

Raney copper catalysts for the water-gas shift reaction II. Initial catalyst optimisation

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Abstract

The initial Raney copper WGS activity based on catalyst volume has been shown to be comparable to industrial and co-precipitated alternatives under varying reaction conditions. The presence of zinc oxide in the Raney copper structure was shown to be necessary for resisting catalyst deactivation due to copper crystallite sintering. Over long operating times, greater stability was maintained by increasing the Raney catalyst zinc content by leaching precursor Cu–Zn–Al alloys with zinc contents of up to a nominal 40 wt% for 1 h. Achieving a high catalyst zinc concentration by leaching alloys with a higher zinc content proved to be more beneficial than by increasing the catalyst zinc concentration by the zinc impregnation process. The addition of concentrated zincate to the caustic solution slowed the leach rate, promoting an increase in copper crystallite size with a corresponding decrease in copper surface area and WGS activity. Leaching precursor alloys with higher zinc contents was effective for increasing the rim zinc content of the Raney catalyst without inhibiting the leach rate and the development of large copper surface areas. A statistically significant correlation was observed between the WGS activity of Raney copper catalysts and their active metal surface areas, demonstrating that the WGS reaction is a structure insensitive reaction over Raney copper. © 1997 Elsevier Science B.V.

Keywords: Water-gas shift reaction; Raney catalyst; Copper catalyst; Synthesis; Sintering

1. Introduction

Caustic leached Raney copper catalysts have been shown to be active for the low temperature water-gas shift reaction (WGS) [1]. This result was not surprising since rim compositions similar to well-known

low temperature WGS ternary Cu–ZnO–Al₂O₃ catalysts were identified.

To achieve highly active, well stabilised Raney copper catalysts for the WGS, a high concentration of zinc in the structure was shown to be essential [1]. Whilst leaching is required to produce operable surface areas, it also results in the depletion of zinc from the resultant catalyst. Partial leaching of a Cu(35)Zn(15)Al(50) alloy demonstrated that the best

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catalyst stability, achieved after the shortest leach time of 1.0 h, corresponded to the highest catalyst zinc content. Increasing the catalyst zinc loading by zinc impregnation during extraction improved stability, but resulted in an overall decrease in activity [1].

Although it is evident that an intimate contact between the copper surface and zinc oxide crystallites has a stabilizing influence on the catalyst activity [1], it is unclear as to whether any promotion of the WGS reaction occurs at the Cu–ZnO interface. Contrasting views of the function of ZnO in the copper-based formulation have previously been proposed. Some authors [2,3] have argued that a synergy exists between copper and zinc whilst others have taken the view that zinc oxide principally acts as a support for maintaining a dispersed copper surface [4]. In a recent review of methanol synthesis over Raney copper catalysts, Wainwright and Trimm [5] concluded that although no unique promotional role could be ascribed to ZnO (or Al_2O_3), there was some evidence that the catalytic activity could be improved by events occurring at the Cu–ZnO interface.

In this publication we have attempted to improve the overall Raney copper catalyst performance, by leaching precursor alloys with increased zinc content (at the expense of copper) in caustic solution for a maximum of only 1 h. Catalyst activity was evaluated as a function of lifetime, operating temperature and reagent feed rate. Characterisation studies on all the catalysts were also conducted.

Controversy still exists with regard to the reaction mechanism [6] and the structure sensitivity of the WGS reaction over Cu–ZnO– Al_2O_3 catalysts [7]. Much evidence has been presented in an attempt to elucidate the precise mechanistic pathway [6,7], but little is known about the structure-sensitivity relationship of the WGS reaction over copper-based catalysts. Recently, structural influences on activity have also been considered. Chinchén and Spencer [8] classified reactions over supported copper catalysts according to the influence of various physicochemical properties of the catalyst on activity. Notably, crystal size and shape effects were regarded as less important in copper catalysts. Sensitive catalytic reactions were identified when the activity under standard reaction conditions was strongly dependent on catalyst composition, size distribution of metal crystallites, nature of catalyst support, catalyst preparation parameters and impuri-

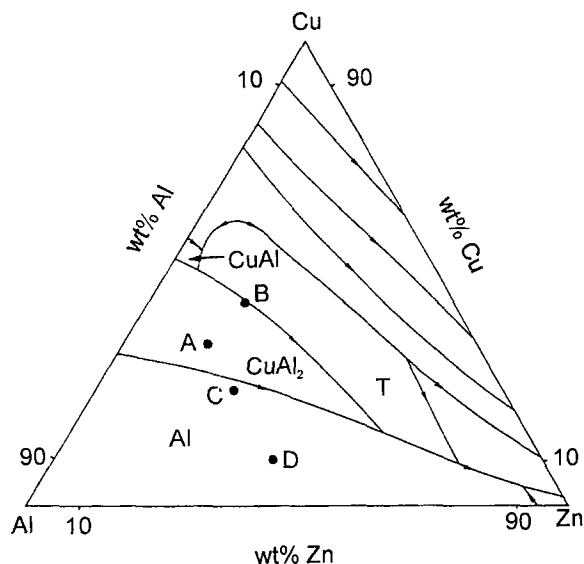
ties in catalyst or reactants. Using this criteria, Chinchén and Spencer [8] found that the WGS reaction over a number of commercial and co-precipitated Cu–ZnO– Al_2O_3 catalysts was a sensitive reaction. A plot of relative WGS activity versus copper metal surface area showed a significant scattering of the experimental points, some of which deviated by almost an order of magnitude from any median line which could be drawn. The sensitivity of the reaction was ascribed to the nature and concentration of adsorbed species, crystal face and morphology, and any alkali impurities. Other authors [2,10] have also presented evidence to suggest that there is no significant relationship between copper surface area and activity.

Using a similar approach to that of Chinchén and Spencer, Ginés et al. [9] also conducted experiments to determine the structure sensitivity of the WGS reaction over Cu–ZnO– Al_2O_3 catalysts. Their results showed that the turnover frequency was not modified by significantly changing several critical catalyst parameters. In addition, the specific reaction rate was always observed to be proportional to the copper surface area. Further, the results of Ginés et al. [9] are in agreement with the findings of several authors [11–14] who proposed that metallic copper is the active site for the WGS reaction, since catalytic activity was generally proportional to the concentration of metallic copper on the surface. Thus, under the reported experimental conditions, they concluded that the WGS reaction was a structure-insensitive reaction over these copper-based catalysts. They reported that an optimum WGS catalyst should contain the metallic copper phase highly dispersed on the mixed oxide support.

In an attempt to further the understanding of the structure sensitivity of the WGS reaction, the relationship between Raney copper surface area and activity has been investigated by us, and the results are presented in this paper.

2. Experimental

Alloys, Raney copper catalysts and a co-precipitated low temperature WGS catalyst were prepared according to the methods described elsewhere [1]. Ternary alloys of nominal compositions



T = ternary phase

Fig. 1. The liquidus projection for the Cu–Zn–Al system showing the compositions of the nominal alloys (●) and specific phase regions of interest: A=Cu(35)Zn(15)Al(50); B= Cu(43)Zn(18)Al(39); C=Cu(25)Zn(25)Al(50); D=Cu(10)Zn(25)Al(50).

Cu(35)Zn(15)Al(50), Cu(43)Zn(18)Al(39), Cu(25)Zn(25)Al(50) and Cu(10)Zn(40)Al(50) were prepared. In this paper they are referred to as alloys A, B, C and D, respectively. Alloys A, C and D were prepared with 50 nominal wt% aluminium in order to produce products containing the maximum amount of primary precipitate CuAl_2 , which is the leachable phase producing Raney copper [15]. Alloy B was included because some authors [16,17] observed that catalysts prepared from these alloys had both greater methanol synthesis

activity and greater mechanical strength than those prepared from alloys with higher Al contents. The nominal alloy A, B, C and D compositions are plotted on the Al–Cu–Zn liquidus projection diagram [15,18] in Fig. 1, and the atomic absorption (AA) analysed bulk composition of the four alloys are shown in Table 1.

Particles (0.5–1.18 mm in diameter) of alloys A, B, C and D were leached for 1 h in 7.1 M aqueous sodium hydroxide at 50°C, and subsequently passivated. The Raney catalyst was transferred under water to the glass passivation reactor (quartz glass 400 mm long, 15 mm i.d., with a porous sintered disk 250 mm from the top of the reactor) directly after washing. Before passivation commenced, excess water retained in the reactor from catalyst transfer was removed by passing a 99.999% pure nitrogen stream at 30 ml min⁻¹ through the reactor. Raney copper catalysts were dried at 120°C in nitrogen (30 ml min⁻¹) for 2.0 h. The reactor was then cooled under nitrogen to room temperature ($\pm 25^\circ\text{C}$) and a nitrous oxide (99.9% purity) flow of 1–2 ml min⁻¹ established. Under these conditions, catalyst temperature was increased to 220°C in 4.0 h and maintained for 16 h.

Characterisation data for the base leached alloys was obtained from atomic absorption (AA), scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX), X-ray diffraction (XRD), differential scanning calorimetry (DSC), pulse N_2O chemisorption, total BET surface area, pore volume and mean pore radii determinations. All these techniques have been detailed elsewhere [1]. The catalyst testing procedures have also been previously described [1]. In all cases, 2 ± 0.1 ml of catalyst was loaded into a fixed-bed, stainless steel microreactor,

Table 1
Alloy bulk compositions

Alloy	Alloy compositions (wt%) ^a					
	Nominal			Analysis		
	Cu	Zn	Al	Cu	Zn	Al
A	35	15	50	40.4	11.3	47.7
B	43	18	39	41.7	20.5	37.5
C	25	25	50	24.8	25.2	48.3
D	10	40	50	13.4	34.0	51.0

^aError: ± 2.0 wt%.

reduced in-situ, and tested for WGS activity and time-on-stream stability under identical experimental conditions ($\text{CO} : \text{H}_2\text{O} = 1 : 22.5$, temperature = 200°C and $\text{GHSV} = 1000 \text{ h}^{-1}$). Catalysts were reduced in a flow of 5% H_2/N_2 (by vol.) at 900 h^{-1} . A temperature of 230°C was maintained for 16 h. After reduction, the reactor was flushed with nitrogen prior to start-up at the relevant temperature. In cases where catalytic performance was investigated as a function of catalyst temperature and GHSV, reactor conditions were returned to those employed at the initial start-up of the catalyst. WGS activity was only recorded *after* steady-state conditions had been achieved.

3. Results and discussion

3.1. Characterisation of the caustic leached alloys

Bulk XRD analysis of alloy A has been detailed elsewhere [1] while the XRD results of alloys A, B and C are presented in Table 2. XRD analysis of alloys, A, B, C and D confirmed the *primary* precipitation products of $\text{Cu}(\text{Zn})\text{Al}_2$ (alloys A, B and C) and of Al (alloy D) as predicted from the liquidus phase diagram shown in Fig. 1. The Zn content of the $\text{Cu}(\text{Zn})\text{Al}_2$ phase is known [15] to increase with increasing alloy Zn level.

Alloy D showed a high secondary concentration of the $\text{Cu}(\text{Zn})\text{Al}_2$ phase whilst alloys B and C demonstrated secondary solidification products of Al. The Al phase content of alloy C was almost equivalent to the amount of $\text{Cu}(\text{Zn})\text{Al}_2$ phase present, as a result of the strong secondary influence of Al precipitation (observed from the liquidus phase diagram, Fig. 1). Alloys B, C and D contained elemental Zn and in each case, some evidence was found for the presence of the binary AlZn phase. The XRD pattern of alloy B

(Table 2) showed traces of CuAl which was impervious to caustic leaching as previously observed for the leaching of alloy A under similar conditions [1]. No evidence of any ternary phase was found. Passivated Raney copper catalysts A, B, C and D produced by leaching in aqueous sodium hydroxide for 1 h 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 A catalyst (prepared under the same conditions and extraction time as the passivated catalysts) showed Cu_2O followed by CuO as the major phase products [1]. Cross-section electron-micrographs of catalysts A, B, C and D revealed clearly identifiable reacted rims and alloy cores. The extent of average leach penetration after 1 h was calculated as 32.0%, 24.0%, 35.2% and 36.5% for catalysts A, B, C and D, respectively. In all cases, two 'leach fronts' were observed (as described elsewhere [1]). Catalyst development was consistent with the *first stage* of leaching which corresponds to the formation of an 'alloy-catalyst' interface in ternary Cu-Zn-Al alloys. Characterisation studies also showed that this stage generally corresponds to a Raney copper catalyst surface morphology best suited for catalysing the WGS reaction [1].

The bulk metal content (determined by AA) of alloys A, B, C and D leached in caustic solution for 1.0 h and passivated are presented in Table 3.

No iron impurities were detected in any of the precursor alloys or catalysts. Any mass defect was considered to be due to catalyst oxygen content. The bulk metal compositions of the 1 h leached alloy A catalyst after air drying [1] and passivating (Table 3) were similar, as expected. Approximately 1.6 wt% more oxygen was associated with the passivated Cu-Zn-Al catalyst. During the *controlled* passivation

Table 2
Crystalline phase of alloys B, C and D and their product Raney copper catalysts before and after reaction

Alloy	Precursor alloy phases	Cat. phases before reaction ^a	Cat. phases after reaction ^a
B	CuAl_2 , Al, Zn, $(\text{AlZn})^b$, CuAl	CuO , Zn, CuAl_2 , Cu, Cu_2O , CuAl	Cu, Zn, CuAl , CuO , $\text{CuAl}_2(\text{tr})^c$
C	CuAl_2 , Al, Zn, (AlZn)	CuO , Zn, Al, Cu, CuAl_2 , $\text{Cu}_2\text{O}(\text{tr})$	Cu, Zn, Al, CuO , $\text{CuAl}_2(\text{tr})$
D	Al, CuAl_2 , Zn, (AlZn)	CuO , Zn, Al, Cu_2O , $\text{Cu}(\text{tr})$	Cu, Zn, CuO , Al

^aPhases listed in *approximate* order of abundance (from left to right).

^bPhase in brackets not conclusively identified.

^c(tr)=trace.

Table 3

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

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

of a caustic leached Cu(50.3)Al(49.7) alloy using N_2O as oxidant, Tomsett et al. [19] calculated that at 200°C, a minimum oxygen uptake equivalent to four monolayers was sufficient to passivate the catalyst. The results in Table 3 show that catalysts prepared from precursor alloys with higher zinc levels contain higher levels of zinc after 1 h of leaching. No significant changes in catalyst compositions were apparent after testing for WGS activity. From cross-sectional EDAX determinations (presented in Table 4) this trend was qualitatively confirmed in the *rim* of the fresh Raney copper catalysts.

EDAX measurements of the alloy core compositions were in good agreement with the AA analysis (Table 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 D are presented in Table 5.

The large amount of Al solidification product present in the alloy precursors of catalysts C and D (Table 2) correlates with 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)Al₂ phase [20], it is feasible to consider that extensive leaching of alloys C and D to produce porous Raney copper may have already occurred within a caustic contact time of only 1 h. The greater extent of leach penetration for catalysts C and D is consistent with this explanation. For alloys A, B, C and D 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

Table 4

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	81.0	12.1	6.9	37.0	15.2	47.8
B	1.0	79.7	13.7	6.6	40.3	21.4	38.3
C	1.0	79.7	15.7	4.6	27.7	26.1	46.2
D	1.0	66.3	27.1	6.6	16.9	31.4	51.7

Table 5

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	30.0 (18.5) ^a	11.8 (4.1)	395 (1538)	4.6 (1.2)
B	1.0	25.4 (13.0)	8.7 (2.5)	569 (2004)	3.5 (0.7)
C	1.0	44.3 (22.0)	18.4 (6.3)	265 (738)	7.3 (2.6)
D	1.0	66.9 (27.0)	12.8 (8.3)	323 (484)	6.2 (4.0)

^aResults in brackets for *used* catalysts.

surface area (catalysts C and D), is accompanied by large amounts of evenly dispersed zinc in the leached rim. In particular, catalyst C exhibits a copper surface area over twice as large as that measured for an industrial WGS catalyst ($8.2 \text{ m}^2 \text{ g}^{-1}$, [1]), as well as a rim Zn content 37% greater than the Zn level associated with the most stable Raney catalyst tested for WGS activity over 1000 h (alloy A leached for 1.0 h [1]). Catalyst C also showed the highest copper surface dispersion and the lowest crystallite size observed for Raney copper catalysts. Catalyst D contained the greatest amount of zinc (Table 3) observed, together with a copper surface area larger than the values determined for all hydroxide/zincate leached alloys previously reported by us [1]. Catalysts C and D have similar pore volumes of 0.399 and $0.334 \text{ cm}^3 \text{ g}^{-1}$ and mean pore radii of 180.1 and 99.8 \AA , respectively.

DSC was used to simulate reduction conditions under 5% H_2/N_2 at a flow rate of 30 ml min^{-1} . Catalysts A, B, C and D were heated from ambient to 300°C at a rate of 5°C min^{-1} . As observed for the reduction of the air-dried alloy A catalysts [1] under similar conditions, a single exothermic phase change between 160°C and 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 [1].

3.2. Activity and stability of caustic leached alloys A, B, C and D

3.2.1. Initial activity

In order to present a complete study of Raney copper catalysts for the WGS reaction, the initial activities of 1 h leached catalysts A, B, C and D 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). Initial catalyst activity was determined at 200°C after steady-state conditions had been achieved. The objective was to compare the performance of the Raney copper system with an industrial catalyst under typical conversion values ($>90\%$). Results are presented in Table 6.

As described elsewhere [1], 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). All Raney copper catalysts (A, B, C and D) are more active under the same experimental conditions than industrial and co-precipitated alternatives. 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. 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. Thus it can be seen that the performance of the Raney copper system is dependent on the manner in which the activity is expressed.

3.2.2. Stability

The long term stability of Raney copper catalysts A, B, C and D under constant reaction conditions are shown in Fig. 2. 'Activity' is expressed in terms of CO conversion for a constant volume of catalyst.

Table 6
Specific activities of Raney copper catalysts produced from leaching various alloy precursors^a

Alloy	Extraction time (h)	Rate (a) ($\times 10^{-3} \text{ mol}_{\text{CO}} \text{ ml}^{-1} \text{ h}^{-1}$)	Rate (b) ($\times 10^{-3} \text{ mol}_{\text{CO}} \text{ g}_{\text{comp}}^{-1} \text{ h}^{-1}$)	Rate (c) ($\times 10^{-4} \text{ mol}_{\text{CO}} \text{ m}_{\text{Cu}}^{-2} \text{ h}^{-1}$)	Rate (d) ($\times 10^{-5} \text{ mol}_{\text{CO}} \text{ m}^{-2} \text{ h}^{-1}$)
A	1.0	3.2	2.13	1.80	7.11
B	1.0	3.28	1.89	2.18	7.47
C	1.0	3.44	3.91	2.12	8.83
D	1.0	3.08	3.67	2.86	5.48
Industrial	—	3.06	3.15	3.84	3.86
Precipitated	—	2.94	2.94	5.55	3.43

^aTemperature= 200°C ; total GHSV= 1000 h^{-1} ; dry gas composition= $10\% \text{ CO}/90\% \text{ N}_2$; $\text{CO} : \text{H}_2\text{O} = 1 : 22.5$; catalyst volume= $2 \pm 0.1 \text{ ml}$.

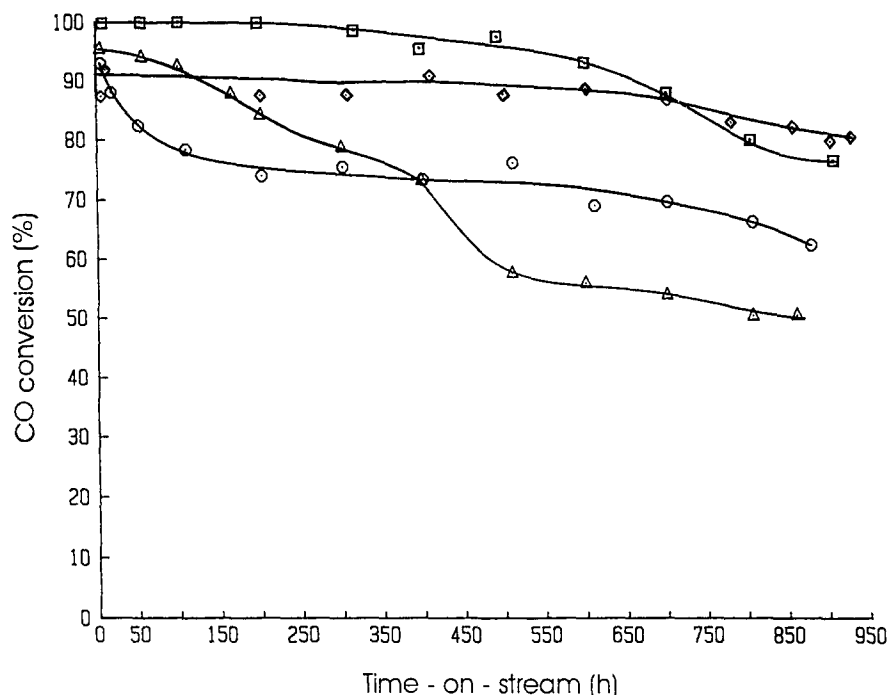


Fig. 2. Stability of various Raney copper catalysts as a function of precursor alloy composition (temperature=200°C; total GHSV=1000 h⁻¹; dry gas composition=10% CO/90% N₂; CO : H₂O=1 : 22.5; catalyst volume=2±0.1 ml): (○)=Cat. A Cu(69.3)Zn(6.9)Al(19.5); (△)=cat. B Cu(73.6)Zn(10.9)Al(14.8); (□)=cat. C Cu(72.4)Zn(13.3)Al(12.9); (◇)=cat. D Cu(61.5)Zn(15.1)Al(19.1).

It can be seen from Fig. 2 that whilst the activity of all Raney copper catalysts decreased over time as a result of sintering, good overall stability after 900 h-on-stream was observed for catalyst D which contained the highest bulk (15.1 wt%) and rim (27.1 wt%) zinc content. The catalyst demonstrated a loss in activity of only 10.2% after 900 h. Based on the correlation shown to exist between Raney copper deactivation and zinc oxide content [1], the high rim Zn concentration of Catalyst D is regarded as the major reason for the overall sustained stability. Catalyst D showed the smallest decrease in copper surface area and the most stable copper crystallite size over the same time period (Table 5). Although the activity of catalyst C decreased by 23.1%, the catalyst remained the most active for at least 700 h-on-stream. Catalysts A and B displayed good initial activities, but deactivated substantially with time, (especially in the case of catalyst B). Both catalysts possessed relatively low concentrations of zinc in the rim and the lowest copper surface areas observed for freshly prepared Raney copper catalysts. Thus it may be concluded that

the caustic leaching of alloys with high levels of zinc under the conditions reported may result in catalysts with increased zinc content, effective for stabilizing high copper surface areas formed during extraction.

3.2.3. Temperature dependence

The effect of temperature on the WGS activity for Raney copper catalysts (A, B, C and D) and an industrial WGS catalyst is shown in Fig. 3. In all cases, 2±0.1 ml of catalyst was tested, and activity expressed in terms of percent CO conversion. In order to clearly demonstrate WGS equilibrium conversion as a function of temperature, numerical data on the temperature dependence of the equilibrium constant (K_p) for the WGS [11] was used to determine the equilibrium conversion of CO for the reaction conditions reported, and the data is presented as a dashed line in Fig. 3.

For all the catalysts investigated, a sharp increase in catalyst activity at temperatures from 200°C was observed, indicating that the Raney copper system may be operated in the typical low temperature WGS

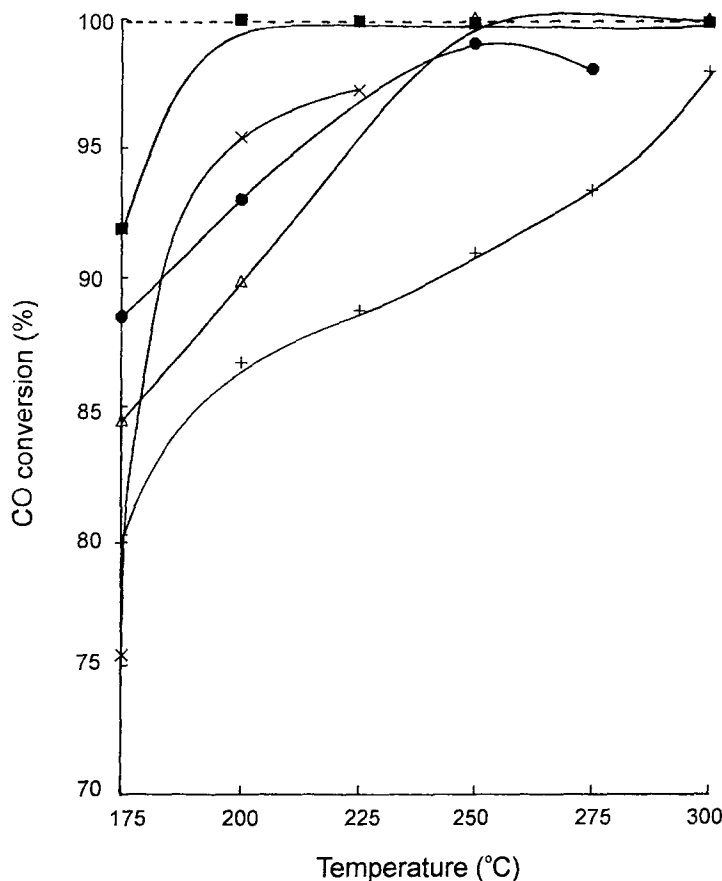


Fig. 3. Effect of temperature on the WGS activity of various Raney copper catalysts (total GHSV=1000 h⁻¹; dry gas composition=10% CO/90% N₂; CO : H₂O=1 : 22.5; catalyst volume=2±0.1 ml): (●)=Cat. A Cu(69.3)Zn(6.9)Al(19.5); (×)=cat. B Cu(73.6)Zn(10.9)Al(14.8); (■)=cat. C Cu(72.4)Zn(13.3)Al(12.9); (△) cat. D Cu(61.5)Zn(15.1)Al(19.1); (+)=Industrial catalyst.

catalyst region [21]. All Raney copper catalysts tested achieved equilibrium conversions at temperatures below that observed for the industrial catalyst, and in particular equilibrium conversion was observed for catalyst C at temperatures from as low as 200°C. The higher activity of catalyst C at lower temperatures may be explained by the high active surface area of copper (18.4 m² g⁻¹), together with a pore volume (0.399 cm³ g⁻¹) and mean pore radii (180.1 Å) sufficiently large enough to eliminate possible diffusion limiting factors, which could prevent the reagent molecules from reaching the active sites in the catalytic network structure.

As the equilibrium conversion of carbon monoxide is enhanced by lower operating temperatures [11], the high activity of Raney copper catalysts at tempera-

tures below 300°C could be advantageous for an industrial operation of such a catalyst system, as it could present lower energy costs [22]. Andreev et al. [22] also observed that for temperatures below 300°C, a Raney copper catalyst manifested a higher catalytic activity than the industrial Chimco Company low temperature BNTK catalyst.

3.2.4. Effect of GHSV on the water-gas shift activity

The activity (presented as percent carbon monoxide conversion) as a function of GHSV for catalysts A, B, C and D and industrial WGS catalyst is presented in Fig. 4.

From Fig. 4 it can be seen that catalyst D which showed good long term stability under constant conditions (Fig. 2), also demonstrated good stability at

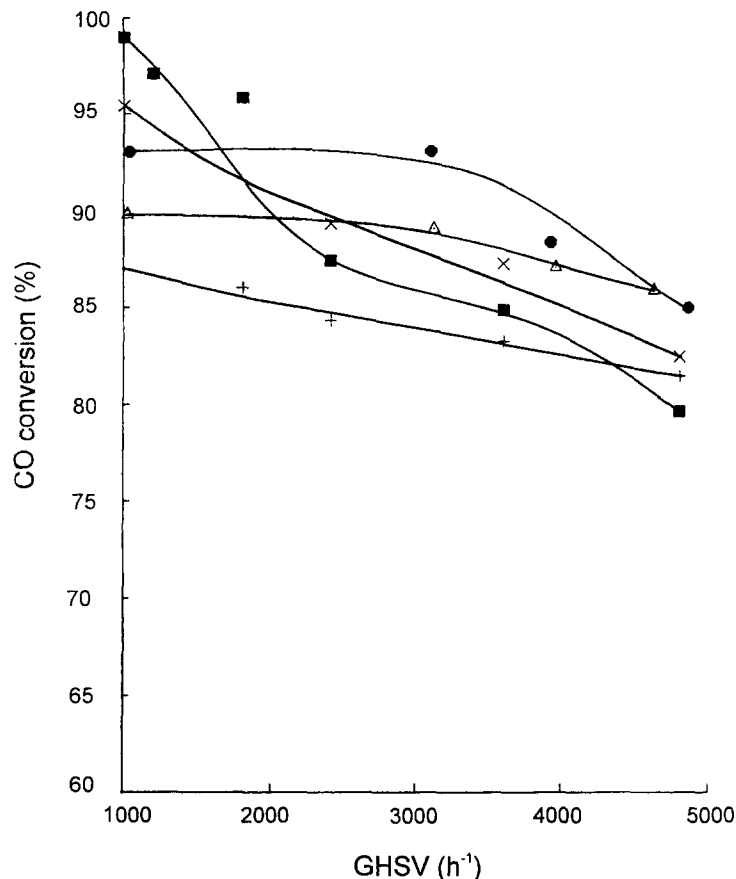


Fig. 4. Effect of GHSV on the WGS activity of various Raney copper catalysts (temperature=200°C; dry gas composition=10% CO/90% N₂; CO : H₂O=1 : 22.5; catalyst volume=2±0.1 ml): (●)=Cat. A Cu(69.3)Zn(6.9)Al(19.5); (×)=cat. B Cu(73.6)Zn(10.9)Al(14.8); (■)=cat. C Cu(72.4)Zn(13.3)Al(12.9); (△)=cat. D Cu(61.5)Zn(15.1)Al(19.1); (+)=Industrial catalyst.

high space velocities. In general, higher space velocities revealed that the catalyst compositions could not sustain initial activities by preventing or minimizing sintering. As expected, the industrial catalyst showed no significant change in catalytic performance at higher space velocities.

3.3. Relationship between water-gas shift activity and copper surface area

The relationship between initial and final WGS rate of reaction and copper surface area for a number of air dried and passivated Raney copper catalysts with different alloy precursor compositions and leach times are shown together with an industrial WGS catalyst

and a co-precipitated WGS Cu–Zn–Al catalyst in Fig. 5.

Analysis of variance (regression) performed on the data presented in Fig. 5 shows that if linearity is assumed, 71% of the variation in activity can be explained by copper surface area. Also, the correlation coefficient, R , between the activity and copper metal area ($R=0.82$) is high enough to suggest that activity and metal surface area are significantly related, since it passes the test described by Barford [23] where

$$|R| > 3/(n+7)^{1/2}, \quad (1)$$

n is the number of observations.

Although a statistically significant correlation exists between the WGS activity of Raney copper catalysts

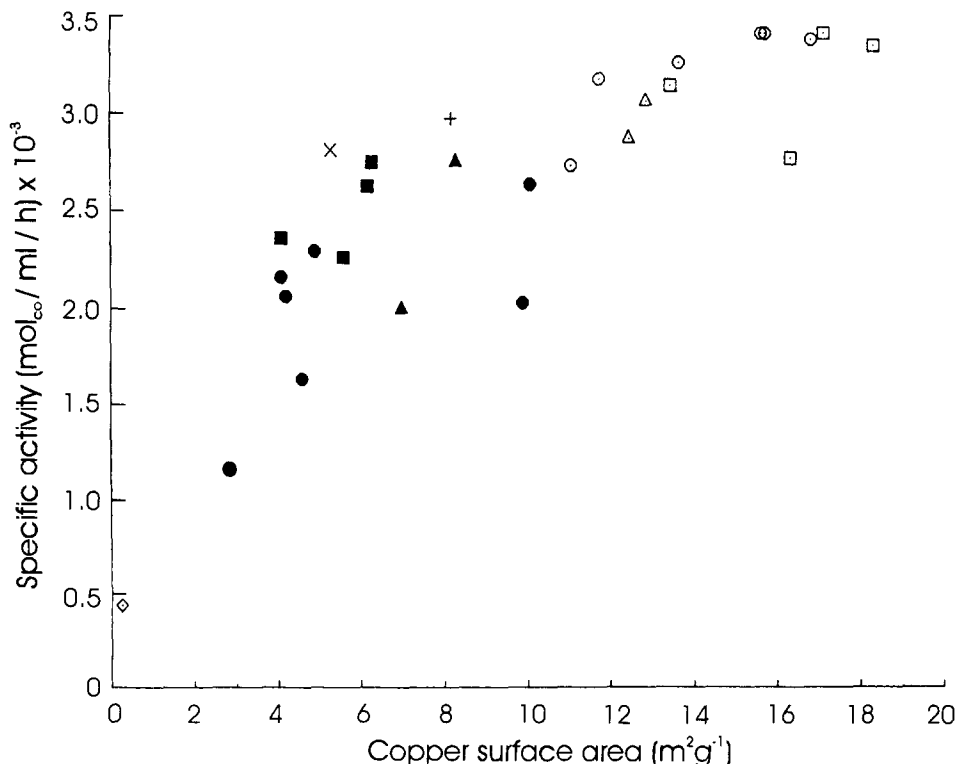


Fig. 5. The dependence of Raney copper WGS activity on copper surface area. Open symbols=initial catalyst activity; closed symbols=final catalyst activity (temperature=200°C; total GHSV=1000 h⁻¹; dry gas composition=10% CO/90% N₂; CO:H₂O=1:22.5; pressure=0.825 kPa; catalyst volume=2±0.1 ml): (○)=Cat. A Cu(69.3)Zn(6.9)Al(19.5); (□)=cat. C Cu(72.4)Zn(13.3)Al(12.9); (△)=cat. D Cu(61.5)Zn(15.1)Al(19.1); (×)=co-precipitated Cu-Zn-Al (initial activity); (+)=industrial catalyst; (◇)=copper powder.

and their active metal surface areas, the scatter of experimental points is greater than that would be expected from experimental error [1]. Our results tend to also suggest the presence of small second-order effects. From Fig. 5 it generally appears that a catalyst copper surface area of only approximately 5 m² g⁻¹ is needed to achieve a CO conversion in excess of 50%, whilst relatively higher CO conversions are only realised with much greater comparative copper surface areas. This trend may be due to the low space velocity (1000 h⁻¹) employed for the measurements.

4. Conclusion

The caustic leaching of precursor alloys rich in zinc proved to be an effective method for increasing the

content of zinc in the Raney copper rim without compromising the formation of high copper surface areas, shown to result in high WGS activity. The residual zinc had a stabilizing influence on the catalyst surface area, and a quantitative relationship was observed between the amount of zinc dispersed in the catalyst rim, and long-term stability. Caustic leached Raney copper catalysts exhibited a high degree of WGS activity in the low temperature region (i.e. 175–300°C) under varying reaction conditions.

An examination of the relationship between WGS activity and Raney copper surface area showed that catalytic activity was to a certain extent, dependent on the magnitude of the copper area. This result supports the suggestion that the WGS reaction over Raney copper is a structure insensitive-reaction, as proposed by Ginés et al. [9] over co-precipitated Cu-ZnO-Al₂O₃ catalysts. Chinchén and Spencer [8] showed

that over Cu–ZnO–Al₂O₃ catalysts prepared by conventional co-precipitation procedures but with variations in catalyst composition and in the *parameters of catalyst preparation*, the WGS reaction is a sensitive catalytic reaction. Whilst the findings of Chinchén and Spencer [8] may seem to be in conflict with our results, Hadden et al. [24] recently concluded that although no single function could describe the relationship between copper surface area and the activity of every catalyst, discrete copper area–activity relationships were evident within groups of catalysts whose precursor species were formed under identical preparation conditions. Within these groups, they identified simple, linear surface area–activity relationships.

Thus it would seem that both catalyst structure and copper surface area are important determinants of WGS activity.

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References

- [1] J.R. Mellor, N.J. Coville, A.C. Sofianos, R.G. Copperthwaite, *Appl. Catal.*, submitted.
- [2] R.G. Herman, K. Klier, G.W. Simmons, B.P. Finn, J.B. Bulko, *J. Catal.* 56 (1979) 407.
- [3] T. Shido, Y. Iwasawa, *J. Catal.* 140 (1993) 575.
- [4] F. Garbassi, G. Petrini, *J. Catal.* 90 (1984) 106.
- [5] M.S. Wainwright, D.L. Trimm, *Catal. Today* 23 (1995) 29.
- [6] J.R. Mellor, Ph.D. Thesis, University of Witwatersrand, Johannesburg, South Africa, 1993.
- [7] C. Rhodes, G.J. Hutchings, A.M. Ward, *Catal. Today* 23 (1995) 43.
- [8] G.C. Chinchén, M.S. Spencer, *Catal. Today* 10 (1991) 293.
- [9] M.J.L. Ginés, N. Amadeo, M. Laborde, C.R. Apestequia, *Appl. Catal. A* 131 (1995) 283.
- [10] G. Petrini, F. Montino, A. Bossi, F. Garbassi, in: G. Pancelet (Ed.), *Preparation of Catalysts 3*, Elsevier, Amsterdam, 1983.
- [11] W.J. Lywood, L. Lloyd, D.E. Ridler, M.V. Twigg, in: M.V. Twigg (Ed.), *Catalysis Handbook*, Wolfe Publishing, London, 1989.
- [12] D.K. Ghorai, N.C. Ganguli, S.P. Sen, *Fert. Tech.* 18 (1981) 40.
- [13] R.W. Bedford, ICI Technical Paper Nr. 4., Imperial Chemical Industries, Billingham, Cleveland, England.
- [14] J.S. Campbell, *Ind. Eng. Chem. Process Des. Dev.* 9 (1970) 588.
- [15] J.B. Friedrich, D.J. Young, M.S. Wainwright, *J. Electrochem. Soc.* 128 (1981) 1840.
- [16] M.S. Wainwright, *Methane Conversion*, Elsevier, Amsterdam, 1988, p. 95.
- [17] H.E. Curry-Hyde, M.S. Wainwright, D.J. Young, *Appl. Catal.* 77 (1991) 89.
- [18] L.F. Mondolfo, *Aluminium Alloys: Structures and Properties*, Butterworths, London, 1976.
- [19] A.D. Tomsett, M.S. Wainwright, D.J. Young, *Appl. Catal.* 12 (1984) 43.
- [20] J.B. Friedrich, D.J. Young, M.S. Wainwright, *J. Electrochem. Soc.* 128 (1981) 1845.
- [21] F.M. Gottschalk, R.G. Copperthwaite, M. van der Riet, G.J. Hutchings, *Appl. Catal.* 38 (1988) 103.
- [22] A. Andreev, T. Haltchev, V. Kafedjiiski, B. Kunev, M. Kalchev, I. Orizariski, D. Shopov, *Proceedings of the Sixth International Symposium on Heterogeneous Catalysis, Part 1*, Sofia, 1987, p. 235.
- [23] N.C. Barford *Experimental Measurements: Precision, Error and Truth*, 2nd ed., Wiley, Chichester, 1985.
- [24] P.A. Hadden, P.J. Lambert, C. Ranson, *Appl. Catal. A* 122 (1995) L1.