For instance, Haining et al. (30) successfully used an $^{129}Xe^{+}$ implanted α-alumina plate to isolate catalytic ethylene hydrogenation activity due to $^{195}Pt^{+}$ ions implanted to the same dose. BET and copper surface areas of the catalysts before and after WGSR are also presented in Table 4.10.

Table 4.10 **Surface area and crystallite diameter of fresh and used ion implanted Raney copper catalysts**

Sample	Ion Implanted	Ion dosage (ions.cm^{-2}) x 10^{13}	S_{BET} (m^2.g^{-1})	S_{Cu} (m^2.g^{-1})	Copper Crystallite Diameter (Å)
1	None	None	18.9 (10.5)*	5.2 (1.0)	913
2	Zn^{+}	2.51	18.5	6.0	791
3	Zn^{+}	5.21	17.1 (12.3)	5.8 (3.4)	819
4	Zn^{+}	8.04	17.0	6.6	720
5	Zn^{+}	8.16	18.2 (9.3)	7.2 (4.1)	660
6	Kr^{+}	4.23**	18.1 (11.0)	6.4 (1.5)	742

* Results in brackets for used catalysts
** Theoretically calculated (Equation 2.6) Kr^{+} ion dosage

From Table 4.10 it is evident that increasing dosage levels correspond to a decrease in average copper crystallite size and slight increases in active metal surface area. The trend is "masked" by less sensitive changes in the total surface area. It is considered that implanting ion dosages well in excess of normal operating levels causes either fragmentation of the existing crystallites, or the emergence of smaller structures from atoms or groups of atoms displaced from the larger copper crystallites (see Section 4.1.3). The overall effect of radiation damage was increased copper surface area which resulted in higher initial catalyst activities as shown in Figure 4.15.

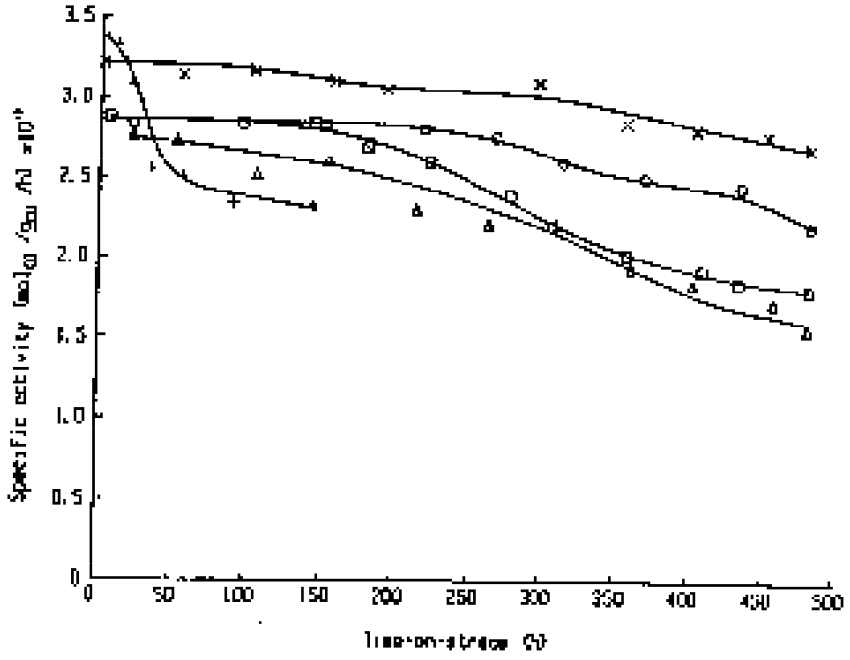

Figure 4.15 Stability of ion implanted Raney copper catalysts^

+ = 4.23 x 10^{13} Kr^+ ions cm^{-2}; △ = No ion implantation;
□ = 5.21 x 10^{13} Zn^+ ions cm^{-2};
⊙ = 8.04 x 10^{13} Zn^+ ions cm^{-2};
× = 8.36 x 10^{13} Zn^+ ions cm^{-2}

^ Temperature = 200°C; Total GHSV = 1000 h^{-1}; Dry gas composition = 10% CO/90% N_2; CO:H_2O = 1:22.5; Catalyst Volume = 2 ± 0.1 ml

WGS activity is observed to be influenced by the active copper surface area but no direct proportionality is apparent (see Chapter 5 for a detailed discussion). Prolonged activity is a function of zinc dosage. Krypton ions demonstrated no stabilizing influence on initial Raney copper activity enhanced by radiation damage, whilst long term stability increased with increasing zinc content. The active form of zinc in the catalyst was not determined, but is considered to be ZnO. An X-ray spectral micro-analysis (10) of an oxidised leached granule showed a localized oxygen concentration of approximately 25 wt% extending into the particle by a distance corresponding to 1/4 of the

overall diameter. The relationship between zinc loading and Raney copper catalyst stability is similar to that found for the Cu-ZnO-$A\ell_2O_3$ catalysts produced by leaching Alloy C with sodium hydroxide (see Section 4.4). Therefore, the correspondence between these two types of catalysts implies that the resulting copper surface area stability (and hence activity) is independent of the origin of the zinc. The stabilizing effect of near-surface low zinc implanted concentrations confirms the conclusions of Friedrich *et al.* (2) who reported that residual zinc in Raney catalysts has a "stabilizing influence" on the catalysts during methanol synthesis (see Section 4.1).

The ion implantation technique confirmed the important role of zinc as a stabilizing support material in Raney copper catalysts operated for the WGSR.

4.3.4 Zinc impregnation

Of considerable importance in the development of catalysts (for the WGSR) is long term stability (1). From the studies of a series of partially leached and ion implanted Raney copper catalysts (Sections 4.4 and 4.5 respectively) zinc oxide was observed to assist in the process of stabilizing copper crystals by acting as a suitable spacer material. Long term stability was found to be related to the level of zinc present in the catalyst which was, in turn, strongly dependent on leach time. Decreased stability resulted from a decrease in zinc oxide concentration in the reacted rim. Varying concentrations of zinc impregnated Raney copper catalysts were produced by leaching Alloy C for 2 hours in solutions of either 0.1; 0.5 or 0.75M sodium zincate in 7.1M sodium hydroxide, according to the procedure outlined in Section 4.2. From the XRD pattern of the 0.5M zincate/hydroxide leached catalyst, zinc oxide (ZnO) was identified as the major precipitated product from the JCPDS file at d-spacings of 2.7944; 2.5974; 2.4591; 1.9087; 1.6195; 1.4742; 1.4124 and 1.3774. Correct relative peak intensities were observed.

AA analysis of the zinc impregnated catalysts and a 7.1M sodium hydroxide leached catalyst are presented in Table 4.11 below:-

Table 4.11 **Bulk composition of zinc impregnated Raney copper catalysts**

Zincate conc. (M)	Extraction time (h)	Composition before WGSR (wt%)		
		Cu	Zn	Aℓ
0	2.0	76.1	3.2	19.7
0.1	2.0	74.9	5.4	17.6
0.5	2.0	71.9	8.1	18.6
0.75	2.0	63.2	14.7	20.8

The results suggest that a higher concentration of zinc in the leach solution corresponds to a greater deposition of zinc into the Raney copper catalyst.

Curry-Hyde *et al.* (6) observed that the relative mass loading of Aℓ in Raney Cu-Zn-Aℓ catalysts leached in a constant zincate/hydroxide solution at various temperatures remained more-or-less the same with an increase in zinc loading. Cross-sectional EDAX analysis of the 0.5M zincate leached catalyst (Table 4.12) showed a 7.2 times zinc excess in the rim compared to a catalyst produced with no zincate added to the caustic leach solution.

Table 4.12 **Rim and core compositions of zinc impregnated Raney copper catalysts**

Zincate conc. (M)	Extraction time (h)	Rim (wt%)			Core (wt%)		
		Cu	Zn	Aℓ	Cu	Zn	Aℓ
0	2.0	90.1	2.9	6.9	39.5	14.2	46.4
0.5	2.0	74.6	21.0	4.4	40.4	13.8	45.9

Curry-Hyde *et al.* (6) used electron microprobe analysis to show that the ZnO concentrations increased steadily across the rim of a zincate/hydroxide leached Cu-Zn-Aℓ alloy pellet towards the surface.

The total and copper surface areas together with copper crystallite diameters of the zincate/hydroxide leached catalysts are presented in Table 4.13. Corresponding pore volumes and mean pore radii are given in Table 4.14.

Table 4.13 **Surface area and crystallite diameter of fresh and used zinc impregnated Raney copper catalysts**

Zincate conc. (M)	Extraction time (h)	S_{BET} ($m^2.g^{-1}$)	S_{Cu} ($m^2.g^{-1}$)	Copper Crystallite Diameter (Å)
0	2.0	32.8	15.8 (10.1)[a]	324 (514)
0.1	2.0	28.2	14.6 (9.7)	345 (519)
0.5	2.0	23.9	11.3 (9.1)	428 (531)
0.75	2.0	9.5	4.2	1012

[a] Results in brackets for used catalysts

Table 4.14 **Pore volume and mean pore radii of zinc impregnated Raney copper catalysts**

Zincate conc. (M)	Extraction time (h)	Pore volume ($cm^3.g^{-1}$)	MPR[a] (Å)
0	2.0	0.197	121.2
0.1	2.0	0.15	133.6
0.5	2.0	0.027	127.8
0.75	2.0	0.028	116.2

[a] MPR = Mean Pore Radii

Total BET surface area was observed to decrease with increasing zincate concentrations in sodium hydroxide (and zinc loading) for similar leach conditions. Curry-Hyde et al. (8) observed a decrease in the diffusion controlled leaching rate when high concentrations of zincate were present in the sodium hydroxide solution. This effect is significant because previous studies (14) using caustic solution showed that the rate of leaching affected the pore spacing and consequently influenced the surface area of the freshly leached material (see Section 4.1.1). It is considered that adding increasingly concentrated zincate to the caustic leach solution effectively slows the rate (for a constant leach time) causing a change in the leaching behaviour. Pore volume and pore radii were observed to generally decrease with decreasing leach rate (Table 4.14). The lower leach rates promoted an increase in copper crystallite size due to their re-arrangement which consequently resulted in a loss of surface area in the leached copper structures. This microsegregation process has been classically regarded (9, 31) to take place through an aging process brought about whilst the alloy was in contact with sodium hydroxide solution. The results in Table 4.13 suggest that this process is also linked to the leaching rate. No evidence of deposits of zinc oxide or alumina decreasing pore volume and pore radii were observed. The leaching process in zincate/hydroxide solutions is therefore regarded as the fundamental determinant of catalyst surface morphology.

The initial activity and stability of Raney copper catalysts produced from leaching Alloy C for 2 hours in varying zincate concentrations is shown in Figure 4.16.

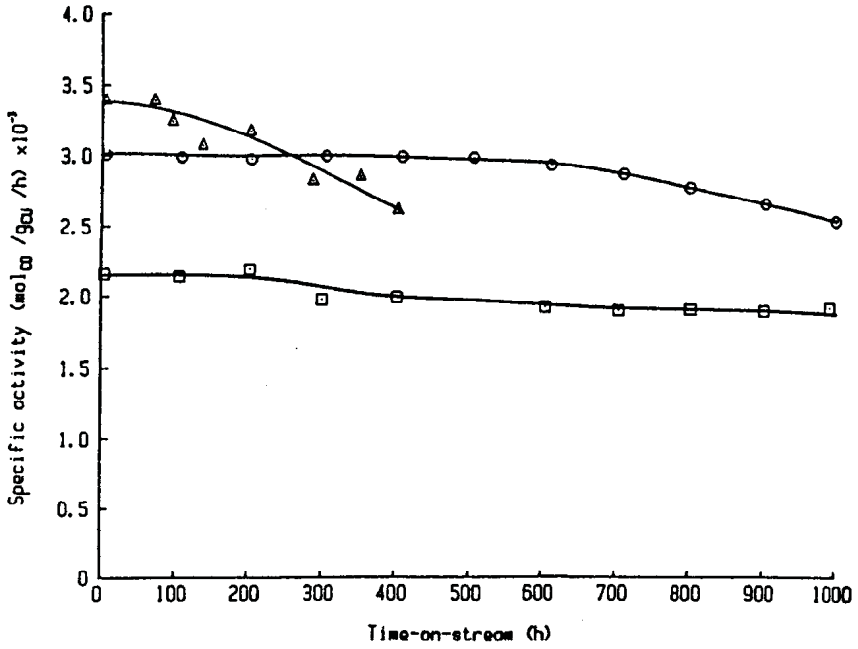

Figure 4.16 **Stability of zinc impregnated Raney copper catalysts[a]**

△ = No zincate added to caustic solution;
⊙ = 0.1M Zincate; ⊡ = 0.5M Zincate

[a] Temperature = 200°C; Total GHSV = 1000h^{-1}; Dry gas composition = 10% CO/90% N_2; CO:H_2O = 1:22.5
Catalyst Volume = 2 ± 0.1ml

From Figure 4.16 it can be seen that while improving the stability of copper crystallites, deposited zinc oxide also causes a decrease in initial catalyst activity due to the smaller surface areas of Raney copper catalysts resulting from leaching in caustic solutions with high concentrations of zincate (Table 4.13). The catalyst prepared by caustic leaching in a solution containing 0.1M zincate showed a 15.4% loss in activity up to 1000 hours-on-stream, whilst the 0.5M zincate leached catalyst lost 10.6% in activity over the same time period. The catalyst leached in only caustic solution demonstrated a 22.8% activity loss in only 400 hours-on-stream. Curry-Hyde *et al.* (8) successfully used zincate/hydroxide leached Raney copper catalysts to demonstrate that methanol synthesis activity is related to

the ZnO loading on the leached surface. The authors concluded that the dispersion of ZnO on the copper surface increased with an increased ZnO loading.

4.4 SUMMARY

Characterisation of partially leached Raney copper catalysts demonstrated that the chemical nature of the reactant surface could be determined by controlling the leaching process. Initial WGS activity at the stated conditions compared favourably to the co-precipitated and industrial catalyst alternatives due to a similar active phase composition and high metallic copper surface areas. Raney copper catalyst deactivation in a poison-free environment was attributed to a zinc oxide deficiency. Stability increased significantly with increased ZnO loading as a result of better contact between the copper surface and ZnO crystallites. The stabilizing effect of incorporated zinc was independent of its original source. The role of aluminium was to produce Raney copper of high surface area. No beneficial effects of residual alumina in the active catalysts were observed.

4.5 REFERENCES

1. W.L. Marsden, M.S. Wainwright and J.B. Friedrich, *Ind. Eng. Chem. Prod. Res. Dev.*, 19, (1980), 551.

2. J.B. Friedrich, M.S. Wainwright and D.J. Young, *J. Catal.*, 80, (1983), 1.

3. "*ICI Catalysts 53-1 Low Temperature Shift Conversion Operating Manual*", Imperial Chemical Industries, Billingham, Cleveland, England.

4. A.J. Bridgewater, M.S. Wainwright, D.J. Young and J.P. Orchard, *Appl. Catal.*, 7, (1983), 369.

5. G. Dearnaley, *Nature*, 256, (1975), 701.

6. H.E. Curry-Hyde, M.S. Wainwright and D.J. Young, *Appl. Catal.*, 77, (1991), 75.

7. H.E. Curry-Hyde, M.S. Wainwright and D.J. Young, *Appl. Catal.*, 77, (1991), 89.

8. H.E. Curry-Hyde, M.S. Wainwright and D.J. Young, in *"Methane Conversion"*, (b.M. Bibby, C.D. Chang, R.F. Howe and S. Yurchak, eds.), Elsevier Science Publishers B.V., Amsterdam, (1988), 239.

9. A.D. Tomsett, H.E. Curry-Hyde, M.S. Wainwright, D.J. Young and A.J. Bridgewater, *Appl. Catal.*, 33, (1987), 119.

10. A. Andreev, V. Kafedjiiski, T Halacher, B. Kunev and M. Kaltchev, *Appl. Catal.*, 78, (1991), 199.

11. M.S. Wainwright, D.J. Young and A.J. Bridgewater, *"Commonwealth of Australia National Energy Research, Development and Demonstration Program"*, Report Nr. 376, (1984).

12. L.F. Mondolfo, *"Aluminium Alloys: Structure and Properties"*, Butterworths, London, (1976).

13. J.B. Friedrich, D.J. Young and M.S. Wainwright, *J. Electrochem. Soc.*, 128, (1981), 1840.

14. J.B. Friedrich, D.J. Young and M.S. Wainwright, *J. Catal.*, 80, (1983), 14.

15. T. van Herwijnen and W.A. de Jong, *J. Catal.*, 34, (1974), 209.

16. J.B. Friedrich, D.J. Young and M.S. Wainwright, *J. Electrochem. Soc.*, 128, (1981), 1845.

17. A. Andreev, T. Haltchev, V Kafedjiiski, B. Kunev, M. Kalchev, I. Orizarski and D. Shopov, "*Proc. VIth Int. Symp. Heterogeneous Catalysis, Part 1*", Sofia, (1987), 235.

18. A.D. Tomsett, M.S. Wainwright and D.J. Young, *App. Catal.*, 12, (1984), 43.

19. H.E. Curry-Hyde, D.J. Young and M.S. Wainwright, *J. Electrochem. Soc.*, 135, (1988), 1902.

20. O. Levenspiel, "*Chemical Reaction Engineering*", Wiley, New York, (1972).

21. N.I. Onuoho, A.D. Tomsett, M.S. Wainwright and D.J. Young, *J. Catal.*, 91, (1985), 25.

22. J.H. de Boer, in "*Structure and Properties of Porous Materials*", (D.H. Everett and F.S. Stone, eds.), Butterworths, London, (1958), 68.

23. A.D. Tomsett, D.J. Young and M.S. Wainwright, *J. Electrochem. Soc.*, 131, (1984), 2476.

24. A.D. Tomsett, D.J. Young and M.S. Wainwright, *Appl. Catal.*, 35, (1987), 321.

25. G. Rasulic, S. Jovanovic and Lj. Milanovic, *Thermochimica Acta*, 62, (1983), 1.

26. F. Chongzheng, M.S. Wainwright and D.L. Trimm, *Appl. Catal.*, 54, (1989), 53.

27. F. Chongzheng, W. Changsui, W. Shengjun, Wi. Youshi, D.L. Trimm and M.S. Wainwright, *Chin. Chem. Lett.*, 1, (1990), 279.

28. W.J. Lywood, "*Catalyst Handbook*", 2nd ed., (M.V. Twigg ed.), Wolfe Publishing, England, (1989).

29. E. Ruckenstein, in "*Metal-Support Interactions in Catalysis, Sintering, and Redispersion*", (S.A. Stevenson, J.A. Dumesic, R.T.K. Baker and E. Ruckenstein, eds.), Van Nostrand Reinhold Company, New York, (1987), 144.

30. I.H.B. Haining, P. Rabette and M. Che, "*Proc. Int. Cong. Catal., 7th*", (1981), 317.

31. A.D. Tomsett, D.J. Young, M.R. Stammbach and M.S. Wainwright, *J. Mat. Sci*, 25, (1990), 4106.

CHAPTER FIVE

THE INITIAL OPTIMISATION OF RANEY COPPER CATALYSTS

5.1 INTRODUCTION

The initial evaluation of Raney copper catalysts for the WGSR showed that zinc was essential for maintaining high catalyst activity. Whilst leaching is required to produce operable surface areas, it also results in the depletion of zinc from the resultant catalyst. Partial leaching of the Cu(35) Zn(15) Aℓ(50) alloy demonstrated that the best catalyst stability (achieved after the shortest leach time of 1.0 hour) corresponded to the highest catalyst zinc content. Increasing the zinc loading during extraction (zinc impregnation) improved stability but decreased activity. Thus, in an attempt to improve the overall Raney copper catalyst performance, precursor alloys with increased zinc content (at the expense of copper) were leached in caustic solution for a maximum of only one hour. Characterisation studies on all the catalysts were conducted. Catalyst activity was evaluated as a function of lifetime, operating temperature and reagent feed rate. Consequently, based on characterisation and activity criteria, an optimal precursor alloy composition of Cu(25) Zn(25) Aℓ(50) (Alloy B) was identified and used for acid leaching studies. A further statistical evaluation of catalyst preparation variables (reported in Chapter 6) was also conducted on Alloy B. A catalyst made from an alloy of nominal composition Cu(43) Zn(18) Aℓ(39) (Alloy E) which was recently reported by Bridgewater *et al.* (1) to produce catalysts of greater mechanical strength to those prepared from alloys containing 50wt%, Aℓ, was also tested.

A literature survey revealed that in general, little research has been conducted on catalysts produced by the acid leaching of ternary Cu-Zn-Aℓ alloys. It was therefore

considered appropriate to conduct characterisation and activity studies of Raney copper catalysts prepared in this manner. Characterisation of Alloy B of nominal composition Cu(25) Zn(25) Al(50) and resultant catalysts prepared by leaching in nitric as well as perchloric acid, was carried out. Nitric acid was chosen as a leachant because of its ability to act as an oxidising agent at high concentrations, and an acid at low concentrations (2). The nitrate counter ion is also considered to be catalytically non poisonous. Perchloric acid was chosen since the perchlorate counter ion is soluble in aqueous solutions (2) and hence easily removed during the catalyst wash. Statistically designed experiments were used to optimise preparation variables. Activity and stability studies were conducted on the most promising catalysts.

5.2 EXPERIMENTAL

Particles (0.5 - 1.18mm in diameter) of Alloys A, B, C, and E were leached for one hour in 7.1M aqueous sodium hydroxide at 50°C, and subsequently passivated according to the detailed description given in Appendix 1. Also, 0.5 - 1.18mm particles of Alloy B were leached for one hour in both nitric and perchloric acids of 5, 14 and 27.5 mass% for characterisation purposes (see Chapter 2, Section 2.1.1). Characterisation data for acid and base leached alloys was obtained from AA, SEM, EDAX, XRD, pulse N_2O chemisorption, total BET surface area, pore volume and mean pore radii determinations (detailed in Chapter 2, Section 2.5). Acid leached Raney copper catalysts were chosen for WGS activity and stability evaluation from the responses generated by two 2^3 *factorially* designed experiments used to evaluate the preparation variables (i.e. particle size range, acid strength and acid/metal ratio) shown to be significant for catalyst activity in the caustic leaching process (see Chapter 6 for details). In this case, Alloy B particles were leached with nitric and perchloric acid. All catalysts were placed on-stream at the relevant start-up temperature. In cases where catalytic performance was

investigated under different experimental conditions (i.e. temperature and GHSV), reactor conditions were returned to those employed at the initial start-up of the catalyst, in order to restore the original activity of the system before proceeding with further testing. If the original activity could not be re-established due to catalyst deactivation, new samples (of similar initial activity obtained under identical conditions) were evaluated. For temperature and GHSV studies, WGS activity was only recorded after steady-state conditions had been achieved.

5.3 RESULTS AND DISCUSSION

5.3.1 Characterisation of caustic leached precursor alloys

Bulk XRD analysis (Table 5.1) of Alloys A, B and E confirmed the primary precipitation products of Al (Alloy A), and Cu(Zn)Al_2 (Alloys B and E) predicted from the liquidus phase diagram (Chapter 2, Figure 2.1). The Zn content of the Cu(Zn)Al_2 phase is known (3) to increase with increasing alloy Zn level.

Table 5.1 Crystalline phases of Alloys A, B and E and their product Raney copper catalysts before and after reaction

Alloy	Precursor alloy phases	Cat. phases before reaction[a]	Cat. phases after reaction[a]
A	Al, $CuAl_2$, Zn (AlZn)[b]	CuO, Zn, Al, Cu_2O, Cu(tr)	Cu, Zn, CuO, Al
B	$CuAl_2$, Al, Zn (AlZn)	CuO, Zn, Al, Cu, $CuAl_2$, Cu_2O(tr)[c]	Cu, Zn, Al, CuO, $CuAl_2$(tr)
E	$CuAl_2$, Al, Zn, (AlZn), CuAl	CuO, Zn, $CuAl_2$, Cu, Cu_2O, CuAl	Cu, Zn, CuAl, CuO, $CuAl_2$(tr)

[a] Phases listed in approximate order of abundance (from left to right)
[b] Phase in brackets not conclusively identified
[c] (tr) = trace

Alloy A showed a high secondary concentration of the

$Cu(Zn)Al_2$ phase whilst Alloys B and E demonstrated secondary solidification products of Al. The Al phase content of Alloy B was almost equivalent to the amount of $Cu(Zn)Al_2$ phase present, as a result of the strong secondary influence of Al precipitation (observed from the liquidus phase diagram - Chapter 2, Figure 2.1). Alloys A, B and E contained elemental Zn and in each case, some evidence was found for the presence of the binary AlZn phase. The XRD pattern of Alloy E (Table 5.1) showed traces of CuAl which was impervious to caustic leaching as previously observed for the leaching of Alloy C under similar conditions (see Chapter 4, Table 4.3). No evidence of any ternary phases was found. Passivated Raney copper catalysts A, B, C and E produced by leaching in aqueous sodium hydroxide for one hour consisted predominantly of crystalline CuO, whilst smaller amounts of Cu_2O were also observed. After reaction and subsequent exposure to air, most copper remained in the zero oxidation state. The XRD pattern of the air-dried Alloy C catalyst (prepared under the same conditions and extraction time as the passivated catalysts) showed Cu_2O followed by CuO as the major phase products. Cross-sectional electron-micrographs of catalysts A, B, C and E revealed clearly identifiable reacted rims and alloy cores. The extent of average leach penetration after one hour was calculated as 36.5%, 35.2%, 32.0% and 24.0% for catalysts A, B, C and E respectively. In all cases, two "leach fronts" were observed (as described in Chapter 4, Section 4.3.1(a)). Catalyst development was consistent with the <u>first stage</u> of leaching which corresponds to the formation of an "alloy-catalyst" interface in ternary Cu-Zn-Al alloys. Initial characterisation studies reported in Chapter 4 also show that this stage generally corresponds to a Raney copper catalyst surface morphology best suited for catalysing the WGSR.

The bulk metal content (determined by AA) of Alloys A, B, C and E leached in caustic solution for 1.0 hour (Section 5.2) and passivated are presented in Table 5.2. Analysis

of catalysts before and after reaction are shown.

Table 5.2 Bulk composition of fresh and used Raney copper catalysts produced from leaching various alloy precursors

Alloy	Extraction time (h)	Composition before WGSR (wt%)			Composition after WGSR (wt%)		
		Cu	Zn	Aℓ	Cu	Zn	Aℓ
A	1.0	61.5	15.1	19.1	59.7	14.8	21.7
B	1.0	72.4	13.3	12.9	69.1	15.0	11.1
C	1.0	69.3	6.9	19.5	70.9	8.6	78.3
E	1.0	73.6	10.9	14.8	74.5	7.3	13.1

No iron impurities were detected in any of the precursor alloys or catalysts and mass deficits were therefore considered to be due to catalyst oxygen content. The bulk metal compositions of the one hour leached Alloy C catalyst after air drying (Table 4.1) and passivating (Table 5.2) were similar, as expected. Approximately 1.6 wt% more oxygen was associated with the passivated Cu-Zn-Aℓ catalyst. During the controlled passivation of a caustic leached Cu(50.3) Aℓ(49.7) alloy using N_2O as oxidant, Tomsett *et al.* (4) calculated that at 200°C, a minimum oxygen uptake equivalent to four monolayers was sufficient to passivate the catalyst. The results in Table 5.2 show that catalysts prepared from precursor alloys with higher zinc levels (Chapter 2, Table 2.1) contain higher levels of zinc after 1 hour of leaching. No significant changes in catalyst compositions were apparent after reactor testing. From cross-sectional EDAX determinations (Table 5.3) this trend was qualitatively confirmed in the rim of the fresh Raney copper catalysts.

Table 5.3 Rim and core compositions of Raney copper catalysts produced from leaching various alloy precursors

Alloy	Extraction time (h)	Rim (wt%)			Core (wt%)		
		Cu	Zn	Al	Cu	Zn	Al
A	1.0	66.3	27.1	6.6	16.9	31.4	51.7
B	1.0	79.7	15.7	4.6	27.7	26.1	46.2
C	1.0	81.0	12.1	6.9	37.0	15.2	47.8
E	1.0	79.7	13.7	6.6	40.3	21.4	38.3

EDAX measurements of the alloy core compositions were in good agreement with the AA analysis (Chapter 2, Table 2.1) of the precursor alloys, demonstrating that the composite alloy cores were unaffected by the caustic leaching reaction.

The BET and copper surface areas, together with crystallite diameter and copper dispersion of Catalysts A, B, C, and E are presented in Table 5.4.

Table 5.4 Surface area, crystallite diameter and copper dispersion of fresh and used Raney catalysts produced from leaching various alloy precursors

Alloy	Extraction time (h)	S_{BET} ($m^2.g^{-1}$)	S_{Cu} ($m^2.g^{-1}$)		Copper crystallite Diameter (Å)		Copper Dispersion (%)	
A	1.0	66.9 (27.0)*	12.8	(8.3)	323	(484)	6.2	(4.0)
B	1.0	44.3 (22.0)	18.4	(6.3)	265	(738)	7.3	(2.6)
C	1.0	30.0 (18.6)	11.8	(4.1)	395	(1538)	4.6	(1.2)
E	1.0	25.4 (13.0)	8.7	(2.5)	569	(2004)	3.5	(0.7)

* Results in brackets for used catalysts

The large amount of Al solidification product present in the alloy precursors of Catalysts A and B (Table 5.1) correlates to the high BET and copper surface areas observed for these two catalysts. As it is known that intergranular phases of Al, Zn and AlZn leach at a faster rate than the $Cu(Zn)Al_2$ phase (Chapter 4, Section 4.3.1(b)) it is feasible to consider that extensive leaching of Alloys A and B to produce porous Raney copper may have already occurred within a caustic contact time of only one hour. The greater extent of leach penetration for catalysts A and B is consistent with this explanation. For Alloys (A, B, C, and E) the level of Al appears to drop more rapidly from initial levels than observed for Zn. Of significant importance is the fact that high copper surface area (catalysts A and B), is accompanied by large amounts of evenly dispersed ZnO in the leached rim. In particular, catalyst B exhibits a copper surface area over twice as large as that measured for the ICI 53-1 (industrial) WGS catalyst (Chapter 6, Table 6.4) as well as a rim Zn content 3% greater than the Zn level associated with the most stable Raney catalyst (Alloy C leached for 1.0 hour, Chapter 4, Table 4.2) tested for WGS activity over 1,000 hours (Chapter 4, Figure 4.12). Catalyst B also showed the highest copper surface dispersion and the lowest crystallite size observed for Raney copper catalysts. Catalyst A contained the greatest amount of zinc (Table 5.2) observed, together with a copper surface area larger than the values determined (Chapter 4, Table 4.11) for all hydroxide/zincate leached alloys. Catalysts A and B have similar pore volumes of 0.334 and 0.399 $cm^3.g^{-1}$ and mean pore radii of 59.6 and 190.1 Å respectively.

In many instances the air drying of catalysts prepared from Alloys A and B led to rapid oxidation and subsequent thermal sintering of the copper crystallites. The result was a decrease in WGS activity brought about by decreases in copper surface area. In some cases the area decreased by more than 40% of the value observed for equivalent passivated catalysts. Tonsett et al. (4) showed that

passivation (as compared to air drying) by oxidation with nitrous oxide caused only very minor changes to the pore structure and surface area of Raney copper. Thus, for this study it was concluded that the controlled oxidation of Raney copper catalysts by passivation in nitrous oxide (see Appendix 1) was necessary and acceptable to prevent the possibility of sintering occurring as a consequence of the pyrophoric nature of Raney copper.

DSC was used to simulate reduction conditions under 5% H_2/N_2 at a flow rate of 30 ml/min. Catalysts A, B, C and E were heated from ambient to 300°C at a rate of 5°C/min. As observed for the reduction of the air-dried Alloy C catalysts (Chapter 4, Section 4.3.1(e)) under similar conditions, a single exothermic phase change between 160 - 210°C was recorded for the catalysts passivated after extraction. The phase change is considered to be due to the formation of elemental copper from copper oxides (see Chapter 4, Section 4.3.1(e)).

5.3.2 Activity and stability of caustic leached Alloys A, B, C and E

(a) Initial activity

The initial activity and stability of Catalysts A, B, C and E were measured using the procedure and conditions described in Chapter 2, Section 2.2. Initial activities of one hour leached Catalysts A, B, C and E are expressed as the rate (per hour) of moles of carbon monoxide converted as a function of: volume of catalyst particles (Rate a), composite (total) mass of catalyst particles (Rate b), specific copper surface area (Rate c) and BET surface area (Rate d). Results are presented in Table 5.5.

Table 5.5 Specific activities of Raney copper catalysts produced from leaching various alloy precursors[a]

Alloy	Extraction time (h)	Rate (a) ($mol_{CO}/ml/h$) x 10^{-3}	Rate (b) ($mol_{CO}/g_{comp}/h$) x 10^{-3}	Rate (c) ($mol_{CO}/m^2_{Cu}/h$) x 10^{-4}	Rate (d) ($mol_{CO}/m^2/h$) x 10^{-5}
A	1.0	3.08	3.67	2.86	5.48
B	1.0	3.44	3.91	2.12	8.83
C	1.0	3.2	2.13	1.80	7.11
E	1.0	3.28	1.89	2.18	7.47

[a] Temperature = 200°C; Total GHSV = 1000 h^{-1}; Dry gas composition = 10% CO/90% N_2; CO:H_2O = 1:22.5; Catalyst Volume = 2 ± 0.1 ml

As described in Chapter 4 the unit density of precursor alloys is dependent on composition, necessitating careful interpretation of activity data involving the mass of Raney catalysts. Based on volume of catalyst, high initial activities are observed to correspond to high copper surface areas (see Table 5.4). All Raney copper catalysts (A, B, C and E) are more active than the industrial ICI 53-1 and co-precipitated alternatives reported in Chapter 4, Table 4.9. Activities expressed in terms of composite mass (Rate b) and specific copper surface area (Rate c) are expectedly low due to the nature of Raney copper (see Chapter 4). Activities based on total surface area turnover frequency (Rate d) demonstrate a greater overall surface efficiency than the industrial and co-precipitated catalysts and implies a higher concentration of active sites per unit surface area in Raney copper catalysts.

(b) Stability

The long term stability of Raney copper catalysts A, B, C and E under constant reaction conditions are shown in Figure 5.1. Rates are expressed in terms of mass of