

## Comparison of Pt and Cu promotional effects in CO<sub>2</sub> Hydrogenation over Co/Al<sub>2</sub>O<sub>3</sub>

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### Introduction

Concern for the consequences of emission of CO<sub>2</sub> to the atmosphere has motivated the study of alternatives for the direct reduction of the emission as well as for recycling of CO<sub>2</sub> by its conversion to liquid fuels [1]. There are many approaches have been perused among them catalytic hydrogenation to liquid hydrocarbons through carbon monoxide is the most attractive one. One of the early studies by Russell et al. [2] on hydrogenation of carbon dioxide using cobalt catalyst showed an improving oil yield with the addition of copper, potassium and ceria. Later, Okabe et al. [3] prepared Co/SiO<sub>2</sub> catalysts derived from acetate and promoted with Ir and these catalysts showed a high selectivity to CO and MeOH. Riedel et al. [4] observed the same product distribution with alkalinized iron catalyst from a feed of H<sub>2</sub>/CO<sub>2</sub> as from H<sub>2</sub>/CO synthesis gas in spite of the lower CO partial pressure due to water-gas shift equilibrium constraints, where as with the cobalt catalyst, the shift CO to CO<sub>2</sub> results in the product distribution being shifted from a FT type distribution to almost exclusively methane. Herein, we report the comparison study of Cu and Pt promotional influence on rate and product distribution of hydrogenation of CO<sub>2</sub>.

### Experimentals

The catalysts used in this study, 0.5%Pt-25%Co/Al<sub>2</sub>O<sub>3</sub> and 0.5%Cu-25%Co/Al<sub>2</sub>O<sub>3</sub> were prepared by a sequential aqueous slurry impregnation method using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as the support. Two impregnation steps were used to load 25% Co followed by 0.5% Pt (0.5% Cu). Between each step, the catalyst was dried under vacuum in a rotary evaporator at 363 K for 2 h. After the second impregnation/drying step, the catalyst was calcined in flowing air at 623 K for 4 h. BET surface area measurements were conducted using a Micromeritics Tri-Star system. An appropriate amount (~0.25 g) of catalyst sample was taken and slowly heated to 433 K for 10 h under vacuum (~50m Torr). The sample then was transferred to the adsorption unit, and the N<sub>2</sub> adsorption was measured at the boiling temperature of nitrogen (77K). Hydrogenation of CO<sub>2</sub> reactions were conducted in a 1 L CSTR. In a typical experiment, 12-15 g of calcined catalyst (80-140 mesh) were reduced *ex-citu* using H<sub>2</sub>:He (1:3) mixture at 623 K for 10h. The reduced catalyst was transferred to a 1 L CSTR which already contained 310 g of melted Polywax, 3000 under flowing nitrogen. The catalyst was reduced *in-situ* using pure H<sub>2</sub> (15 slph) for 24 h at 503 K. Three Brooks mass flow controllers were used to control the flow rate of CO<sub>2</sub>, H<sub>2</sub>, and N<sub>2</sub>. Hydrogenation of CO<sub>2</sub> was conducted at 493 K, 1.99 MPa and a constant space velocity of 4.0 SL/h/g catalysts with different H<sub>2</sub>:CO<sub>2</sub> ratios. The effluent gases were analyzed online using a Micro GC equipped with a TCD detector, while the liquid products condensed at 273 K and 373 K traps were analyzed separately using a HP 5890 GC with capillary column DB-5 and a HP 5790 GC with Porapak Q packed column.

### Results and Discussion

On both catalysts, as the H<sub>2</sub>/CO<sub>2</sub> ratio decreases CO<sub>2</sub> conversion also decreased but differs in the product selectivity. Cu promotes to form more C<sub>2</sub> and C<sub>3</sub> compare to Pt and as

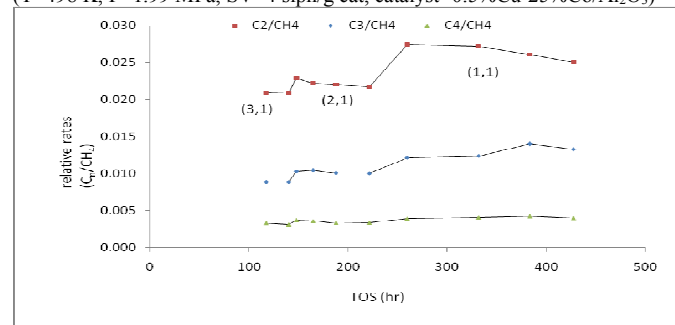
seen from Table 1 that the chain growth probability ( $\alpha$ ) increased from 0.32 to 0.39 as the H<sub>2</sub>/CO<sub>2</sub> decrease. In addition, Cu catalyst shown higher CO<sub>2</sub> conversion compare to Pt under our experimental conditions indicate Cu promotes CO<sub>2</sub> hydrogenation better than the conventional Pt based catalysts. Figure 1 shows the effect of H<sub>2</sub>/CO<sub>2</sub> ratio on relative rates of HC (C<sub>n</sub>/CH<sub>4</sub>) with time on stream of Cu-Co-Al<sub>2</sub>O<sub>3</sub> catalyst. The relative rates of C<sub>2</sub>/CH<sub>4</sub> and C<sub>3</sub>/CH<sub>4</sub> increases with decreasing H<sub>2</sub>/CO<sub>2</sub> quite considerably where as C<sub>4</sub>/CH<sub>4</sub> remains the same. It show that the major product formation from CO<sub>2</sub> hydrogenation is methane (80-93 %) and less amount of C<sub>2</sub>, C<sub>3</sub>,C<sub>4</sub> are only formed irrespective of the catalyst system. This could be explained on the basis that the attainable CO partial pressure rather very low to establish FT regime, which is an important criterion of inhibition of product desorption.

**Table 1. Effect of H<sub>2</sub>:CO<sub>2</sub> ratio on product distribution**

(T = 498 K, P = 1.99 MPa, SV = 4 slph/g catalyst)

Feed composition (H <sub>2</sub> :CO <sub>2</sub> :N <sub>2</sub> )	CO <sub>2</sub> conversion (%)	Selectivity (C %)				$\alpha$ (C <sub>2</sub> – C <sub>3</sub> )
		CH <sub>4</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	
Pt-Co-Al <sub>2</sub> O <sub>3</sub>						
3:1:0	40	89.0	2.69	1.64	1.15	0.33
2:1:1	26.3	86.3	3.31	2.09	0.99	0.36
Cu-Co-Al <sub>2</sub> O <sub>3</sub>						
3:1:0	46.3	92.2	3.8	2.4	1.2	0.32
2:1:1	36.2	81.9	3.6	2.5	1.1	0.39

**Figure 1. Effect of H<sub>2</sub>:CO<sub>2</sub> ratio on rates of HC formation with time-on-stream**  
(T=498 K, P=1.99 MPa, SV=4 slph/g cat, catalyst=0.5%Cu-25%Co/Al<sub>2</sub>O<sub>3</sub>)



### References

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