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Catalysis Today 45 (1998) 245–250

CATALYSIS TODAY

Development of high performance Raney Cu-based catalysts for methanol synthesis from CO_2 and H_2

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Abstract

Catalytic hydrogenation of CO_2 into methanol has been investigated over Raney Cu-based catalysts. The Raney catalysts leached in NaOH/ZnO solutions showed high activities and selectivities for methanol synthesis. The deposition of Zn on the surface of Cu particles increased the surface area and the specific activity of Raney Cu–M. Raney Cu–Zr developed was significantly more active than a commercial catalyst. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: CO_2 hydrogenation into methanol; Raney Cu–Zr catalyst; Methanol activity; Leaching in NaOH/zincate solutions

1. Introduction

Catalytic hydrogenation of carbon dioxide is one of the crucial issues and processes to present a serious option for the global warming control. In particular, methanol synthesis has been considered to play an important role in the transportation of hydrogen energy derived from natural energy such as solar energy, hydropower and so on.

In previous studies the authors have reported that metal oxides such as Ga_2O_3, Al_2O_3, ZrO_2 and Cr_2O_3 contained in Cu/ZnO-based catalysts have an important role to improve simultaneously, the activity and the selectivity [1,2]. Unlike Cu/ZnO-based catalysts, Raney copper catalysts have not been widely reported in the literature as practical catalysts for methanol synthesis. However, 20 years ago Wainwright [3] has been the first to report the potential use of Raney Cu and Raney Cu–Zn as catalysts to produce methanol from syngas to use as synthetic liquid fuel. Recent works of Wainwright and Trimm [4] on methanol synthesis and WGS reactions from syngas showed that the alkaline leaching of copper/zinc/aluminium alloy to produce Zinc-promoted Raney Cu leads to an excellent mixing of the components and consequently allows a high activity for methanol synthesis by improving the surface area and the porosity of the catalyst. This work also demonstrated that the production of MeOH was promoted by copper and the major role of zinc oxide, and that carbon dioxide is the major reactant forming methanol under the industrial conditions. On the basis of these studies, it is completely

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PII: S0920-5861(98)00223-5

legitimate to envisage an interesting route for the methanol synthesis directly from CO_2 and H_2 over an optimal Raney Cu catalyst. In this conference, we report an unprecedented high catalytic performance for methanol synthesis from CO_2 and H_2 over a new metal-promoted Raney Cu catalysts.

2. Experimental

Raney Cu–M catalysts (M=Metal added to Cu/Al alloy) were prepared by leaching of the metal alloys in moderately stirring NaOH aqueous solution and/or a sodium zincate ($Na_2Zn(OH)_4$)/NaOH solution which was prepared by adding ZnO to NaOH aqueous solution. The concentrations of NaOH were respectively 250 g NaOH in 1 kg H_2O for NaOH leaching solution and 300 g NaOH in 1 kg H_2O for NaOH–zincate leaching solution. Leaching in zincate gives zinc deposition on the catalyst. The Raney Cu catalysts prepared after leaching were washed with distilled water until completely removing Na from the catalyst. The catalysts were stored in distilled water to avoid the re-oxidation of the metallic particles. The total specific surface area of the catalyst after reaction was determined by flow nitrogen adsorption at 77 K. The total copper surface area of each catalyst after reaction was determined by the technique of N_2O reactive frontal chromatography (RFC) after re-reducing the post-reaction catalyst with hydrogen at 523 K [5]. The catalyst fixed in a flow reactor was reduced in H_2 at 523 and 573 K during 2 h under 5 MPa before flowing CO_2 and H_2 feed gas mixture (CO_2/H_2=1/3). The reaction products were analysed by adequate gas chromatographs connected to the reactor.

3. Results and discussion

3.1. General features of CO_2 hydrogenation over Raney Cu catalysts

When a mixture of CO_2/H_2 passes over Raney Cu–M catalysts at the operating conditions described above, the main products of the reaction were methanol, water, and carbon monoxide. Dimethyl ether, methane and methyl formate were also produced but the selectivities of the by-products were less than 0.1%.

3.2. Role of ZnO contained in the leaching solution for the preparation of Raney Cu catalysts

Table 1 shows the atomic composition of Raney Cu and Raney Cu–Zr 1 at.% leached in NaOH and NaOH–zincate solutions and those after reaction. Overall chemical compositions of catalyst samples were measured using inductively coupled plasma with atomic emission spectroscopy (ICP–AES). Samples were dissolved in aqua regia before dilution in distilled water.

For both catalysts the presence of zincate leads to a significant deposition of metallic zinc. Zn metal associated to copper is obtained after a full leaching of a Cu/Al-based alloy in the conditions described before (vide supra). The chemical reaction occurring during

Table 1
Compositions and activities of Raney Cu catalysts leached with aqueous solutions of NaOH and zincate[a]

Catalyst (alloy)	Leaching solution	Composition of catalyst (at.%)	S_{Cu} (m^2/ml)	Activity (g-CH_3OH/l-cat h)	Specific activity (mg-CH_3OH/m^2-Cu h)
Cu/Al (1/2)	NaOH	Cu/Al 98.6/1.4	6.0	239	39.8
	Zincate	Cu/Al/Zn 98.4/0.5/1.1	7.4	540	73.0
Cu/Al+Zr (1 at%)	NaOH	Cu/Al/Zr 89.5/7.6/2.9	12.7	415	32.7
	Zincate	Cu/Al/Zr/Zn 89.9/5.0/2.9/1.9	18.2	814	44.7

[a] Leaching and reaction conditions are the same as those of Fig. 1.

this step could be described as follows:

$$Al(metal) + NaOH + 3H_2O = NaAl(OH)_4 + \frac{3}{2}H_2$$

$$Zn^{2+} + H_2 = Zn + H_2O.$$

The amounts of metallic zinc deposited on the surface were 1.1% for Raney Cu and 1.9% for Raney Cu–Zr (1 at.%).

3.3. *Influence of the metal added to Cu/Al alloy on the activity and the specific activity of Raney Cu catalysts*

Fig. 1 shows methanol synthesis activities and specific activities of Raney Cu–M (1 at.%) catalysts leached in aqueous solutions of NaOH or NaOH/zincate under the same reaction conditions. Raney Cu–Zr has exhibited the best activity among the catalysts tested. At the present stage of this study, the reason why Zr has a strong effect for enhancing the activity and the copper surface of Raney Cu is not clear. However, Zr might be very important to enhance the interdispersion of Zn into copper and then allows a higher Cu surface area. On the other hand, for every catalyst tested, the presence of zincate in the leaching solution led to the deposition of Zn on the surface of Cu particles and had a strong effect to improve the activity and the Cu surface area (respectively, by 95% and 50% for Raney Cu–Zr). The highest activity due to the presence of zincate seems to be partially related to the increase in Cu surface area (Table 1). Fig. 1 shows also another important finding which indicates that zincate doping leads to better specific activity. As it was reported in others works [6], the increase in copper surface area could be related to the formation of smaller copper particles on the surface of Raney copper due to the slower rate of leaching when the zincate is present. Therefore the nature of precursor alloy and leaching solution both were found to be key steps in the preparation of high performance Raney Cu for methanol synthesis from CO_2 and H_2.

3.4. *ZnO concentration*

The influence of ZnO concentration in the leaching solution on the composition of Raney Cu–Zr (1 at.%) and its activity has been examined by varying the concentration of ZnO from 0 to 91 g in 1 kg H_2O (which corresponds to maximum concentration of ZnO). It is clearly shown in Table 2 that the content of zinc metal in the catalyst after reaction increased with ZnO concentration. On the other hand, the Cu surface area and the activity of Raney Cu–Zr (1 at.%) are significantly improved by increasing the ZnO concentration. Therefore, the chemical composition

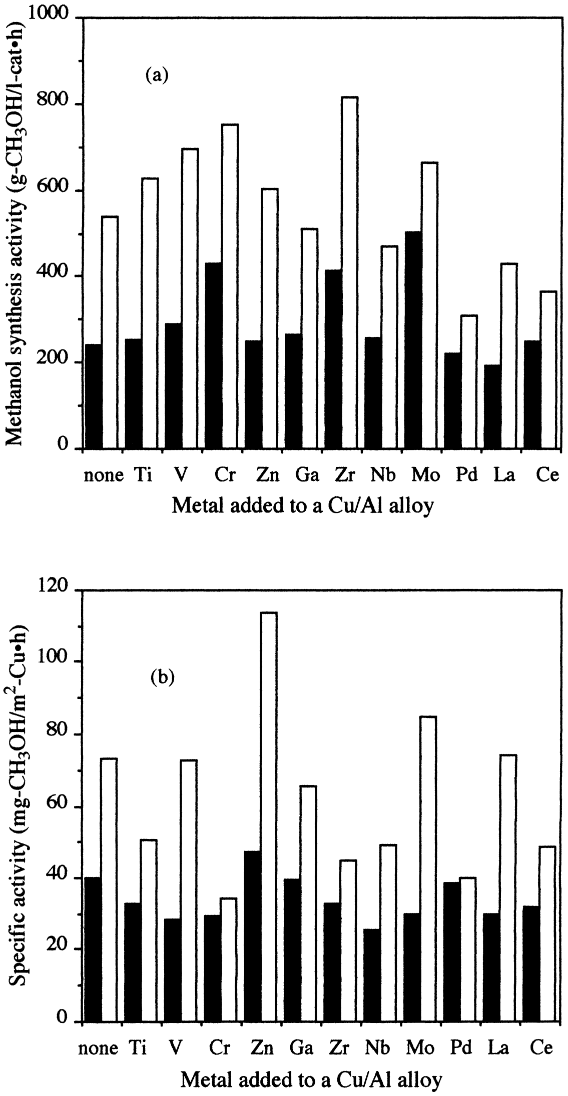

Fig. 1. Effect of metal added to Cu/Al alloy on: (a) the methanol synthesis activity and (b) the specific methanol synthesis activity of Raney Cu catalysts leached in aqueous solutions of NaOH (20%, ■) and zincate (NaOH+ZnO, □). Conditions for leaching alloys: 313 K in N_2. Reaction conditions: 523 K, 5 MPa, SV=18 000 h^{-1}, $H_2/CO_2=3$.

Table 2
Effect of ZnO concentration on the composition and the activity of Raney Cu/Zr(1) leached with aqueous solution of NaOH and zincate

[ZnO] in a leaching solution(2) (g-ZnO/kg-H$_2$O)	Composition(3) (Cu/Al/Zr/Zn) (at.%)	S_{area}(4) (m^2/ml-cat)	S_{Cu}(4) (m^2/ml-cat)	Methanol activity(5) (g-CH$_3$OH/l-cat h)		Specific activity(6) (mg-CH$_3$OH/m^2-Cu h)
91(a)	94.6/1.5/1.8/2.1	26.1	18.8	931(a)	842(b)	44.7
84(b)	92.5/3.2/2.3/2.0	29.2	19.1	936	838	43.7
67(c)	93.4/2.5/2.2/1.9	28.1	19.5	939	836	43.6
51(d)	93.3/2.7/2.3/1.5	31.4	20.9	923	809	38.7
34(e)	–	23.5	16.5	881	798	48.4
27(f)	94.3/2.6/2.1/1.2	12.6	9.4	721	738	78.6

(1)Zr content in CuAl$_2$ alloy was 1 at.%.

(2)Conditions of preparation: leaching in an aqueous solution of NaOH/ZnO in the stream of N$_2$ at 323 K for 1 h before fixing the temperature at 333 K. The concentrations of NaOH were (a) 341, (b) 333, (c) 316, (d) 300, (e) 283, (f) 276 g in 1 kg H$_2$O.

(3)By elemental analysis of the post-reaction catalyst.

(4)Surface area and Cu surface area were measured after the reaction at 523 K following the reduction at 573 K.

(5)Conditions – reduction: (a) 523 K, (b) 573 K, 2 h in pure H$_2$; reaction: 523 K, 5 MPa, SV=18 000 h^{-1}, H$_2$/CO$_2$=3.

(6)Specific activity was calculated by dividing the activity (4-b) by Cu surface area (3).

and the texture of Raney copper tested changed by the addition of zincate and increasing the content of metallic zinc deposited on the surface of Cu particles had an important role to improve both the activity and the Cu surface area of Raney Cu catalyst.

3.5. Temperature of leaching the alloy

Table 3 reveals that leaching temperature influences also the surface area and the activity of Raney Cu catalysts. An optimum range of temperature for leaching the alloy was between 293 and 333 K. The activity of Raney Cu–Zr (1 at.%) reached a maximum at 333 K. The highest Cu surface was obtained for the catalyst leached at 323 K. When the temperature was increased between 293 and 333 K, the activity and specific activity increased. This is another experimental result showing that there is a strong interdependence between the activity of the catalyst and its Cu surface area. On the other hand, as shown in Table 3, increasing the temperature between 293 and 333 K leads to the increase in the amount of zinc metal deposited on the surface of the catalyst. However, if the temperature of leaching the alloy is over 333 K, the activity of the catalyst and its Cu-surface area significantly decreased with the increase in the temperature. At high temperature a strong interaction between copper and zinc could affect the dispersion of Cu

Table 3
Effect of leaching temperature on the composition and the activity of Raney Cu/Zr(1) leached with aqueous solution of NaOH and zincate

Leaching(2) temperature (K)	Composition(3) (Cu/Al/Zr/Zn) (at.%)	S_{area}(3) (m^2/ml-cat)	S_{Cu}(3) (m^2/ml-cat)	Methanol activity(3) (g-CH$_3$OH/l-cat h)		Specific activity(3) (mg-CH$_3$OH/m^2-Cu h)
293	91.2/4.7/2.3/1.3	32.0	19.0	881(a)	742(b)	38.8
313	93.0/3.3/2.2/1.5	34.7	19.0	900	782	41.0
323	93.4/2.7/2.3/1.7	33.4	21.7	906	801	36.9
323–333(a)	93.5/2.7/2.3/1.5	31.4	20.9	923	809	38.7
333	93.8/2.4/2.0/1.8	24.5	19.8	927	816	41.2
343	94.3/1.9/2.0/1.8	24.0	18.4	911	817	44.0
353	95.1/1.3/1.9/1.7	23.2	17.3	877	790	45.7

(1)Zr content in CuAl$_2$ alloy was 1 at.%.

(2)Conditions of preparation: leaching in an aqueous solution of NaOH(300 g)/ZnO(51 g) in 1 kg H$_2$O in the stream of N$_2$. (a) 1 h leaching at 323 K and then the temperature was fixed at 333 K.

(3)Same conditions as described in Table 2.

Table 4
Effect of Zr content in the Cu/Al/Zr alloy on the composition and the activity of Raney Cu/Zr(1) leached with aqueous solution of NaOH and zincate

Zr(1) (at.%)	S_{area}(2) (m^2/ml-cat)	S_{Cu}(2) (m^2/ml-cat)	Methanol activity(2) (g-CH_3OH/l-cat h)		Specific activity(2) (mg-CH_3OH/m^2-Cu h)
0.5(a)	15.2	15.1	766(a)	678(b)	44.9
1.0(a)	24.5	19.8	923	816	41.2
1.0(b)	26.1	18.8	931	842	44.8
1.5(a)	32.2	21.8	928	831	38.1
1.5(b)	31.2	20.6	942	853	41.4
2.0(a)	32.4	21.9	853	769	35.1
3.0(a)	28.6	7.9	712	700	88.1

(1)Alloy leached in an aqueous solution of: (a) NaOH(300 g)/ZnO(51 g) in 1 kg H_2O in the stream of N_2 at 323 K for 1 h before fixing the temperature at 333 K; (b) NaOH(341 g)/ZnO(91 g) in 1 kg–H_2O in the stream of N_2 at 323 K.
(2)Same conditions as mentioned in Table 2.

particles. Consequently, keeping the temperature in a moderate range leads to leach completely the alloy without affecting the physical structure of the catalyst.

3.6. Zr content

Table 4 shows the catalytic behaviour of Raney Cu–Zr as a function of Zr content. These data indicate that the optimum amount of Zr in the mother alloy should be between 1 and 2 at.%. In this range, the activity and the surface area increased and passed by a maximum for Raney Cu–Zr (1.5 at.%). The correlation previously found between the Cu-surface area and the activity is confirmed by investigating the effect of Zr content in the precursor alloy. In addition, the elemental analysis of the samples obtained after reaction showed that Zr and Zn are present in post-reaction catalyst. The amounts of Zn and Zr deposited depend on the concentration of ZnO in the leaching solution and on the initial content of Zr metal in the precursor alloy.

3.7. Catalytic performances of the optimum Raney Cu catalysts and those of a commercial catalyst for methanol synthesis from CO_2 and H_2

Catalytic performances of the best Raney Cu obtained (Raney Cu–Zr 1.5 at.%) were compared with those of the optimum multicomponent catalyst developed in our laboratory and the commercial catalyst tested in the same conditions for methanol synthesis from CO_2 and H_2 (Table 5). The initial activity (with the catalyst reduced at 523 K) of Raney Cu was (30%) higher than commercial catalyst and 10% higher than the multicomponent catalyst. In addition, the Raney Cu–Zr (1.5 at.%) exhibited a higher specific activity which was 57% higher than the commercial catalyst and 25% higher than that of the multicompo-

Table 5
Catalytic performances of a typical Raney Cu based catalyst compared with those of an optimal Cu/ZnO-based multicomponent catalyst and a commercial catalyst

Catalyst	S_{area}(3) (m^2/ml-cat)	S_{Cu}(3) (m^2/ml-cat)	Methanol activity(3) (mg-MeOH/ml-cat h)		Specific activity(3) (mg-MeOH/m^2-cat h)
Raney Cu/Zr(1)	31.2	20.6	941(a)	853(b)	41.4
$Cu/ZnO/ZrO_2/Al_2O_3$	90.7	26.4	845	839	31.8
Commercial catalyst(2)	72.5	34.5	626	591	17.1

(1)Conditions of preparation: leaching of an alloy $CuAl_2$/Zr containing 1.5 at.% of Zr in an aqueous solution of NaOH(341 g)/ZnO (91 g) in 1 kg-H_2O in the stream of N_2 at 333 K.
(2)$Cu/ZnO/Al_2O_3$.
(3)Same conditions as described in Table 2.

nent catalyst. These findings clearly indicated that the synergetic alloying between copper and the metallic components is more exerted in the case of Raney Cu catalyst than in the case of mixture oxides' catalysts.

4. Conclusion

In summary, this study clearly showed that Raney Cu catalyst prepared in the optimal conditions determined was highly active for methanol synthesis from CO_2 and H_2. For every Raney Cu–M catalyst, the presence of zincate with NaOH in the leaching aqueous solution led to the deposition of Zn on the surface of Cu particles. The degree of zinc deposition was improved by increasing in an optimum range ZnO concentration in the leaching solution. The presence of Zn along with Cu on the surface of Raney Cu catalyst had a strong double effect: to increase the surface area and to enhance the specific activity. Raney Cu–Zr (1.5 at.%) was the most active catalyst among Raney Cu–M catalysts tested. The initial activity of the present catalyst was significantly higher than that of a commercial catalyst tested in the same reaction conditions.

Acknowledgements

This work was in part supported by New Energy and Industrial Technology Development Organization (NEDO).

References

[1] M. Saito, T. Fujitani, M. Takeuchi, T. Watanabe, Appl. Catal. A 138 (1996) 311–318.

[2] M. Saito, T. Fujitani, I. Takahara, T. Watanabe, M. Takeuchi, Y. Kanai, K. Moriya, T. Kakumoto, Energy Convers. Mgmt 36 (1995) 577.

[3] M.S. Wainwright, Proceedings on Alcohol Fuels, Sydney, August 1978, p. 8.

[4] M.S. Wainwright, D.L. Trimm, Catal. Today 23 (1995) 29.

[5] G.C. Chinchen, K.C. Waugh, D.A. Whan, Appl. Catal. 251 (1986) 101.

[6] H.E. Curry, M.S. Wainwright, D.J. Young, in: D. Bibby, C.C. Chang (Eds.), Methane Conversion, Stud. Surf. Sci. Catal. 36 (1988) 239–244.