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**PROBE MOLECULE STUDIES:
ACTIVE SPECIES IN ALCOHOL SYNTHESIS**

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1. OBJECTIVE AND SCOPE OF WORK

The goal of this research is to develop a better understanding of the mechanisms of formation of alcohols and other oxygenates from syngas over supported catalysts. Probe molecules will be added in situ during the reaction to help delineate reaction pathways and identify reaction intermediate species. The key of our study is to investigate how the species generated by these probe molecules interact with surface species present during oxygenate formation.

One of the catalysts chosen for this investigation is Co/Cu/ZnO/Al₂O₃. Detailed motivations for studying this system as well as using CH₃NO₂ as the probe molecule were given in a previous report^[2].

2. SUMMARY OF PROGRESS

(A) BET surface areas and XRD patterns of Cu/ZnO/Al₂O₃ and Co(5%)/Cu/ZnO/Al₂O₃ suggested that the addition of Co did not significantly change the Cu/ZnO/Al₂O₃ structure.

(B) Co(10%)/Cu/ZnO/Al₂O₃ was prepared in the same way as Co(5%)/Cu/ZnO/Al₂O₃^[3]. CO hydrogenation was conducted over this catalyst under the same conditions used for Co(5%)/Cu/ZnO/Al₂O₃^[3].

(C) Different amounts of C₂H₄ were added to the steady state CO hydrogenation reaction over Co(5%) and Co(10%)/Cu/ZnO/Al₂O₃. For both these catalysts, increases in propanol and

decreases in methanol production were observed as the C_2H_4 level was increased.

(D) Blank runs with $H_2/He/CH_3OH/C_2H_4$ over Co(5%) and Co(10%)/Cu/ZnO/ Al_2O_3 catalysts were conducted and showed that under the reaction conditions used C_2H_4 does not react with CH_3OH .

3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

(A) BET Surface Area and XRD

Table 1 lists the results of BET surface area measurements of two catalyst samples, Cu/ZnO/ Al_2O_3 and Co(5%)/Cu/ZnO/ Al_2O_3 , after similar treatment (calcination, reduction, CO hydrogenation^[3], H_2 flush at 290°C overnight, passivation at room temperature with O_2 (2% in He)). The unchanged BET surface area suggests that the Co addition did not change the bulk structure of the Cu/ZnO/ Al_2O_3 which may further imply that the added Co is associated only with the surface of the Cu/ZnO/ Al_2O_3 .

Table 1. BET Surface Area of Co(0%, 5%)/Cu/ZnO/ Al_2O_3

CATALYST	BET Surface Area, $m^2/g\text{-cat}$		
	<u>RUN 1</u>	<u>RUN 2</u>	<u>Average</u>
0% Co	54.5	60.2	57
5% Co	56.5	64.1	60

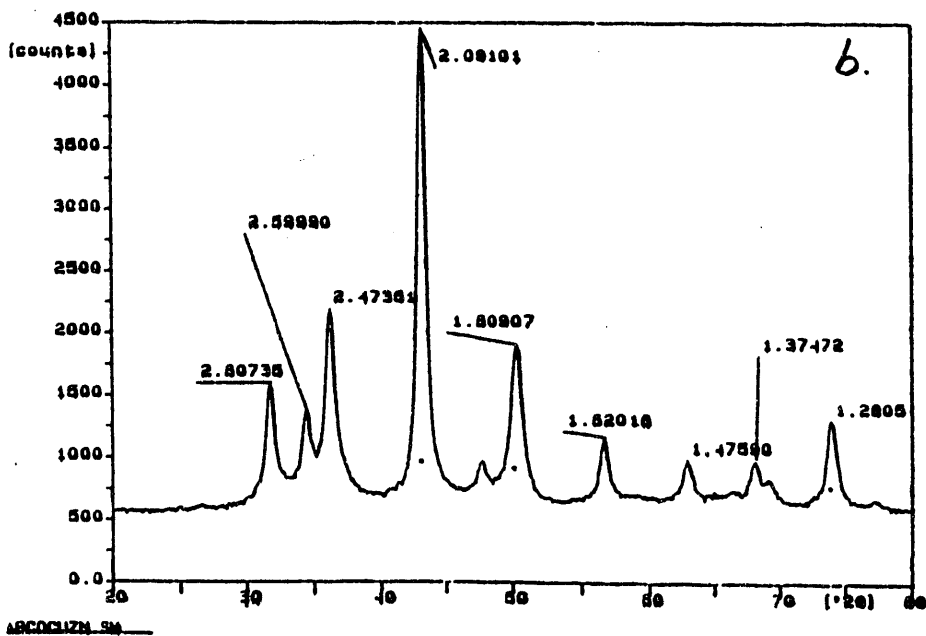
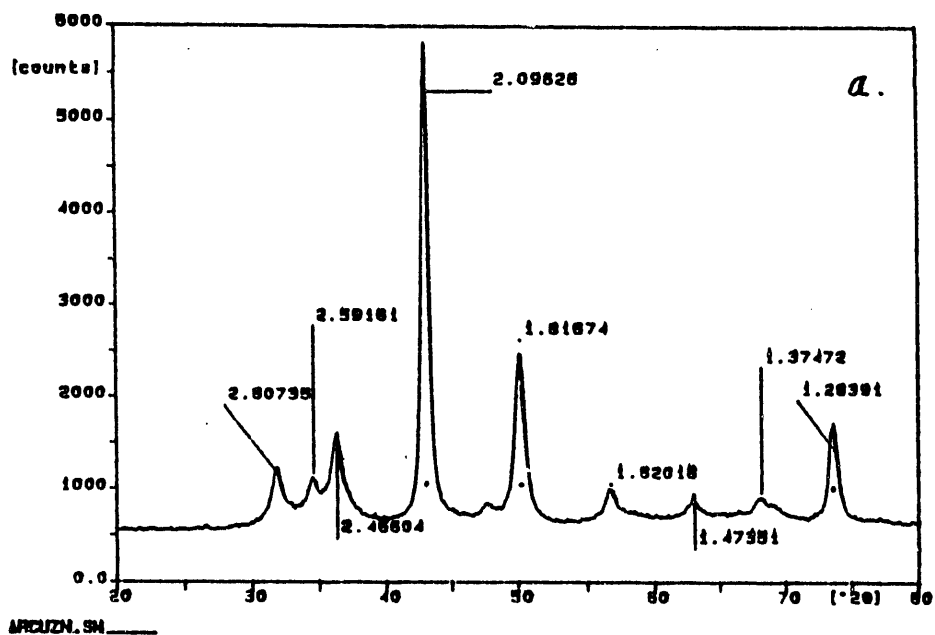


Figure 1. XRD Patterns of (a) Cu/ZnO/Al₂O₃ and (b) Co(5%)/Cu/ZnO/Al₂O₃ after Reactions.

The XRD patterns of Cu/ZnO/Al₂O₃ and Co(5%)/Cu/ZnO/Al₂O₃ after reactions (see Figure 1) show similar Cu/ZnO structures which further suggests that there is no bulk structure change caused by cobalt addition.

(B) CO hydrogenation

Co(10%)/Cu/ZnO/Al₂O₃ was prepared in the same way as Co(5%)/Cu/ZnO/Al₂O₃^[3]. CO hydrogenation was also carried out over Co(10%)/Cu/ZnO/Al₂O₃ at the same reaction conditions used for Co(5%)/Cu/ZnO/Al₂O₃, i.e. 500 psi, 290 °C, H₂:CO=2, and GHSV=7600 hr⁻¹. The comparison of the CO hydrogenation results over these two catalysts are given in Table 2.

The data in Table 2 provides the following facts:

1) the comparison of the specific rates (μmol/g-cat/min) of products shows that increased Co loading does not suppress the formation rate of any products except dimethylether;

2) the comparison of both the rate and the selectivity (mole ratio of C in alcohols and hydrocarbons) shows that the increased Co loading provided slight increases in the production of alcohols as well as a promotion of hydrocarbon production.

The promotion of hydrocarbons with increased Co loading suggests an increased surface area of Co⁰. The promotion of alcohols and the suppression of dimethylether suggest that the Co addition might have altered the surface state of the Cu/ZnO, possibly the oxidation states of Cu. Planned characterization studies like TPR, XRD, and XPS will be very

Table 2. Comparison of CO Hydrogenation over Co(5,10%)/Cu/ZnO/Al₂O₃ at 500psi, 290°C, H₂:CO=2, GHSV=7600 hr⁻¹.

<u>PRODUCTS</u> <u>(-CO₂, -H₂O)</u>	<u>μmol/g-cat/min</u>		<u>Mole Ratio of C</u>	
	<u>Co(5%)</u>	<u>Co(10%)</u>	<u>Co(5%)</u>	<u>Co(10%)</u>
CH ₃ OH	14.4	20.2	51.8	46.5
CH ₃ OCH ₃	0.5	0.1	3.7	0.5
CH ₃ CH ₂ OH	1.0	1.8	7.2	8.4
CH ₃ CH ₂ CH ₂ OH	0.3	0.3	2.8	2.2
CH ₃ (CH ₂) ₃ OH	0.0	0.1	0.0	0.0
CH ₄	5.0	8.4	18.0	19.0
C ₂ H ₄ +C ₂ H ₆	1.4	4.1	10.2	17.6
C ₃ + HCs	0.5	1.0	6.2	5.8
<u>CO₂ :</u>	13.3	18.5		
	<u>Total Conversion of CO (%)</u>			
	1.2	1.7		

helpful to understand further the role of Co.

(C) Effect of C₂H₄ Addition

As reported previously^[3], C₂H₄ was added as a probe molecule to the CO hydrogenation reaction over the Co(5%)/Cu/ZnO/Al₂O₃ catalyst and a simultaneous increase in propanol and decrease in methanol was observed. During this reporting period, different amounts of C₂H₄ were added to the steady state CO hydrogenation over Co(5%)/ and Co(10%)/Cu/ZnO/Al₂O₃. With both of these catalysts, further increases in propanol

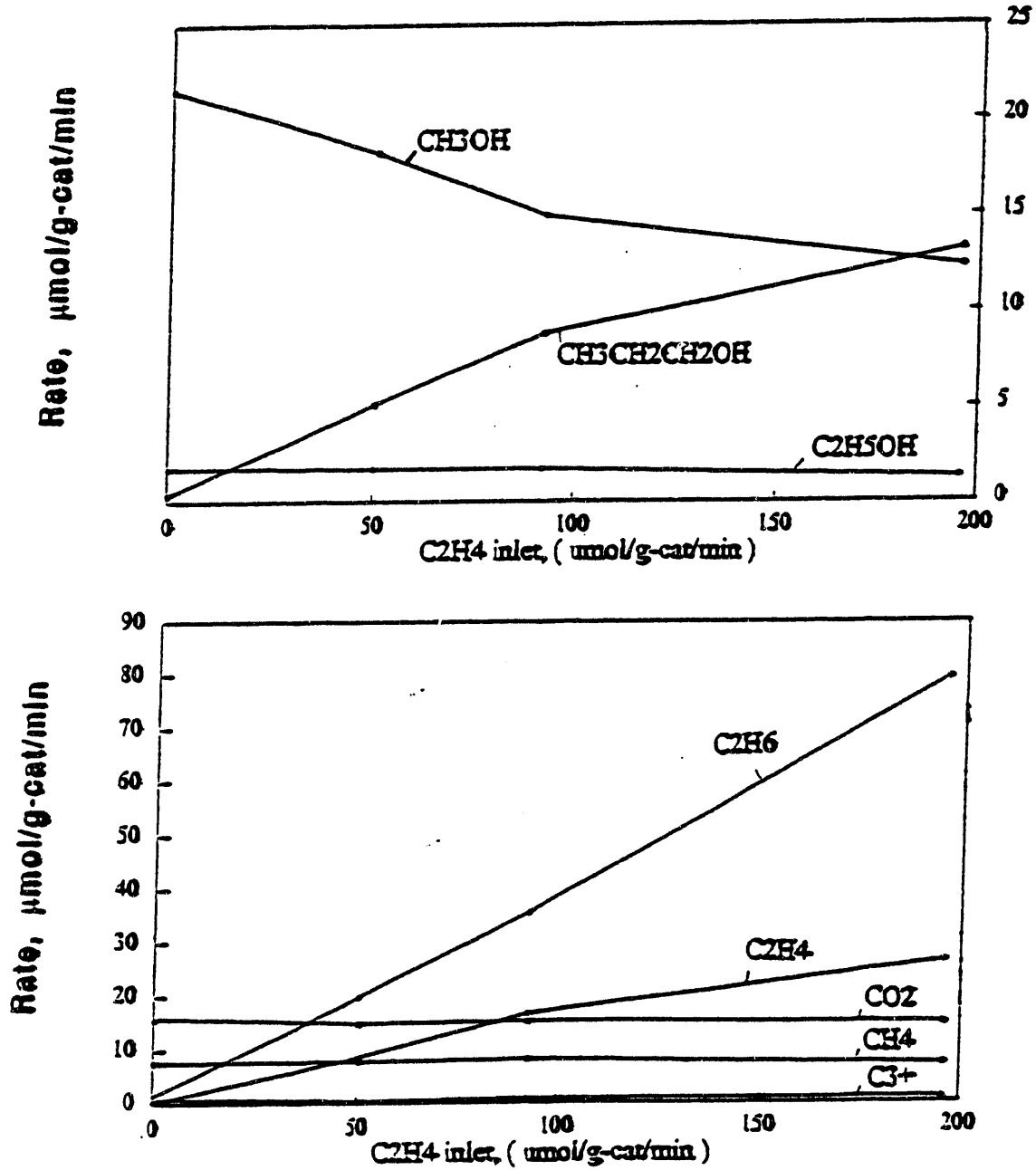


Figure 2. Effect of C₂H₄ addition on CO hydrogenation over Co(10%)/Cu/ZnO/Al₂O₃ at 500 psi, 290 °C, H₂/CO = 2, and GHSV = 7600 hr⁻¹

and decreases in methanol were observed as the C_2H_4 level increased. The steady state data obtained with Co(10%)/Cu/ZnO/Al₂O₃ is plotted in Figure 2. The increase in propanol with the C_2H_4 level supports the existence of a hydroformylation pathway. However, the concomitant decrease in methanol suggests the involvement of the methanol intermediate in a 2nd pathway for propanol production. This is consistent with the observation reported in the study of CH_3NO_2 addition^[3]. The fact that hydrocarbons and CO_2 were not affected and most of the added C_2H_4 was hydrogenated into C_2H_6 suggests that propanol forms readily with the supply of C_2H_4 on the surface under the CO hydrogenation reaction. In other words, the formation of propanol from CO/H₂ over this type of catalyst can be limited by the insufficiency of surface C_2H_4 . This raises the question of whether Co simply supplies surface C_xH_y species or if it has a more complex role. On the other hand, is the role of Cu/ZnO that of supplying undissociated CO or some type of methanol precursor, such as CH_xO surface species? Further investigations are required to answer these questions.

(D) Blank Reactions

C_2H_4 and CH_3OH were added sequentially into the H₂/He stream (17+113 cc/min) passing through the reactor loaded with catalyst at 500 psig and 290°C. The steady state data listed in Table 3 shows that:

- 1) C_2H_4 does not react with CH_3OH to form propanol over

Table 3. $H_2/He/+C_2H_4/+CH_3OH$ over $Co/Cu/ZnO/Al_2O_3$
at 500 psig, 290°C, GHSV=7600 hr^{-1} .

CATALYST	PM		PRODUCTS						
	$C_2H_4^*CH_3OH$		CH_4	C_2H_4	C_2H_6	C_3+	CH_3OH	DME	CO_2
			($\mu mol/g-cat/min$)						
0% Co**	880.		0.4	0.2	877.4	0.9	0.0	0.0	0.0
	880.	35.	4.9	2.7	872.4	0.5	46.1	2.0	9.3
5% Co	87.		0.1	0.0	87.0	0.0	0.0	0.0	0.0
	87.	35.	2.2	0.0	93.2	0.1	0.9	0.9	3.1
10% Co	63.		0.0	0.0	63.2	0.1	0.0	0.0	0.0
	63.	35.	1.5	2.1	61.0	0.2	14.4	0.8	3.4

* C_2H_4 amounts were estimated from the total carbon number of the exit.

** The original catalyst calcined and reduced the same way as the catalysts with Co addition, but without wet impregnation.

the $Cu/ZnO/Al_2O_3$ with or without Co addition;

2) Catalysts with or without Co addition, Co(0%)/ and Co(5%)/ and Co(10%)/ $Cu/ZnO/Al_2O_3$, are all very good C_2H_4 hydrogenation catalysts;

3) The catalyst surface with Co addition retains CH_3OH in the absence of CO.

4. PLANS FOR THE NEXT REPORTING PERIOD

The experiments listed below are planned for the next reporting periods:

a) Blank reaction of $CO/H_2/+C_2H_4$ over empty reactor to

evaluate the extent of C_2H_4 hydrogenation if any on the reactor walls;

b) Preparation of a $Co(0\%)/Cu/ZnO/Al_2O_3$ catalyst with $H_2O + HNO_3$ of the same pH as the cobalt nitrate solution and using the same procedure as in the preparation of the $Co(5\%)/$ and $Co(10\%)/Cu/ZnO/Al_2O_3$ catalysts to get a comparable base catalyst;

c) Preparation of a $Co(5\%)/Al_2O_3$ catalyst as another base catalyst;

d) CO hydrogenation and probe molecule (CH_3NO_2 , C_2H_4) addition over $Co(0\%)/Cu/ZnO/Al_2O_3$ and $Co(5\%)/Al_2O_3$, and CH_3NO_2 addition to $Co(10\%)/Cu/ZnO/Al_2O_3$;

e) XRD, TPR and XPS experiments with selected catalyst samples.

5. REFERENCES

- [1] DOE Quarterly Report, No.1&3, 1991, under Grant No. DE-FG22-90PC-90305.
- [2] DOE Quarterly Report, No.5, 1991, under Grant No. DE-FG22-90PC-90305.
- [3] DOE Quarterly Report, No.7, 1992, under Grant No. DE-FG22-90PC-90305.

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