn)Al₂-phase leach residue. This conclusion has already been reached (4) on the basis of electron probe microanalysis data and is thereby confirmed. A possible mechanism for this process has been proposed elsewhere (4) and involves reprecipitation of an oxidized Zn species near the leaching front. As that front recedes the zinc redissolves as shown in the microprobe profiles of Fig. 6. In the second stage of reaction (times of 1.5 to 2.75 h) both Al and Zn are leached from the alloy, the Zn remaining at relatively high levels until the alloy core of the leaching particle is exhausted. In the third and final stage of reaction the Zn content is lowered rapidly as the residual soluble metals are removed. The

TABLE 5

Carbon Monoxide Chemisorption on Partially Leached Raney Catalysts at 77.5 K

Extraction time (h)	V _m (cm ³ STP/g composite material)	Chemisorbed carbon monoxide, ΔV _{CO}		
		cm ³ /g composite material	cm ³ /g active material	ΔV _{CO} /V _m
0.75	8.59	0.843	1.48	0.098
1.0	9.88	1.08	1.58	0.110
1.5	15.23	1.21	1.36	0.079
2.0	15.75	1.53	1.61	0.097
2.75	14.27	2.47	2.48	0.173
3.5	9.19	2.95	2.95	0.321
4.5	7.52	2.38	2.38	0.316
Industrial ^a	16.84		3.25	0.193

^a Reduced (493 K, 101.3 kPa, 24 h under CO/CO₂/H₂ = 19.5/5.5/75 vol%).

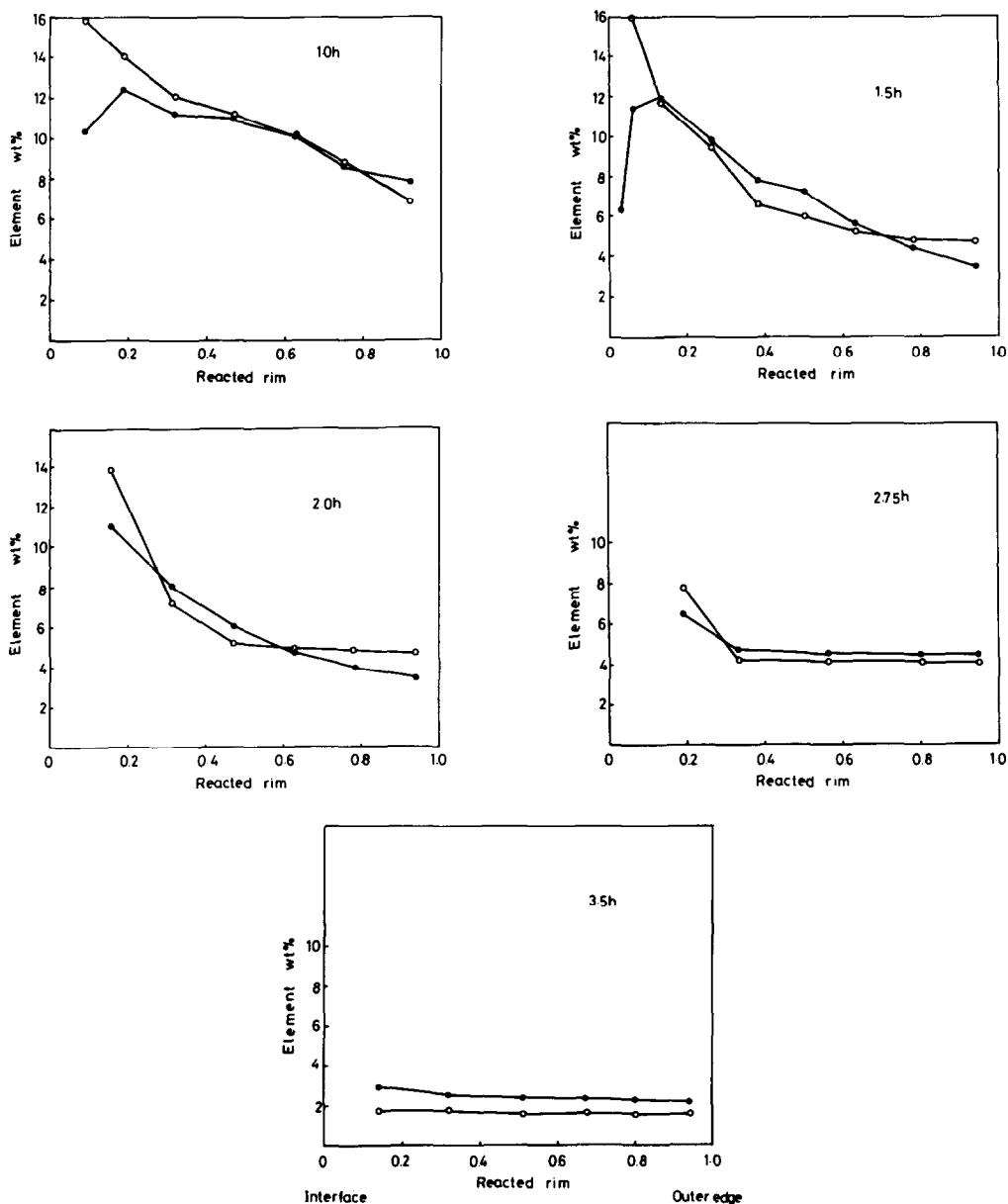


FIG. 6. Zinc (●) and aluminum (○) concentration profiles in the porous copper grains of the active catalyst material for extraction times of 1.0 to 3.5 h.

changing chemistry of the catalyst is reflected in its morphological development.

The enlargement of pore volume per unit mass of leached rim is seen in Table 2. In the short leaching times of 0.75 and 1.0 h the variation in pore volume is probably due to the incomplete formation of all pores in the active rim and possibly to the pres-

ence of oxide. During the next stage the pore volume increases as the Al and Zn contents are progressively lowered. After the leach reaction reaches the centre of the particle, a further increase in pore volume occurs as the residual Al and Zn are removed. The total pore volume occurs as the residual Al and Zn are removed. The total

TABLE 6
CO and H₂ Adsorption on Raney Catalysts at 473 K

Catalyst	Carbon monoxide adsorption		Hydrogen adsorption	
	V _{CO} (cm ³ /g active material)	V _{CO} /V _m	V _{H₂} (cm ³ /g active material)	V _{H₂} /V _m
Al-36Cu-15Zn, 2.75 h extraction	1.76	0.159	1.42	0.128
Al-36Cu-15Zn, 4.5 h extraction	1.52	0.275	0.626	0.113
Al-50Cu, 3.0 h extraction	1.03	0.263	0.187	0.048
Al-50Zn, 4.5 h extraction	0.113	0.106	0.141	0.132
Industrial ^a	1.33	0.093	3.20	0.222

^a Reduced (493 K, 101.3 kPa, 24 h under CO/CO₂/H₂ = 19.5/5.5/75 vol%).

pore volume is determined by the total amount of material removed from the Cu(Zn)Al₂ phase. The size of the pores however, is determined in part by the rate of the leaching reaction.

Pore radii are seen in Table 3 to increase with increasing extent of leach reaction, the increase occurring in the stages already noted. The results for the initial leaching stage are anomalous as a consequence of the duplex layer structure of the reacted rim and also possibly as a result of the presence of oxide, and will not be discussed. During the second and third stages of reaction, the interpore distances are calculated to have increased. This trend is qualitatively confirmed by the experimental measurement of crystallite size. The leaching reaction must be accompanied by microsegregation within the alloy at the reaction front in a plane parallel to that front (3, 4). The distance over which diffusion of the alloy constituents can occur is clearly a function of the rate at which the reaction front advances. This distance determines the maximum interpore spacing. Since the reaction rate slows with increasing leaching time (3, 4), it follows that the interpore distance should increase. For a total pore vol-

ume which increases with time, this implies that the average pore radius must increase with leaching time, as was in fact observed. An important consequence is that surface area will be in part determined by the rate at which the leaching reaction is carried out.

Surface areas of the reacted rim are seen in Table 2 to reach a maximum after about 1.5 h leaching time and then to decline. However, a continuous decline in surface area per unit mass of reacted rim would be predicted from the above argument. Thus the interpore separation is expected to increase with time as the reaction rate slows and the pore size is expected to increase with time as the residual soluble elements are removed. The apparent maximum at the 1.5 h leaching time is again due to the incomplete formation of all pores in the active rim and for leaching times greater than 1.0 h the surface area per unit mass of porous product decreases monotonically with increasing reaction time. The presence of oxide during the early stages of leaching could also contribute to this apparent anomaly.

Catalytic Activity

Catalytic activity data shown in Table 4

are seen to go through a maximum with leaching time when compared on a mass basis and on a surface area basis. The most active catalyst is produced when the alloy is leached for 2.75 h. This catalyst is more active than the industrial methanol synthesis catalyst when measured under the same conditions. Activity data in Table 4 show that the catalyst produced by extracting the alloy for 2.75 h is five times more active than that produced by complete extraction after 4.5 h. This increase in activity cannot be attributed entirely to an increase in total surface area since the ratio of activities normalised with respect to surface area is 2.2. The increased activity must therefore result from some chemical difference in the catalyst.

Bulk chemical analysis of these partially leached samples by atomic absorption spectroscopy shows that as the leaching time increases, the zinc content of these particles decreases from 15 wt% zinc in the initial alloy to 3.3 wt% zinc in the final catalyst. The composition data in Table 1 show that the active catalyst layer in the sample leached for 2.75 h contains approximately three times the zinc concentration present in the fully leached alloy. The method of catalyst preparation and the reaction conditions used to measure catalyst activity are thought to result in the surface zinc being present as an oxide (1). It therefore appears that the increase in activity resulting from partial leaching of the alloy may be attributed to both increased surface area and to significant levels of zinc oxide on the catalyst surface.

Chemisorption Measurements

In a previous investigation (1) we have studied the chemisorption of CO and H₂ in order to obtain estimates of the relative amounts of copper and zinc oxide on the surface of fully leached alloys. In the current study it has been found that negligible amounts of hydrogen were adsorbed on all

catalysts at 77.5 K. However, significant quantities of CO were adsorbed on all catalysts and the results are presented in Table 5. It can be seen that the amount of CO chemisorbed per gram of active material increases with leaching time up to a period of 3.5 h. The amounts of CO chemisorbed when corrected to take into account the differences in total surface area of the catalysts are also presented in Table 5. From these results it can be seen that catalysts leached for periods of 0.75 to 2.0 h chemisorb less than a third of the CO which is adsorbed per unit surface area on a fully leached catalyst. The catalyst prepared by extracting the alloy for 2.75 h chemisorbed approximately half as much CO as the fully extracted catalyst. Since both Raney copper and Raney zinc have been shown to chemisorb CO (1), it is difficult to quantify the effects shown in Table 5. However, the results do show that there is an increase in the surface copper concentration with leaching time.

The results of additional adsorption experiments conducted at 473 K are presented in Table 6. The CO adsorbed per unit surface area on the alloy extracted for 2.75 h was again approximately half the amount adsorbed on the fully leached catalyst. However, the catalyst prepared by leaching for 2.75 h adsorbed 20% more H₂ than the fully leached sample. The results for the adsorption of CO and H₂ on Raney copper and Raney zinc are also presented in Table 6. When corrected to take into account differences in total surface area, Raney copper adsorbed 2.4 times the amount of CO and slightly greater than one-third that of the H₂ adsorbed on Raney zinc. The results in Table 6 confirm the presence of a zinc species on the catalyst surface. It is of interest to note that the industrial catalyst, which has a lower activity than the catalyst prepared by leaching the alloy for 2.75 h, appears to have a higher zinc and lower copper surface concentration. This is to be expected from the chemical composition data in Table 1.

Electron Microprobe Analyses

Figure 6 shows the zinc and aluminum profiles obtained by microprobe analysis of the copper grains formed in alloy samples that had been leached for periods from 1 to 3.5 h.

The results in Table 4 show that the activity per unit surface area for the catalyst produced by leaching the alloy for 2.75 h is 1.5 times that of one leached for 2 h and 1.1 times that leached for 3.5 h. From Fig. 6 it can be seen that the concentration of zinc in the copper grains is approximately 6, 4.4, and 2.4 wt% in the catalysts leached for 2, 2.75, and 3.5 h, respectively. It is therefore suggested that catalyst activity is very dependent on the surface zinc oxide concentration, a value of approximately 4 wt% being optimal for this catalyst system. This value is, of course, a bulk analysis result: the relationship between it and the surface concentration is unknown. These results and those of the chemisorption studies suggest that there is a complex interaction between the copper and zinc oxide species in determining catalyst activity.

CONCLUSIONS

The activity of methanol synthesis catalysts prepared from a Cu-Zn-Al alloy by the Raney method can be greatly increased by controlling the leaching process. This is achieved through modification of both the

chemical nature of the surface and the pore structure of the catalyst. Copper is the major component influencing catalyst activity, whilst surface zinc oxide appears to promote stability and activity of the catalyst.

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