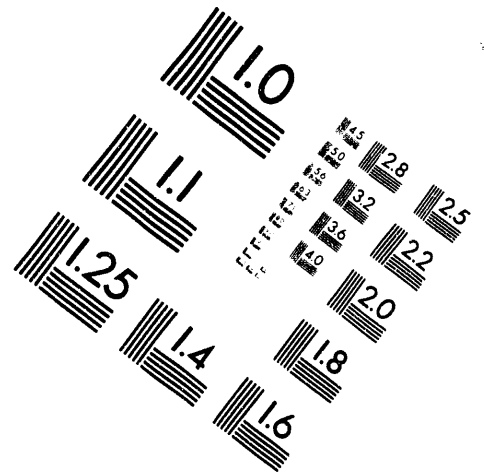
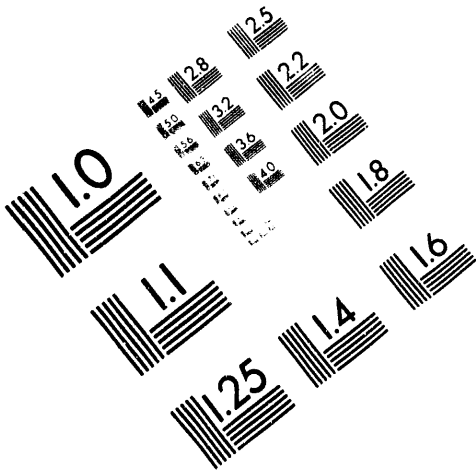




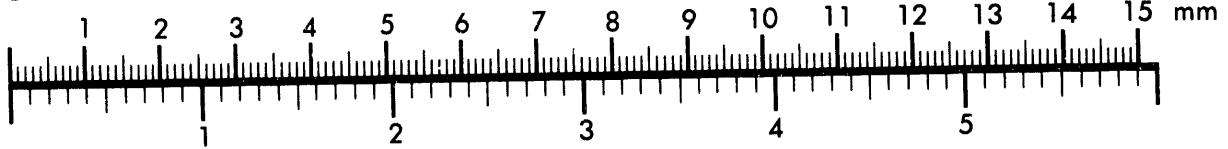
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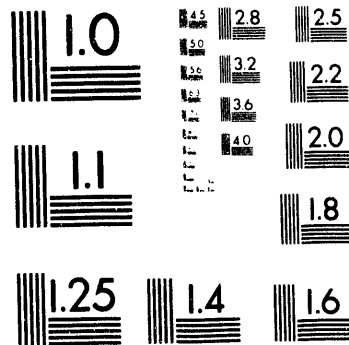
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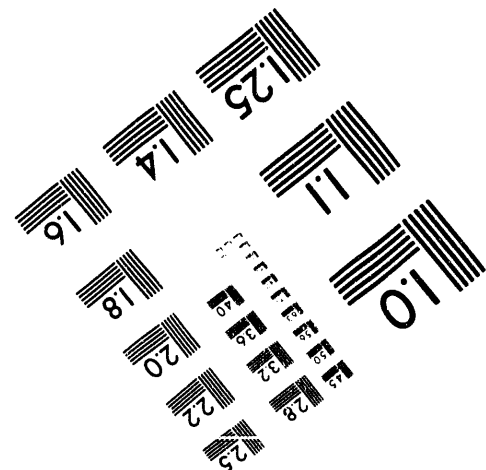
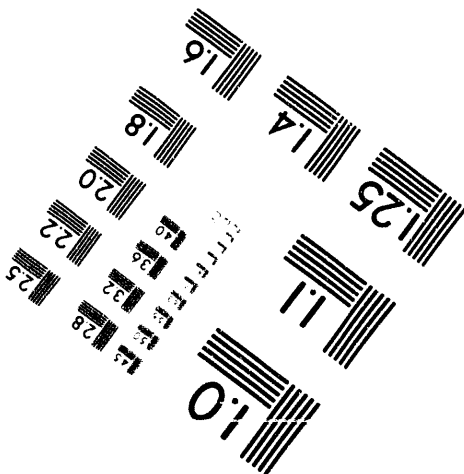
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DOE QUARTERLY REPORT, No.10, January 1993 - March 1993

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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 are 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.

The catalysts chosen for this investigation is Co/Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>. Detailed motivations for studying this system as well as using CH<sub>3</sub>NO<sub>2</sub> as the probe molecule were given in a previous report<sup>[1]</sup>.

## 2. SUMMARY OF PROGRESS

(A) X-ray photoelectron spectroscopy (XPS) experiments were carried out on calcined and reduced samples of Co(0%)/Cu/ZnO and Co(10%)/Cu/ZnO catalysts.

(B) The extent of reduction of the copper and cobalt phases in the Co(0, 5 and 10%)/Cu/ZnO catalysts was estimated from XPS, TPR, and XRD results<sup>[2]</sup>.

(C) A Co(5%)/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared to be used as a base catalyst for the study of probe molecule addition.

(D) CO hydrogenation under the same conditions used before<sup>[2]</sup> was conducted over the Co(5%)/Al<sub>2</sub>O<sub>3</sub> catalyst as well as a Co/Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst (ZC45) prepared by coprecipitation method<sup>[3]</sup>.

## 3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

### (A) XPS Experiments

The calcined and reduced samples of Co(0%)/Cu/ZnO and Co(10%)/Cu/ZnO catalysts were studied by XPS. Figure 1 shows the XPS patterns of Cu 2p

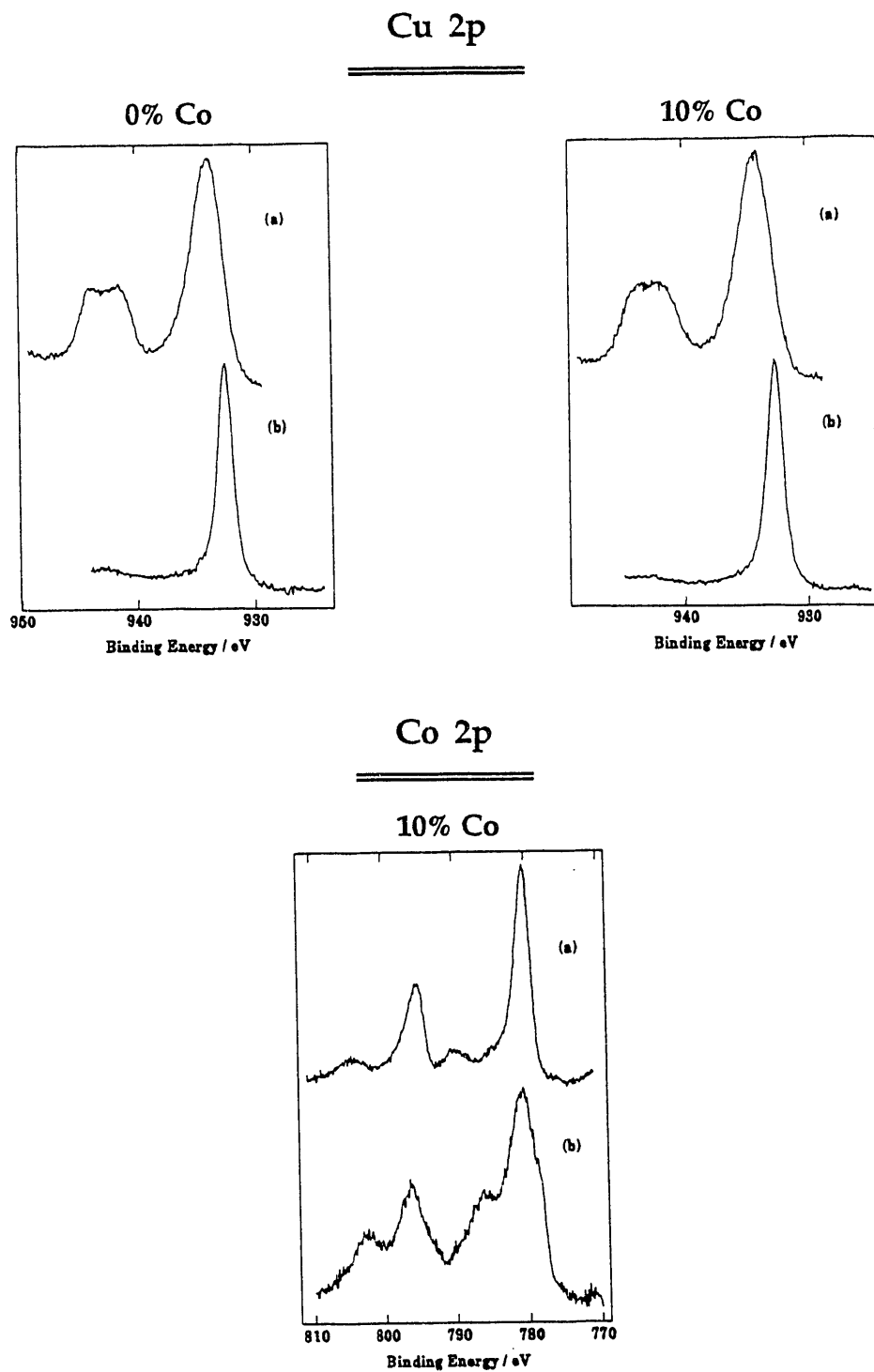


Figure 1. XPS Patterns of Cu 2p and Co 2p in (a) oxidized and (b) reduced samples of Co(0%)/Cu/ZnO and Co(10%)/Cu/ZnO catalysts.

and Co 2p in both oxidized and reduced catalysts. Table 1 lists both the measured and the reference values of photoelectron (2p, 3/2), Auger energy and the Auger parameter for Cu. Both Cu 2p peak shape and the Auger parameters indicate the reduction to copper metal. It is clearly shown by the results of this study that copper was completely reduced in both samples prior to the reaction and cobalt was only partially reduced in the 10% Co catalyst.

Table 1. Measured and reference values of photoelectron, Auger energy and Auger parameter ( $\alpha$ ) for Cu.

Sample		2p 3/2	Auger Energy	$\alpha$
Oxi/Red	wt% of Co		(LMM)	
Oxidized	0	933.76	569.04	1851.32
Oxidized	10	934.14	569.23	1851.51
Reduced	0	923.42	567.75	1851.27
Reduced	10	932.67	568.04	1851.23
Copper <sup>[4]</sup>				
Cu		932.67	567.95	1851.32
Cu <sub>2</sub> O		932.40	569.80	1849.40
CuO		933.80	568.70	1851.70

#### (B) Estimation of the Reduction Extent of Copper and Cobalt Phases.

Both the XRD<sup>[2]</sup> and XPS results show that in the reduced samples of Co(0, 5 and 10%)/Cu/ZnO catalysts, copper was completely reduced. Using this information (100% reduction of copper phase), the reduction extent of cobalt in the cobalt containing catalysts was estimated from the H<sub>2</sub> uptake amounts obtained by temperature programmed reduction<sup>[2]</sup>. The results are listed in Table 2. It is shown that the cobalt phase (Co<sub>3</sub>O<sub>4</sub>) in the 5% Co catalyst was nearly completely reduced but in the 10% Co catalyst only partially

reduced.

The evidences of complete reduction of copper suggest that surface  $\text{Cu}^0$  is the active element for methanol formation and the suppression of methanol by addition of cobalt<sup>[2]</sup> seems mainly caused by blocking the surface  $\text{Cu}^0$ . The partial reduction of cobalt in the  $\text{Co}(10\%)/\text{Cu}/\text{ZnO}$  catalyst might be the reason why the increase of hydrocarbon formation with increased loading of Co from 5% to 10% was insignificant.

Table 2. Estimation of the reduction extent of cobalt phase in  $\text{Co}(5 \text{ and } 10\%)/\text{Cu}/\text{ZnO}$  catalysts from the TPR data.

Catalysts ( wt% of Co )	H <sub>2</sub> -Uptake ( μmol/g-cat )			Co Reduction ( % )
	Measured	Calculated*		
	CuO+Co <sub>3</sub> O <sub>4</sub>	CuO	Co <sub>3</sub> O <sub>4</sub>	
0	5.10	5.10	-	-
5	5.91	4.85	1.13	94.2
10	5.90	4.59	2.26	58.1

\* Assuming 100% reduction of copper.

#### (C) Preparation of $\text{Co}(5\%)/\text{Al}_2\text{O}_3$ .

In the attempt to distinguish the behavior of probe molecule on Co surface from Cu surface, a  $\text{Co}(5\%, \text{wt})/\text{Al}_2\text{O}_3$  catalyst was prepared by wet impregnation of  $\alpha\text{-Al}_2\text{O}_3$  (  $1 \text{ m}^2/\text{g}$  ) with cobalt nitrate. The pretreatment for this catalyst followed the same procedures as for the impregnated  $\text{Co}/\text{Cu}/\text{ZnO}$  catalysts<sup>[5]</sup>.

#### (D) CO Hydrogenation over the $\text{Co}(5\%)/\text{Al}_2\text{O}_3$ and ZC45.

CO hydrogenation reaction was conducted under the same conditions



used before (500 psig, 290 °C, GHSV=6000~60000 hr<sup>-1</sup>)<sup>[2]</sup> over both the Co(5%)/Al<sub>2</sub>O<sub>3</sub> catalyst and a Co/Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst (ZC45) prepared by coprecipitation method.

The steady state CO hydrogenation data over Co(5%)/Al<sub>2</sub>O<sub>3</sub> catalyst is reported in Table 3 with the data obtained over Co(5%)/Cu/ZnO catalyst<sup>[2]</sup> for comparison. As expected, the catalyst made mainly hydrocarbons. This result suggests that this catalyst is a good candidate for studying the behavior of probe molecule addition to CO/H<sub>2</sub> over Co<sup>o</sup> surface.

Table 3. Steady State Data of the CO Hydrogenation over Co(5%)/Al<sub>2</sub>O<sub>3</sub> and Co(5%)/Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> at 500 psig; 290°C; H<sub>2</sub>:CO = 80:40 (cc/min); GHSV = 6000~60000 hr<sup>-1</sup>.

PRODUCTS	ACTIVITY		SELECTIVITY*	
	Co(5%)/Al <sub>2</sub> O <sub>3</sub>	Co(5%)/Cu/ZnO	Co(5%)/Al <sub>2</sub> O <sub>3</sub>	Co(5%)/Cu/ZnO
	<u>μmol/g-cat/min</u>		<u>%, μmol</u>	
<b>OXYGENATES:</b>	<b>14.5</b>	<b>26.6</b>	<b>2.3</b>	<b>76.4</b>
CH <sub>3</sub> OH	10.8	23.9	1.7	68.7
CH <sub>3</sub> OCH <sub>3</sub>	0.0	0.8	0.0	2.3
CH <sub>3</sub> CH <sub>2</sub> OH	3.3	1.5	0.5	4.2
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	0.4	0.4	0.1	1.2
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	0.0	0.0	0.0	0.0
<b>HYDROCARBONS:</b>	<b>618.5</b>	<b>8.2</b>	<b>97.7</b>	<b>23.6</b>
CH <sub>4</sub>	515.8	5.3	81.5	15.3
C <sub>2</sub> H <sub>4</sub> +C <sub>2</sub> H <sub>6</sub>	41.3	1.9	6.5	5.4
C <sub>3</sub> +HCs	61.4	1.0	9.7	2.9
<b>CO<sub>2</sub>:</b>	<b>43.3</b>	<b>16.3</b>		
<b>TOTAL:</b>	<b>676.3</b>	<b>51.1</b>		
	<u>Carbon conversion, %</u>			
	<b>2.5</b>	<b>1.5</b>		

\* CO<sub>2</sub> is not included.

The Co/Cu/Zn/Al catalyst prepared by coprecipitation (ZC45) has an atomic ratio of the metals Co : Cu : Zn : Al = 0.5 : 1.0 : 1.25 : 1.1, and contains 10.6 wt% Co. The steady state data of CO hydrogenation over this catalyst is presented in Table 4 and 5. In Table 4, it is compared with the published data over a Co/Cu/Al catalyst (with Co : Cu : Al = 1.05 : 1.0 : 2.01) which was prepared in a similar way<sup>[3]</sup>. It shows that under our condition (290°C, 500 psig) the overall activity of ZC45 was comparable to that of Co/Cu/Al under higher pressure (735 psig) and at lower temperature (275 °C). The most significant difference in selectivity was in methanol formation which might be due to the different Co:Cu ratios and different reaction temperatures. In Table 5, the reaction data obtained with ZC45 is compared with the data obtained with Co(10%)/Cu/ZnO catalyst prepared by impregnation method<sup>[2]</sup>. It shows that the activities for higher alcohols and hydrocarbons over ZC45 (Cu:Co=2) were only slightly higher than those over the Co(10%)/Cu/ZnO catalyst (Cu:Co≈3), but ZC45 produced much less methanol than the Co(10%)/Cu/ZnO catalyst. Thus the higher selectivities observed for higher alcohols as well as hydrocarbons were mainly caused by suppression of methanol.

Table 4. CO hydrogenation data over Co/Cu/Zn/Al (ZC45) and Co/Cu/Al<sup>[3]</sup>

Conditions for Co/Cu/Al catalyst:						
P = 735 psig, T = 275 °C, GHSV = 5000 hr <sup>-1</sup> , CO:H <sub>2</sub> = 2.						
ACTIVITY ( μmol-C/g-cat/min )	SELECTIVITY ( wt % )					
	HC	Alc	CH <sub>3</sub> OH	C <sub>2</sub> +OH	CH <sub>4</sub>	C <sub>2</sub> +HC
98.0	46.0	54.0	29.2	24.8	16.4	29.6
Conditions for Co/Cu/Zn/Al (ZC45):						
P = 500 psig, T = 290 °C, GHSV = 6000 hr <sup>-1</sup> , CO:H <sub>2</sub> = 2.						
ACTIVITY ( μmol-C/g-cat/min )	SELECTIVITY ( wt % )					
	HC	Alc	CH <sub>3</sub> OH	C <sub>2</sub> +OH	CH <sub>4</sub>	C <sub>2</sub> +HC
98.4	61.8	38.2	4.1	34.1	18.9	42.9

Table 5. Steady State Data of the CO Hydrogenation over ZC45 and Co(10%)/Cu/ZnO /Al<sub>2</sub>O<sub>3</sub> at 500 psig; 290°C; H<sub>2</sub>:CO = 80:40 (cc/min); GHSV = 6000~60000 hr<sup>-1</sup>.

PRODUCTS	ACTIVITY		SELECTIVITY*	
	ZC45	10%-Co	ZC45	10%-Co
	<u>μmol/g-cat/min</u>		<u>% , μmol</u>	
<b>OXYGENATES:</b>	<b>8.6</b>	<b>25.5</b>	<b>37.0</b>	<b>67.3</b>
CH <sub>3</sub> OH	4.2	22.3	18.1	58.9
CH <sub>3</sub> OCH <sub>3</sub>	0.0	0.2	0.0	0.4
CH <sub>3</sub> CH <sub>2</sub> OH	3.1	2.1	13.3	5.6
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	0.8	0.8	3.5	2.1
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	0.5	0.1	2.1	0.3
<b>HYDROCARBONS:</b>	<b>14.7</b>	<b>12.4</b>	<b>63.0</b>	<b>32.7</b>
CH <sub>4</sub>	7.9	9.6	33.8	25.4
C <sub>2</sub> H <sub>4</sub> +C <sub>2</sub> H <sub>6</sub>	3.0	2.0	12.7	5.3
C <sub>3</sub> + HCs	3.8	0.8	16.5	2.0
<b>CO<sub>2</sub>:</b>	<b>55.5</b>	<b>20.1</b>		
<b>TOTAL:</b>	<b>78.8</b>	<b>57.9</b>		
	<u>Carbon conversion, %</u>			
	<b>2.1</b>	<b>1.7</b>		

\* CO<sub>2</sub> is not included.

#### 4. PLANS FOR THE NEXT REPORTING PERIOD

The following experiments are planned for the next reporting periods:

a) CO hydrogenation reactions over a series of Cu/Co/Cr catalysts prepared by coprecipitation method by Murty's group<sup>[6]</sup>. Comparing the activities and selectivities within the series and with the ZC45, a catalyst producing the most C<sub>2</sub>+ alcohols will be selected for further mechanistic study by probe molecule addition.

b) Studies of probe molecule addition over the selected catalyst and the Co(5%)/Al<sub>2</sub>O<sub>3</sub>.

c) Characterization studies of the selected catalyst and the Co(5%)/Al<sub>2</sub>O<sub>3</sub>.

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