

Methanol Synthesis over Raney Copper-Zinc Catalysts

I. Activities and Surface Properties of Fully Extracted Catalysts

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The activity of fully extracted Raney copper-zinc catalysts for the methanol synthesis reaction, and the associated physical and chemical properties of these catalysts, have been examined. The Raney catalysts were prepared by leaching a series of Al-Cu-Zn alloys containing approximately 50 wt% Al and differing Cu/Zn ratios with aqueous NaOH until complete reaction had taken place. Hydrogenation of a mixture of carbon monoxide and carbon dioxide showed that Raney catalysts prepared from alloys containing approximately 50 wt% Al, 30-36 wt% Cu, and 14-20 wt% Zn had the greatest activity for methanol synthesis. The active component for these Raney catalysts was found to be metallic copper and the activity exhibited a maximum for catalysts containing approximately 97 wt% copper. The residual zinc in these catalysts was found to provide a promotional effect to catalytic activity. The surface areas of the catalysts increased from 17 to 39 m²g⁻¹ with increasing zinc content of the precursor alloy. The catalysts exhibited a narrow pore size distribution with the pore radius decreasing with increasing alloy zinc level. Carbon monoxide and hydrogen adsorption were used to determine the nature of the catalyst surface.

INTRODUCTION

The catalytic conversion of synthesis gas to methanol is an important industrial process. The modern low-pressure (20-100 atm) methanol synthesis catalysts are usually based on Cu-ZnO/Cr₂O₃ or Cu-ZnO/Al₂O₃ compositions. These mixed oxide catalysts, produced by co-precipitation methods, have been studied by Herman *et al.* (1) and have been found to be considerably more active than the separate catalytically active components. Raney copper-zinc catalysts have recently been shown to be very active in the synthesis of methanol (2). These Raney catalysts are produced from aluminum-copper-zinc alloys by extraction of aluminum and zinc with aqueous sodium hydroxide. The use of Raney copper-zinc catalysts has also been reported for other reactions (3, 4).

Characterisation studies of the physical and chemical properties of the Cu-Zn oxide catalysts have recently been reported

(1, 5). The enhanced activity of these catalysts does not vary smoothly with the Zn/Cu ratio. Two activity maxima at Zn/Cu ratios of 7/3 and 1/2 have been observed. Herman *et al.* (1) have performed a detailed investigation into the role of the individual components in these oxide catalysts. It is their belief that a solid solution of copper in zinc oxide is responsible for catalytic activity and that the active component is Cu¹ dissolved in the ZnO. This is not the view held by Andrew (6) who, in a study of methanol and water gas shift catalysts, presents the case for copper being the sole active component. Andrew (6) also states that the role of zinc oxide is to absorb poisons that may be present in the synthesis gas.

Little is known about the structure and chemical properties of Raney catalysts prepared from Al-Cu-Zn alloys, although these catalysts have activities comparable to those of the commercial catalysts. In view of the unusual way in which the Raney catalysts are formed, a study of their physi-

cal and chemical properties seems appropriate.

The present work is divided into two parts. Part I (this paper) provides information on the activity and the physical and chemical properties of fully extracted Al-Cu-Zn alloys of differing Cu/Zn ratios. The subsequent paper (Part II) describes the effect of leaching time on the activity, physical, and chemical properties of Raney copper-zinc catalysts produced from an alloy of composition shown to be optimal in activity when fully leached.

METHODS

Catalyst Preparation

The Raney catalysts were prepared from alloys containing nominally 50 wt% aluminum with varying amounts of copper and zinc. Alloys were prepared from high-purity metals (Al > 99.9%, Zn > 99.8%, Cu > 99.5%) and the method of preparation is fully described by Marsden *et al.* (2). Alloy compositions are given in Table 1.

Catalysts were prepared from 500 to 700- μm alloy pieces obtained by crushing and screening the quenched alloy. A 20-g sample of the alloy was placed in 111 g of dis-

tilled water at 50°C. After purging the reaction vessel with hydrogen, 111 g of 40% (w/w) caustic solution was added over a time period of 0.75 h so that the reaction temperature was maintained at $50 \pm 2.5^\circ\text{C}$. No means of stirring was provided. The extent of reaction was monitored by measuring the hydrogen evolution with a wet gas meter. After complete reaction had taken place the catalyst pieces were thoroughly washed with distilled water until the pH of the wash water was 7. Fine particles produced by the leaching process were removed by sieving through a 350- μm screen.

A conventional low-temperature methanol synthesis catalysts, designated C79-4, obtained from United Catalysts Inc., Kentucky, was also studied. The properties of this catalyst, which is an improved version of the copper-based catalyst described in the patent by Casey and Chapman (7), were compared with those of the Raney catalysts. The United Catalysts material was obtained as $\frac{3}{16}$ -in. pellets and was therefore crushed and screened to 500–700 μm to achieve a size similar to that of the Raney catalysts. A supported copper catalyst was also studied. A solution of copper nitrate was deposited on 500 to 700- μm pieces of

TABLE I
Composition of Fully Leached Raney Copper-Zinc Catalysts and Their Starting Alloys

Sample	Alloy composition (wt%)			Catalyst composition (wt%)			H ₂ evolution (litres)		Leaching time (h)
	Cu	Zn	Al	Cu	Zn	Al	Calculated from AAS	Experimental	
1	50.6	0	50.2	98.7	0	1.6	13.4	13.5	3.0
2	44.6	5.3	50.7	98.0	0.8	1.1	14.0	13.8	3.0
3	39.3	9.8	50.3	97.5	1.4	1.3	14.2	14.5	4.0
4	36.2	13.6	51.2	96.9	2.1	1.5	14.6	14.4	4.5
5	33.5	17.1	49.7	97.1	2.8	1.6	14.6	14.5	5.0
6	30.3	20.6	50.2	94.5	4.4	2.1	14.9	14.6	5.5
7	24.6	26.0	49.8	90.0	8.7	2.0	15.3	15.0	6.0
8	17.2	33.0	48.5	64.4	33.0	3.9	14.7	15.1	5.5
9	0	52.0	48.8	0	99.8	0.8	—	13.7	4.0
Industrial ^a				70.9	21.9	6.1			

^a Reduced (495 K, 101.3 kPa, 24 h under CO/CO₂/H₂ = 19.5/5.5/75 vol%).

low-surface-area silica (Davison Chemicals, Md.) which had a BET surface area of approximately $50 \text{ m}^2\text{g}^{-1}$. The excess water was slowly removed until the silica pieces were dry. The impregnated silica pieces were then calcined at 523 K at 101.3 kPa under a gas mixture containing 19.5% CO, 5.5% CO₂, and 75% H₂ for 24 h. This material had a BET surface area of $42 \text{ m}^2\text{g}^{-1}$ and a copper crystallite diameter of 250 Å.

The compositions of the alloys and their resultant catalysts were determined by atomic absorption spectroscopy analysis on acid-digested samples. The reduced industrial catalyst and the copper-on-silica catalysts were also analyzed by the same method. Prior to acid digestion, the industrial methanol catalyst and the copper-on-silica catalyst were reduced for 24 h (493 K, 101.3 kPa) under synthesis gas (19.5 mol% CO, 5.5 mol% CO₂, 75 mol% H₂). The copper and zinc levels were determined by the standard addition technique, while the aluminium content was determined by comparing the unknown with matched standards.

Activity Measurements

The catalyst activity was evaluated in an apparatus similar to that of Marsden *et al.* (2). A premixed gas containing 19.5 mol% CO, 5.5 mol% CO₂, and 75 mol% H₂ (Commonwealth Industrial Gases Ltd.) was fed from a high-pressure cylinder to a 9.5-mm-o.d. U-tube reactor. The gas mixtures were produced from high-purity H₂ (>99.9%), CO (>99.5%), and CO₂ (>99.9%). The impurities present which are known to poison the catalysts were S (<0.005 ppm) and N₂ (<0.06%). The chloride content was not determined but was thought to be less than 0.005 ppm. No purification of the gas mixture was performed. The reactor was immersed in a vigorously stirred molten salt bath. The pressure in the reactor gas was controlled using a back-pressure regulator. The flow rate of the exit gases was measured at atmospheric pressure using a wet gas meter. The compositions of the reactant

and product gases from the reactor were determined by gas chromatography using a Gowmac model 552 gas chromatograph with a thermal conductivity detector. A Porapak T column (3-m × 6.3-mm-o.d. aluminium) operating isothermally at 409 K using hydrogen as the carrier gas gave excellent separation of CO, CO₂, dimethyl ether, water, and methanol. Peak areas were measured using a Spectra-Physics Minigrator electronic integrator. A gravimetric standard mixture containing CO, CO₂, and dimethyl ether in hydrogen (Commonwealth Industrial Gases Ltd.) was used daily to calibrate the gas chromatograph. The response of methanol relative to dimethyl ether was determined by independent experiments. The measurements of catalyst activities were carried out in a flow reactor at a gaseous hourly space velocity (GHSV) of 12000 h^{-1} (calculated on the basis of a pressure of 101.3 kPa absolute and a temperature of 273 K with a CO/CO₂/H₂ = 19.5/5.5/75 vol% mixture at 3450 kPa and a reaction temperature of 513 K.

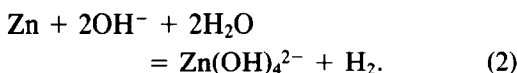
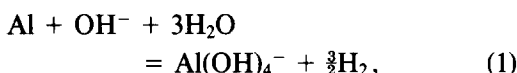
Adsorption Studies

The adsorption of nitrogen at 77.5 K was measured using a Micromeritics 2100E ORR surface area, pore volume analyser. The Raney catalysts were transferred to the adsorption vessel under water which was removed by evacuation. The samples were evacuated at room temperature for 2 h and then at 423 K for an additional 15 h. The industrial methanol synthesis catalyst and the copper-on-silica catalyst were reduced for 24 h (493 K, 101.3 kPa) under flowing synthesis gas (19.5 mol% CO, 5.5 mol% CO₂, 75 mol% H₂) before evacuation at 423 K for 15 h. A nitrogen adsorption-desorption isotherm was measured for each sample. Samples were weighed by difference in the adsorption vessel on completion of each experiment. Separate samples were also used for carbon monoxide and hydrogen adsorption. Samples were evacuated by the procedure described for the adsorption of nitrogen. Carbon monoxide and hydrogen

isotherms were measured in the temperature range of 77.5 to 473 K.

RESULTS

Alloy and catalyst compositions measured by atomic absorption spectroscopy are presented in Table 1. Bulk analyses of the catalysts obtained by atomic absorption spectroscopy showed there was very little or no oxide present. The chemical reactions involved in the leaching of the Al-Cu-Zn alloys with caustic solution may be represented as (8):



From a knowledge of the original alloy and final catalyst compositions together with the stoichiometry of the leaching reaction, the total volume of hydrogen generated was calculated. The results in Table 1 are seen to be in close agreement with the experimental quantity measured with the wet gas meter.

Product analysis by gas chromatography showed that for the Raney catalysts there was high selectivity to methanol (more than 99% with respect to carbon conversion) and only at considerably longer contact times did any traces of dimethyl ether appear in the analysis. The activities of the Raney catalysts are shown in Table 2 and are based on carbon conversion to methanol per gram of catalyst and also per unit total surface area of the catalyst. The activity at 513 K of Raney zinc (sample 9) was zero. The activity of the industrial catalyst is given in Table 2 and it is evident that the industrial catalyst is more active than the fully leached Raney catalysts.

The nitrogen isotherms for the Raney catalysts presented in Fig. 1 are smoothed curves obtained from the experimental data. The shape of the nitrogen isotherms indicates a Type A hysteresis loop as classified by de Boer (9). The pore size distribu-

TABLE 2
Activity Data for Raney Catalysts

Sample	Rate (mol/g cat./h)	Rate (mol/m ² /h)
1	2.26×10^{-3}	1.33×10^{-4}
2	2.33×10^{-3}	1.25×10^{-4}
3	5.40×10^{-3}	2.47×10^{-4}
4	7.35×10^{-3}	3.00×10^{-4}
5	7.90×10^{-3}	2.95×10^{-4}
6	5.04×10^{-3}	1.72×10^{-4}
7	2.29×10^{-3}	7.48×10^{-5}
8	1.63×10^{-3}	4.18×10^{-5}
9 ^a	—	—
Industrial ^b	2.38×10^{-2}	3.25×10^{-4}

^a The activity of this catalyst was less than could be measured by the analytical procedure.

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

tion determined from the nitrogen isotherm (10) is based on the procedure of Pierce (11) as modified by Orr and Dalla Valle (12). The pore size distribution for the Raney catalysts are plotted in Figs. 2 and 3. The nitrogen isotherm and the associated pore size distribution for the reduced industrial catalyst are presented in Fig. 4. Data derived from the physical adsorption isotherms are given in Table 3. The surface area, S_{BET} , was calculated from the BET equation. The pore volume, v_p , is the cumulative volume calculated from the pore size distribution procedure and then converted to liquid volume. The values of r_p , corresponding to the maximum in the $\Delta v_p/\Delta r_p$ plots (Figs. 2 and 3), are also presented in Table 3. The "average" pore radius, r_a (Table 3), is the radius of an equivalent uniform cylinder having the volume $v_{0.95}$, calculated as normal liquid at a relative pressure of 0.95, and is given by: $r_a = 2v_{0.95}/S_{\text{BET}}$ (10). The agreement between the maximum pore radius, r_p , and the "average pore radius," r_a , though not perfect is reasonably close. The monolayer volume, v_m , was calculated from the BET equation isotherm and is presented in Table 3.

Carbon monoxide and hydrogen chemisorption were measured at 77.5 K by the

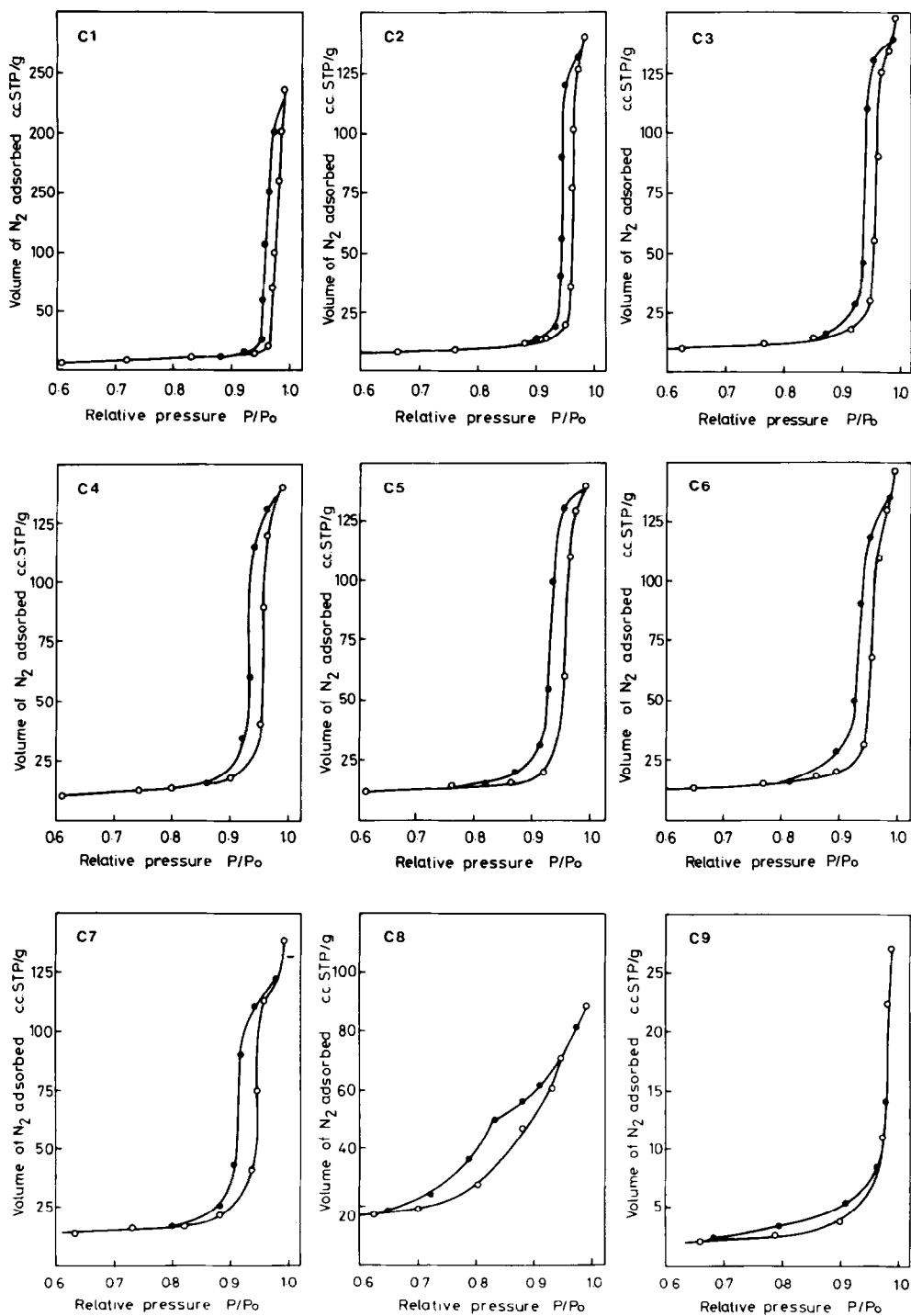


FIG. 1. Nitrogen isotherms for Raney catalysts measured at 77.5 K.

TABLE 3
 Pore Structure of Raney Catalysts from N₂ Isotherms at 77.5 K

Catalyst	Surface area, S_{BET} (m ² g ⁻¹)	V_m (cm ³ STP g ⁻¹)	Pore volume, v_p (cm ³ g ⁻¹)	r_p (Å)	r_a (Å)	Interpore distance ^a (Å)	Copper crystallite diameter ^b (Å)
1	17.0	3.91	0.385	229	422 ^c	194	112
2	18.6	4.27	0.242	177	200	182	112
3	21.9	5.03	0.241	169	185	171	104
4	24.5	5.67	0.239	160	159	160	—
5	26.8	6.16	0.238	142	154	138	104
6	29.4	7.00	0.233	136	127	137	—
7	30.6	7.04	0.238	115	114	119	70
8	39.0	8.96	0.138	50	58	69	62
9	4.6	1.07	0.042	No pore maxima		—	—
Industrial ^d	73.3	16.84	0.366	42/70	72	—	—

^a Calculation based on pores, r_p , as hexagonally arrayed nonintersecting cylinders.

^b Determined by X-ray analysis (11).

^c Calculated at $v = 0.99 P_0$.

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

method adopted by Freel *et al.* (13) in their study of Raney nickel catalysts. The chemisorption of carbon monoxide was determined by measuring an isotherm on the original evacuated catalyst at 77.5 K; the sample was then evacuated for 2 h at 203 K and a second isotherm was measured at 77.5 K. The volume of chemisorbed carbon monoxide was defined as the difference between the second carbon monoxide isotherm and the first carbon monoxide iso-

therm. The types of isotherms obtained are illustrated by data from catalyst 4 shown in Fig. 5. As expected, the volume of chemisorbed carbon monoxide is independent of pressure. The chemisorption data have also been normalised to surface area by dividing the amounts chemisorbed by the V_m value calculated from the N₂ isotherm. See Table 4.

Hydrogen chemisorption was calculated in a similar way, the volume of chemisorbed hydrogen being taken as the difference between an original isotherm at 77.5 K and a second isotherm at 77.5 K following evacuation at 77.5 K for 2 h. The isotherms for catalyst 4 are presented in Fig. 5. Similar isotherms were found for the other catalysts. It should be noted that there is negligible difference between the two measurements. All catalysts showed either zero or negligible hydrogen chemisorption measured under these conditions. This confirms the result of Wainwright and Anderson (14) who showed that no hydrogen chemisorption takes place on Raney copper at 77.5 K.

Carbon monoxide and hydrogen adsorption were also measured on selected cata-

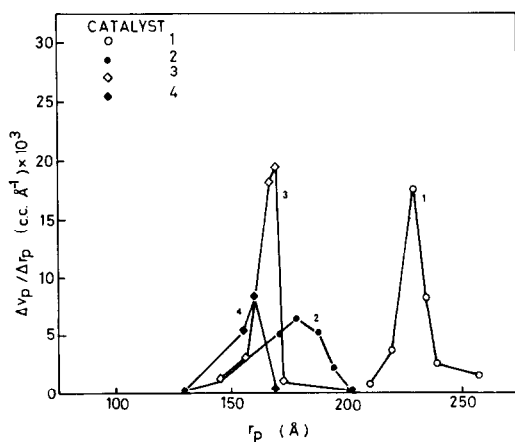


FIG. 2. Pore size distributions for catalysts 1-4 from the nitrogen isotherms at 77.5 K.

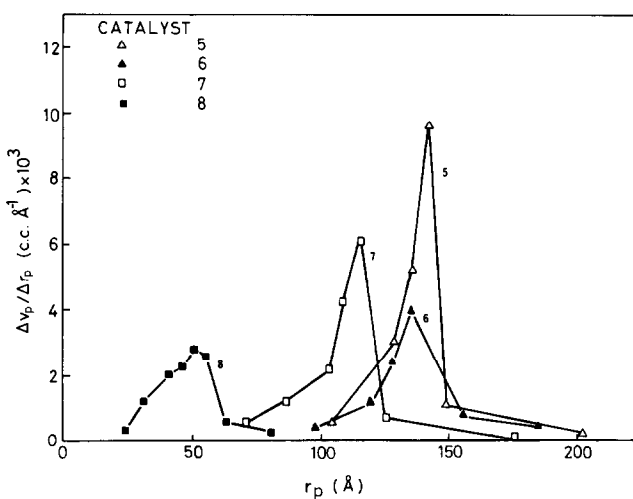


FIG. 3. Pore size distributions for catalysts 5-8 from the nitrogen isotherms at 77.5 K.

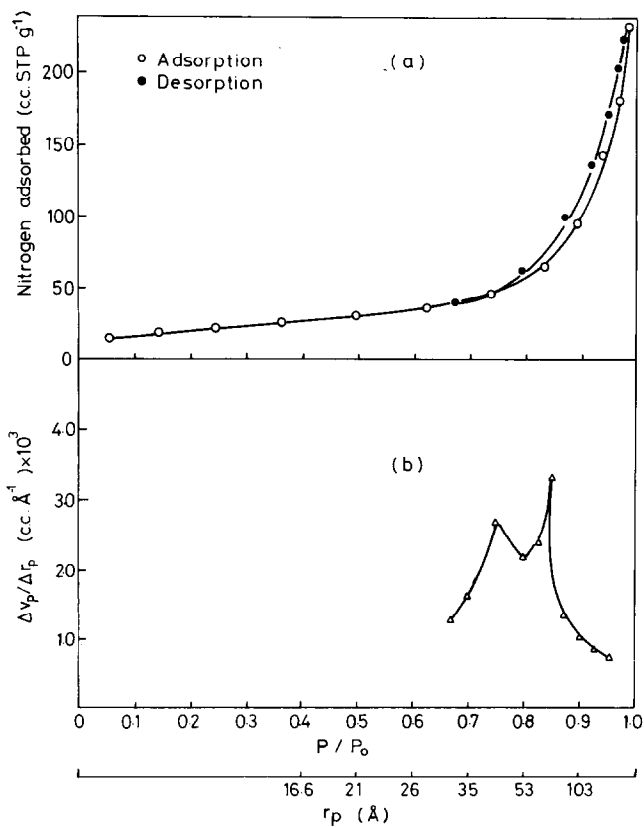


FIG. 4. Pore size distributions from the nitrogen isotherm at 77.5 K on the industrial catalyst C79-4: (a) nitrogen isotherm; (b) pore size distribution curve.

TABLE 4

Chemisorption of CO on Raney Catalysts at 77.5 K

Catalyst	V_m (cm^3 STP/g)	ΔV_{CO}^a	$\Delta V_{\text{CO}}/V_m$
1	3.91	1.67	0.427
2	4.27	1.92	0.450
3	5.03	2.03	0.404
4	5.67	2.18	0.384
5	6.16	2.02	0.328
6	7.00	1.90	0.271
7	7.04	1.72	0.244
8	8.96	0.31	0.035
9	1.07	0.14	0.131
Industrial ^b	16.84	3.25	0.193

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

lysts at temperatures between 203 and 473 K and pressures in the range 1–26 kPa. Figure 6 shows the type of isotherm obtained for catalyst 1 at 473 K. The effect of temperature on the adsorption of carbon monoxide and hydrogen on Raney copper and Raney zinc is shown in Fig. 7. Adsorption data for the catalysts at 473 K are reported in Table 5.

DISCUSSION

The leaching morphology and leaching kinetics of the quenched Al–Cu–Zn alloys have been described elsewhere (15, 16). The alloy $\text{Cu}(\text{Zn})\text{Al}_2$ phase leaches to leave copper while the aluminium-based solution leaches to leave void space. Alloy 1 has as its primary precipitate the phase CuAl_2 while alloys 2–6 have as their primary precipitate the phase $\text{Cu}(\text{Zn})\text{Al}_2$. The $\text{Cu}(\text{Zn})\text{Al}_2$ phase can contain up to 3 wt% zinc (17). The $\text{Cu}(\text{Zn})\text{Al}_2$ phase in alloys 7 and 8 is present as the secondary precipitate. The primary precipitate for alloy 9 is a solid solution of zinc in aluminium.

Surface Physical Properties

Pore radii in the catalysts under discussion are always large enough to support mass transfer processes involved in the re-

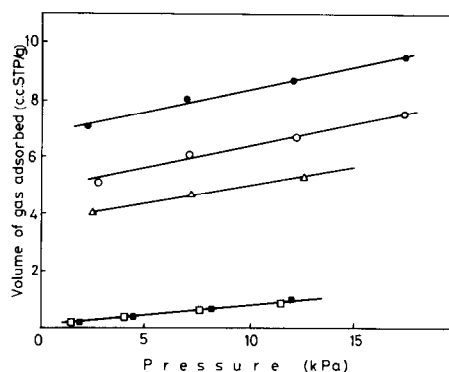


FIG. 5. Adsorption of CO and H_2 on Raney copper-zinc (sample 4) at 77.5 K: ●, CO on catalyst evacuated at 423 K, CO^{I} ; ○, CO on catalyst evacuated at 203 K, CO^{II} ; △, N_2 on catalyst evacuated at 423 K; ■, H_2 on catalyst evacuated at 423 K, H_2^{I} ; □, H_2 on previous sample after evacuation at 77.5 K, H_2^{II} .

action being catalyzed without imposing diffusion limitations. A study of pore development is nevertheless of interest as it provides information on the manner in which a high-surface-area Raney catalyst is formed. Thus compositional and phase constitutional variables in the precursor alloys in large part determine the pore geometry of their product catalysts. Since the pore geometry determines catalyst surface area, it is an important factor in designing alloys for Raney catalyst production.

The surface areas of the fully leached Raney catalysts increase as the zinc content of the precursor alloy is increased. Simultaneously the pore radii, r_p and r_a , decrease. It can be seen from Figs. 2 and 3 that for the

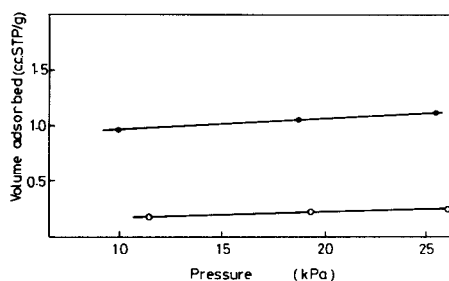


FIG. 6. Adsorption of CO and H_2 on Raney copper (sample 1) at 473 K. ●, CO on catalyst evacuated at 473 K; ○, H_2 on catalyst evacuated at 473 K.

TABLE 5

Carbon Monoxide and Hydrogen Adsorption on Raney Catalysts at 473 K

Catalyst	Carbon monoxide adsorption		Hydrogen adsorption	
	V_{CO} ($\text{cm}^3 \text{g}^{-1}$)	$V_{CO/A_2} V_m$	V_{H_2} ($\text{cm}^3 \text{g}^{-1}$)	V_{H_2}/V_m
1	1.03	0.263	0.187	0.048
4	1.52	0.275	0.626	0.113
8	1.64	0.183	1.39	0.155
9	0.113	0.106	0.141	0.132
Industrial C79-4 ^a	1.33	0.093	3.20	0.222

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

Raney catalysts the pore radii are distributed in a narrow range. By varying the zinc content of the starting alloy and leaching to completion it is possible to produce Raney copper-zinc catalysts with a range of surface areas whilst maintaining a narrow pore size distribution.

The surface area, pore volume, and average pore radius, r_a , of catalyst 1 are in good agreement with the determinations of Wainwright and Anderson (14) who studied the surface and pore structure of a Raney copper catalyst of similar composition. The pore volumes of catalysts 2-7 remain rea-

sonably constant but at lower values than catalyst 1. Since the catalysts are essentially the leach residues of the $\text{Cu}(\text{Zn})\text{Al}_2$ phase, and since the composition of this phase varies only slightly through the series of alloys under consideration, the variation in observed pore volume is presumably to be attributed to the behaviour of the other major alloy phase. In alloy 1 this phase is a frozen eutectic of composition $\text{Cu}_{19}\text{Al}_{81}$, whereas in the other alloys it is an aluminium-zinc solid solution containing a maximum of 3 wt% copper. Leaching of this latter phase appears to leave no residue, the amount of copper being too small to form a coherent structure. However, leaching of the $\text{Cu}_{19}\text{Al}_{81}$ eutectic in alloy 1 may well leave a residue of low surface area containing large-diameter pores, thereby explaining the unusually high pore volume of catalyst 1.

The pore radii, r_p and r_a , for catalysts 2-7 decrease while the surface area increases indicating that for catalysts 2-7 the number of pores per gram of catalyst is increasing. Catalyst 8 has a much lower pore volume but its surface area is higher than those of the other Raney copper-zinc catalysts. Sample 9, produced from the Al-Zn alloy, shows a very low surface area with no defined pore distribution but with an "average" pore radius of 48 Å. In contrast to the Raney catalysts, the industrial catalyst when reduced was found to have a surface area of $73.3 \text{ m}^2\text{g}^{-1}$ and a pore volume of $0.366 \text{ cm}^3\text{g}^{-1}$. The industrial catalyst reveals a broad pore size distribution with pores in the range of 40-70 Å. This is similar to the results of Herman *et al.* (1) who found that a catalyst of composition $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3 = 60/30/10$ exhibited a pore distribution in the range of 40 to 120 Å. The BET argon surface area of that catalyst was $33.4 \text{ m}^2\text{g}^{-1}$ after use.

Copper crystallite diameters measured for some catalysts by X-ray diffraction line broadening (15) are presented in Table 3. Interpore distances were calculated for the range of catalysts studied on the basis of

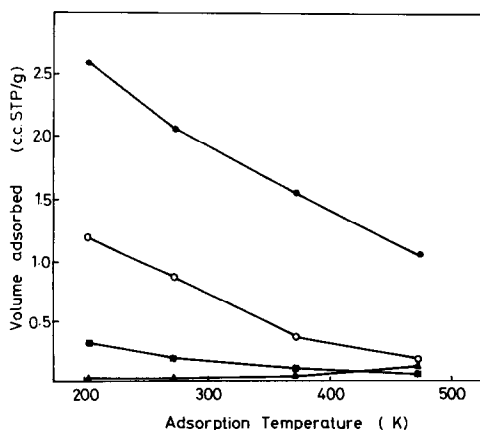


FIG. 7. Adsorption of CO and H₂ on Raney copper (sample 1) and Raney zinc (sample 9) at temperatures between 203 and 403 K: ●, CO on Raney copper; ○, H₂ on Raney copper; ■, CO on Raney zinc; △, H₂ on Raney zinc.

hexagonally arrayed nonintersecting cylinders. Such a model is consistent with the open-ended cylindrical pores indicated by the Type A hysteresis loops in Fig. 1. The inter pore distances are compared with the copper crystallite diameters in Table 3. The considerable agreement between the two results indicates good correlation between the two methods. It is concluded that the microstructural rearrangement accompanying leaching takes place on an exceedingly small scale and that pore size and crystallite size are interdependent, the pores being separated by a single microcrystal of copper. Andrew (6) in his study of catalysts for methanol synthesis and water gas shift states that highly active copper catalysts are made from aggregates of copper crystals about 50–70 Å in size. It is of interest to note that catalysts made by the Raney method have copper crystallites of similar magnitude.

Catalytic Activity

From the catalytic activity data in Table 2 it can be seen that on a mass basis there is an increase in activity from catalysts 1 to 5 and then a decrease in activity in those catalysts whose zinc content in the precursor alloy is 20 wt% or more. However, on a surface area basis catalysts 1–5 have essentially the same activity with perhaps a slight increase in activity for catalyst 5. Again there is a decrease in activity for those cata-

lysts which have a high zinc content in the precursor alloy. Compositional analysis in Table 1 shows that the copper content of each of catalysts 1–5 is greater than 97%. These results are highlighted in Fig. 8 where catalyst activity has been plotted against catalyst copper content. It is suggested that the active component in the fully extracted Raney copper–zinc catalysts for the hydrogenation of carbon monoxide to methanol is copper.

Several authors have concluded that copper is not active for methanol synthesis. Natta (18) in his review on methanol synthesis states that pure cupric oxide is practically inactive for the synthesis of methanol but small amounts of promoters are sufficient to raise its activity to relatively high values. Under reaction conditions the oxide would presumably have been reduced to yield copper metal. Herman *et al.* (1) in an investigation of binary Cu/Zn oxide methanol catalysts found that the activities at 523 K of pure ZnO and reduced copper oxide were zero within detection limits. However, the BET argon surface area of the reduced CuO catalyst measured by Herman *et al.* (1) was only $1.4 \text{ m}^2\text{g}^{-1}$. We have shown that a Raney copper catalyst with a BET nitrogen surface area of $17.0 \text{ m}^2\text{g}^{-1}$ has good catalytic activity.

To resolve the question of the catalytic activity of copper we prepared a copper-on-silica catalyst with a BET nitrogen surface

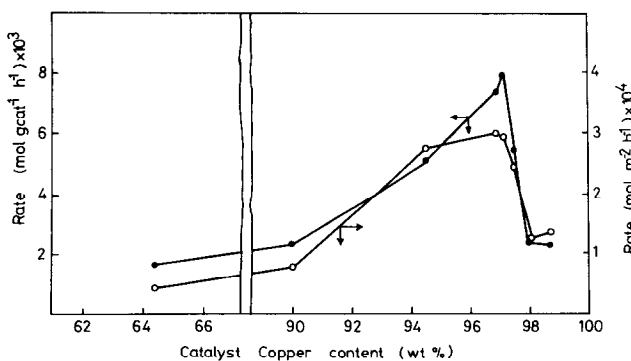


FIG. 8. Activity of the Raney catalysts versus catalyst copper content.

area of $41.5 \text{ m}^2\text{g}^{-1}$ and tested the catalyst under the reaction conditions described previously. The supported copper catalyst was found to have an initial activity of $2.1 \times 10^{-3} \text{ mol/g copper/h}$. This supports the argument that copper is an active catalyst component in the production of methanol from carbon monoxide and hydrogen. The negligible activities observed by Herman *et al.* (1) were presumably a result of the copper sintering. Raney copper appears to be resistant to sintering, at least in the short term. This is perhaps not surprising in view of the catalyst morphology.

The activity of the supported copper catalyst was found to drop to zero within 3 h of being on stream, presumably due to sintering of the catalyst. Raney copper, prepared from alloy 1, was found to lose approximately 50% of its initial activity in the first 5 h on stream before the catalyst attained steady-state conversion. However, a Raney catalyst prepared from alloy 4, which contained 14% zinc, showed little loss in activity before steady-state conversion was attained in the same time period. This suggests that the residual zinc in the Raney catalysts not only increases the catalyst activity but also has some stabilising effect on the catalyst.

A number of authors have investigated the Cu-ZnO catalyst to determine the role of the individual components. Shimomura *et al.* (5) established that the variation of catalytic activity over the Cu-Zn composition range followed closely the variation of effective surface area determined by CO chemisorption. Herman *et al.* (1) suggested that the interaction between the copper and the zinc oxide in conventional catalyst systems is very important in determining catalytic activity. These authors found that up to 12% Cu dissolved in ZnO and they believe that the active component of these oxide catalysts is Cu^{I} dissolved in ZnO. Andrew (6) states that for the Cu-ZnO methanol synthesis catalyst, the catalyst activity is proportional to the copper surface area of the tableted catalyst. Kung (19)

in his review of methanol synthesis concludes by saying that, while progress has been made in characterising the working catalysts, important information on the surface condition of methanol synthesis catalysts is still lacking. Surface characterisation of the Raney catalysts would seem appropriate for determining the nature of the catalyst surface.

Surface Chemical Properties

In this study the chemisorption of carbon monoxide and hydrogen has been employed to give a qualitative estimation of the extent of the catalyst surface that exists as copper or zinc oxide. Figure 7 shows the effect of temperature on the adsorption of carbon monoxide and hydrogen on the Raney copper and zinc surfaces. The adsorption of these gases on the Raney copper and Raney zinc catalysts provides information useful in interpreting the adsorption behaviour of catalysts prepared from the ternary Al-Cu-Zn alloys. The adsorption of carbon monoxide and hydrogen on Raney copper and Raney zinc at 437 K is presented in Table 5. This temperature is close to that at which the methanol synthesis reaction takes place. In order to take into account the differences in surface area of the various catalysts the volume of adsorbate chemisorbed has been divided by the monolayer volume obtained using nitrogen adsorption. Raney copper is seen to adsorb considerably more carbon monoxide than Raney zinc at 473 K. A similar result was obtained at 77.5 K. Raney copper and Raney zinc adsorbed only a small amount of hydrogen at 473 K. After accounting for the lower total surface area of Raney zinc the amount of hydrogen adsorbed was approximately three times that of Raney copper.

Since the Raney catalysts are prepared by a completely different method from conventional catalysts it is important to determine the chemical nature of the zinc and copper under reaction conditions. From the knowledge of the composition of the reactant mixture and the necessary thermody-

dynamic data using a free-energy minimisation computer program, SOLGAS (20), the catalyst in equilibrium with the gas mixture at 513 K and 3450 kPa was found to consist of metallic copper and zinc oxide. With this free-energy minimisation program we did not consider the case of a solid solution of copper in zinc oxide. The X-ray diffraction analysis did not reveal the presence of α -brass which has been reported to be formed in Cu/ZnO catalysts for the water-gas shift reaction (21).

Carbon monoxide and hydrogen adsorption on catalysts prepared from the ternary alloys was also measured at 473 K. The results are presented in Table 5. Carbon monoxide adsorption on the Raney catalysts increases as the zinc content of the precursor alloy increases until 33% zinc in the precursor alloy is attained. After taking into account the monolayer coverage there is a maximum adsorption of carbon monoxide on the catalyst which had 15% Zn in the precursor alloy. This corresponds to the alloy whose resultant catalyst was shown to have maximum catalytic activity for the methanol synthesis reaction. Hydrogen adsorption on the Raney catalysts shows similar trends to those observed for carbon monoxide adsorption. Taking into account the differences in overall surface areas, a maximum adsorption of H₂ is attained for a catalyst derived from a precursor alloy containing 33% Zn.

The activity data in Table 2 together with the adsorption data at 473 K suggest that zinc oxide on the catalyst surface promotes the methanol synthesis reaction and that metallic copper and zinc oxide are together important in determining catalyst activity. The high zinc content of the industrial methanol synthesis catalyst is reflected in the adsorption data of Table 5, which suggest a higher surface zinc oxide concentration than in the Raney catalysts. This material also had higher catalytic activity than the Raney catalysts. In order to achieve greater activities in catalysts prepared by the Raney method it therefore seems to be

necessary to increase their surface concentration of zinc oxide.

CONCLUSIONS

The Raney catalysts have been shown to have an optimal alloy composition for the synthesis of methanol at 50 wt% aluminium, 30–36 wt% copper, and 14–20 wt% zinc. Greatest activity was exhibited by catalysts containing approximately 97 wt% copper. The fully extracted Raney copper-zinc catalysts have been shown to have a narrow pore size distribution with the "average" pore radius decreasing with increasing precursor alloy zinc content. The surface area for the range of catalysts studied was found to increase with increasing precursor alloy zinc content. The active component for these Raney catalysts for the synthesis of methanol was shown to be copper. Carbon monoxide and hydrogen adsorption studies in the temperature range 77–473 K were used to indicate the copper and zinc oxide levels on the catalyst surface. The variation of alloy zinc content permits control of the catalyst surface area and pore radii as well as conferring a slight promotional effect to the catalyst activity.

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