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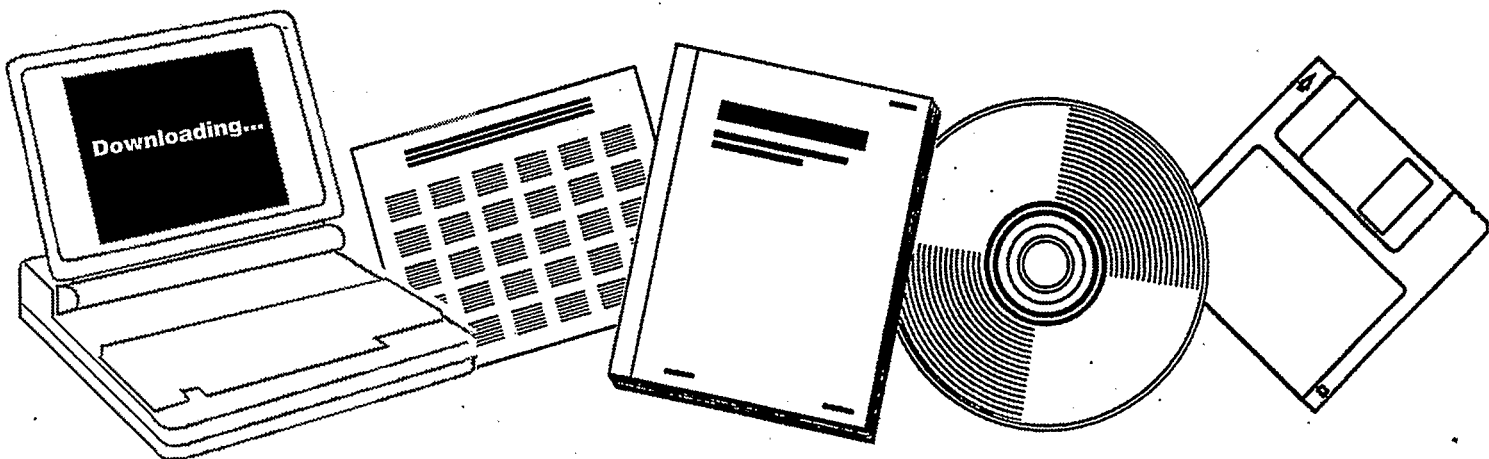
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**PROBE MOLECULE STUDIES: ACTIVE SPECIES IN  
ALCOHOL SYNTHESIS. NINTH QUARTERLY REPORT,  
OCTOBER 1992--DECEMBER 1992**

**PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL  
AND PETROLEUM ENGINEERING**

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

9th Quarterly Report  
October 1992 - December 1992

Donna G. Blackmond (PI)  
Irving Wender (Co-PI)  
Rachid Oukaci  
Jian Wang

Department of Chemical and Petroleum Engineering  
University of Pittsburgh  
Pittsburgh, PA 15261

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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) Pretreatment of a Co(0%)/Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> to be used as a base catalyst was carried out.

(B) XRD experiments were carried out with the calcined and reduced samples of the 0%-Co, 5%-Co and 10%-Co catalysts.

(C) Temperature programmed reduction was performed with the 0%-Co, 5%-Co and 10%-Co catalysts.

(D) CO hydrogenation under the same conditions used for the 5%-Co and 10%-Co catalysts was conducted over the Co(0%)/Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst.

(E) CH<sub>3</sub>NO<sub>2</sub> addition to the steady state reaction of CO hydrogenation was conducted over both the 0%-Co and the 10%-Co catalysts.

## 3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

(A) Preparation of Co(0%)/Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>.

A Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst with 0% loading of Co was pretreated by performing the same incipient wetness impregnation as for the 5%-Co<sup>[1]</sup> and

10%-Co samples<sup>[3]</sup> but with HNO<sub>3</sub> instead of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, at the equivalent pH value. The rest of the treatments were the same as for the 5%-Co and 10%-Co samples<sup>[2,3]</sup>.

#### (B) XRD

Figure 1 gives the XRD patterns of the calcined and reduced samples of 0%-Co, 5%-Co and 10%-Co catalysts. It shows that: (a) Co<sub>3</sub>O<sub>4</sub> was the only Co phase detected and it was detected only in the calcined 10%-Co catalyst; this oxide phase disappeared after reduction; (b) the patterns of the reduced samples showed almost complete reduction of copper in all the samples.

#### (C) TPR

TPR experiments were performed using an Altamira Instruments, Inc. system with a TCD detector. About 60 mg of each calcined catalyst sample was loaded in a fixed bed quartz reactor. Prior to TPR, the sample was first heated up in flowing O<sub>2</sub> (5% in He, 30 cc/min) to 350°C at 5°C/min, held for 8 hours, then cooled down to 50°C. After flushing with Ar (30 cc/min) at 50°C for 30 min, TPR was started with 5% H<sub>2</sub> in Ar flowing at 20 cc/min, and the temperature was increased at 1°C/min up to 500°C. The amount of H<sub>2</sub> uptake by the catalyst during the reduction process was calculated based on the peak area of the TCD response vs. time. The TCD response was calibrated with controlled pulse(s) of Ar into the 5% H<sub>2</sub> in Ar (20 cc/min).

Figure 2 gives the TPR profiles and the integrated amounts of total H<sub>2</sub>-uptake of the 0%-, 5%- and 10%-Co catalysts. It shows that the addition of Co increased the H<sub>2</sub>-uptake. No peak (H<sub>2</sub>-uptake) was observed at temperatures higher than 250°C (upto 500°C).

#### (D) CO Hydrogenation over Co(0%)/Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>

CO hydrogenation over Co(0%)/Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> was conducted under the same conditions used for the 5% and 10%-Co catalysts except that a lower catalyst loading in the reactor was used. The steady state data of the CO hydrogenation over the 0%-Co catalyst was compared with the data obtained

over 5%-Co and 10%-Co catalysts in Table 1. The overall activities of the 5%- and 10%-Co catalysts were similar but about five times less than that of 0%-Co catalyst. The addition of 5% Co suppressed methanol and dimethylether formation by an order of magnitude with a smaller suppression of ethanol, a small increase in propanol, and insignificant effect on hydrocarbons. The increase in Co loading, from 5% to 10%, only slightly suppressed methanol and dimethylether with small increases in ethanol, propanol, butanol and hydrocarbons. CO<sub>2</sub> formation was not significantly affected by Co addition.

#### (E) CH<sub>3</sub>NO<sub>2</sub> Addition over both 0%-Co and 10%-Co Catalysts

The data collected at steady state CO hydrogenation in both the absence and presence of CH<sub>3</sub>NO<sub>2</sub> over both 0%-Co and 10%-Co catalysts are presented in Table 2 together with the data previously reported for the 5%-Co catalyst. The steady state data obtained after CH<sub>3</sub>NO<sub>2</sub> addition was ended is also given in Table 2 (under I'), which shows that the original steady state of CO hydrogenation could be re-established and the deactivation effect of nitromethane was insignificant. The effects of the CH<sub>3</sub>NO<sub>2</sub> addition on the CO hydrogenation products is shown in Figure 3. Figure 4 shows the formation of nitrogen compounds, (CH<sub>3</sub>)<sub>n</sub>NH<sub>3-n</sub>, n = 0, 1, 2, 3, during the in-situ addition of CH<sub>3</sub>NO<sub>2</sub>.

As reported before<sup>[2]</sup>, over Co(5%)/Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, the formation of all alcohols was suppressed to the same extent, by 40% (II/I=0.6), and the formation of hydrocarbons was hardly affected except for a small increase in CH<sub>4</sub>. Methylamines were formed with almost 100% nitrogen conversion to trimethylamine, and no NH<sub>3</sub> was detected.

Over Co(10%)/Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, the formation of all alcohols was suppressed with the formation of ethanol and propanol suppressed to the same extent, by 20% (II/I=0.8), and that of methanol to a greater extent, by 40% (II/I=0.6), while the production of all hydrocarbons was enhanced. Methylamines and very small amount of NH<sub>3</sub> were formed with 73% nitrogen conversion to trimethylamine.

Over Co(0%)/Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, the formation of methanol was enhanced

while the formation of ethanol was suppressed and hydrocarbons were not significantly affected. Methylamines and  $\text{NH}_3$  were formed with 64% nitrogen conversion to trimethylamine.

#### 4. DISCUSSION

##### Characterization

The XRD pattern of the calcined 10%-Co sample shows that before reduction the cobalt was present as  $\text{Co}_3\text{O}_4$ . The disappearance of the  $\text{Co}_3\text{O}_4$  phase in the reduced 10%-Co catalyst suggests that most cobalt was reduced. The increase in  $\text{H}_2$  uptake of the 5%-Co sample in TPR compared with the 0%-Co sample provided another evidence of cobalt reduction. TPR study of supported  $\text{Co}^{\text{III}}$  have shown that the most intense TPR peaks for Co appear between 250~500°C. In the present study, with the addition of cobalt no peak at temperature higher than 250°C was observed in the TPR profiles but there was a slight upward shift of the TPR peak. This suggests that the reducibility of cobalt was improved by copper. The fact that no  $\text{Co}^0$ , neither other cobalt phase, was detected by XRD in any of the reduced cobalt-containing catalysts suggests that the cobalt phase was well dispersed.

The XRD patterns of the reduced 0%, 5%, and 10%-Co samples showed that in all the samples after reduction copper existed mainly in  $\text{Cu}^0$ . The similar BET surface area<sup>Ⓜ</sup> measured with the samples both before and after cobalt impregnation suggests that the bulk structural characteristics of the catalyst remained the same after cobalt addition.

Overall, the characterization results provided the following information: (a) the bulk structure of the  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst was not significantly affected by the addition of cobalt; (b) the cobalt added was reduced and well dispersed.

##### CO Hydrogenation

With the addition of cobalt, both 5% and 10%, the formation rate of



methanol dropped by an order of magnitude while changes in other products were all relatively small. This shows that the main role of the cobalt was to reduce methanol drastically and that the changes in selectivity with the addition of Co is mainly due to the selective suppression of methanol. This might be explained as the result of selective covering of the copper sites by cobalt or changing of the electron environment of copper by the presence of cobalt. With the addition of 5%-Co, hydrocarbon formation did not increase and when the cobalt loading was increased from 5% to 10% only methane increased. It suggests that the reduced cobalt was very finely dispersed, which is consistent with the characterization result.

Studies<sup>[5]</sup> in the literature have shown that uniform distribution of Co over Cu/ZnO, high Co dispersion, and an intimate contact of Co with Cu in the catalyst is necessary for selective production of C<sub>2</sub><sup>+</sup> alcohols. However, it is still not clear whether the formation of C<sub>2</sub><sup>+</sup> alcohols over these adjacent Co-Cu sites requires any specific interaction between the Co and Cu, such as forming certain ensemble or alloy of cobalt and copper. In this study, the absolute rates of higher alcohols did not increase significantly with the addition of cobalt, which was finely dispersed. The results suggest that the active sites for higher alcohol formation require specific Co-Cu interaction and that such specific Co-Cu sites were not created by the cobalt impregnation. Therefore, the addition of cobalt by the impregnation method used in this study mainly suppressed methanol formation and only slightly promoted higher alcohol formation.

### **CH<sub>3</sub>NO<sub>2</sub> Addition to the CO Hydrogenation**

It has been reported that the Cu/ZnO catalyst is also active for amine alkylation reactions<sup>[6]</sup> and that the lower substituted amines, R(R')NH, trap the methanol intermediate, CH<sub>2</sub>O (z=1,2), to form higher substituted amines, R(R')NCH<sub>3</sub><sup>[7]</sup>. This is consistent with the results obtained in this study in the sense that over both 5% and 10%-Co catalysts methanol was suppressed while CH<sub>3</sub>NO<sub>2</sub> was converted into methylamines, mainly the highest substituted methylamine, trimethylamine, i.e. CH<sub>3</sub>NO<sub>2</sub> was reduced to methylamine and

the formation of higher substituted amines diverted the methanol intermediates. The interesting points raised from this study are that ethanol and propanol were all suppressed simultaneously as methanol was suppressed, and that over the 5%-Co catalyst they were all suppressed to the same extent (by 40%) with no promotion in hydrocarbon formation. Over the 10%-Co catalyst ethanol and propanol were all suppressed by 20% and methanol by 40% with a promotion in hydrocarbon formation. This suggested that the methanol intermediates were also involved in the formation of higher alcohols but not via the aldol-condensation mechanism as proposed for the higher alcohol formation over alkali promoted Cu/ZnO based catalysts<sup>8</sup>.

In the previous study using probe molecule addition to CO hydrogenation over supported Ru<sup>9</sup>, CH<sub>3</sub>NO<sub>2</sub> was found to generate the CH<sub>x</sub> (x≤3) surface species via C-N bond cleavage. The CH<sub>x</sub> (x≤3) surface species was found to be the chain growth intermediate in the formation of C<sub>2</sub>+ hydrocarbons as it incorporated into the C<sub>2</sub>+ hydrocarbons randomly. The fact that the addition of CH<sub>3</sub>NO<sub>2</sub> to the CO hydrogenation over the 5%-Co catalyst did not promote the formation of C<sub>2</sub>+ hydrocarbons suggests that the CH<sub>x</sub> (x≤3) surface species were not generated from the added CH<sub>3</sub>NO<sub>2</sub> under the reaction condition. This can be explained as either that the C-N bond cleavage did not occur or that the bond was cleaved in a manner such that the CH<sub>x</sub> (x≤3) surface species was not generated. The fact that over the 10%-Co catalyst hydrocarbons were promoted and ethanol and propanol were suppressed to a lesser extent than methanol while small amount of NH<sub>3</sub> was detected might be the evidence that some CH<sub>x</sub> species were generated from CH<sub>3</sub>NO<sub>2</sub> and that they were involved also in the formation of higher alcohols. Although it is not clear how the CH<sub>x</sub> species was generated in this case, it is possibly related to the amount and state of cobalt.

The 0%-Co catalyst was studied as a base case to understand the behavior of CH<sub>3</sub>NO<sub>2</sub> on the catalyst surface without the presence of cobalt. Since this catalyst demonstrated an activity for methanol formation an order of magnitude higher than the cobalt-containing catalysts. The catalyst loading for the reaction was much lower than the other two catalysts and the CH<sub>3</sub>NO<sub>2</sub>

added based on per gram catalyst was much higher. The increase in methanol with the addition of  $\text{CH}_3\text{NO}_2$  over this catalyst seems to be caused by the excessive addition of  $\text{CH}_3\text{NO}_2$  which significantly increased  $\text{CO}_2$ .  $\text{CO}_2$  is known to have a promotion effect on methanol formation over Cu/ZnO catalysts. It is interesting to notice that with  $\text{CH}_3\text{NO}_2$  addition over this catalyst ethanol was suppressed and methylamines, mainly trimethylamine, as well as small amount of  $\text{NH}_3$  were formed but hydrocarbons did not increase. This observation is consistent with what was suggested by the results over the cobalt-containing catalysts in the aspects that: (a)  $\text{CH}_3\text{NO}_2$  was converted into methylamines and mainly the highest substituted amine, trimethylamine; (b) the diversion of methanol intermediate via the formation of higher substituted methyl-amine suppressed ethanol. The fact that hydrocarbons were not promoted suggested that the  $\text{CH}_x$  species was not generated from  $\text{CH}_3\text{NO}_2$  over  $\text{Cu}^0$ .

## 5. PLANS FOR THE NEXT REPORTING PERIOD

The following experiments are planned for the next reporting periods:

- a) Preparation of a Co(5%)/ $\text{Al}_2\text{O}_3$  catalyst as another base catalyst.
- b) Characterization, CO hydrogenation and probe molecule ( $\text{CH}_3\text{NO}_2$ ,  $\text{C}_2\text{H}_4$ ) addition over Co(5%)/ $\text{Al}_2\text{O}_3$  and a Co/Cu/ZnO/ $\text{Al}_2\text{O}_3$  catalyst prepared by coprecipitation from a research group in Argentina.
- c) XPS experiments with selected catalyst samples.

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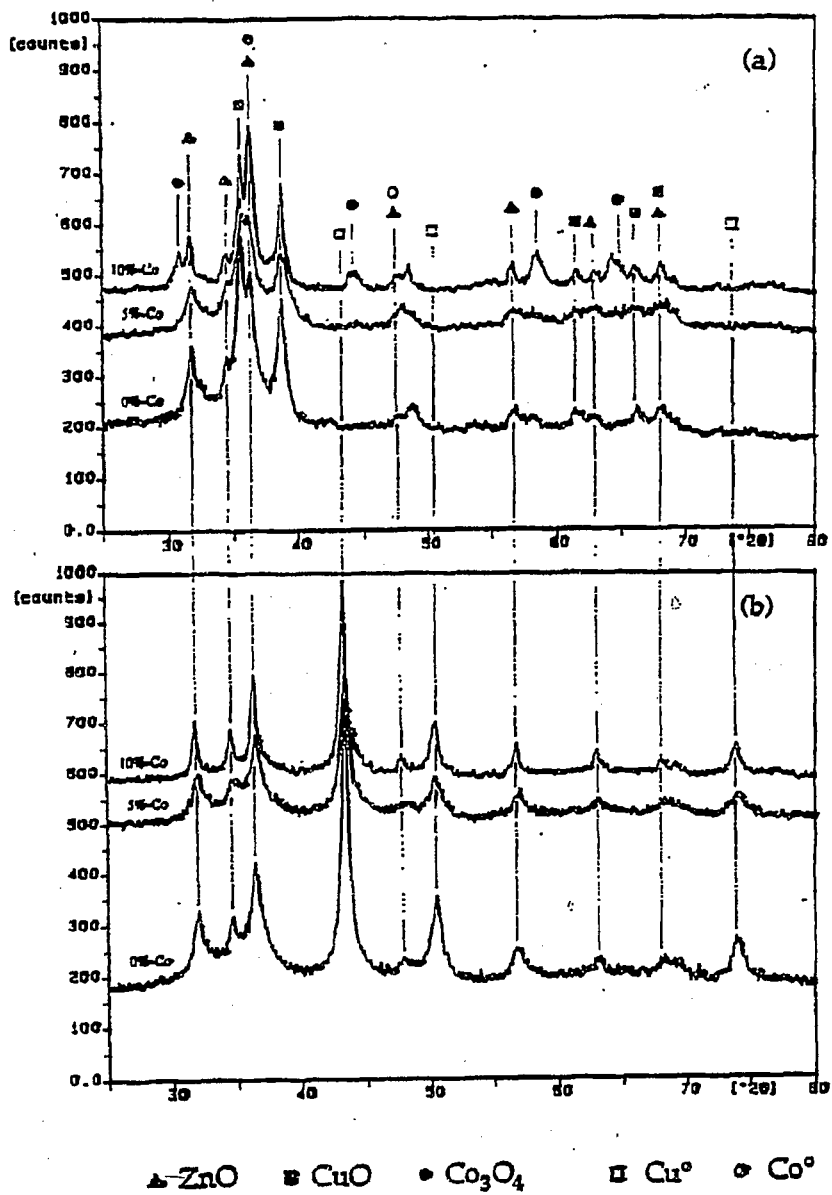


Figure 1. XRD Patterns of (a) calcined and (b) reduced samples of 0%-Co, 5%-Co and 10%-Co catalysts.

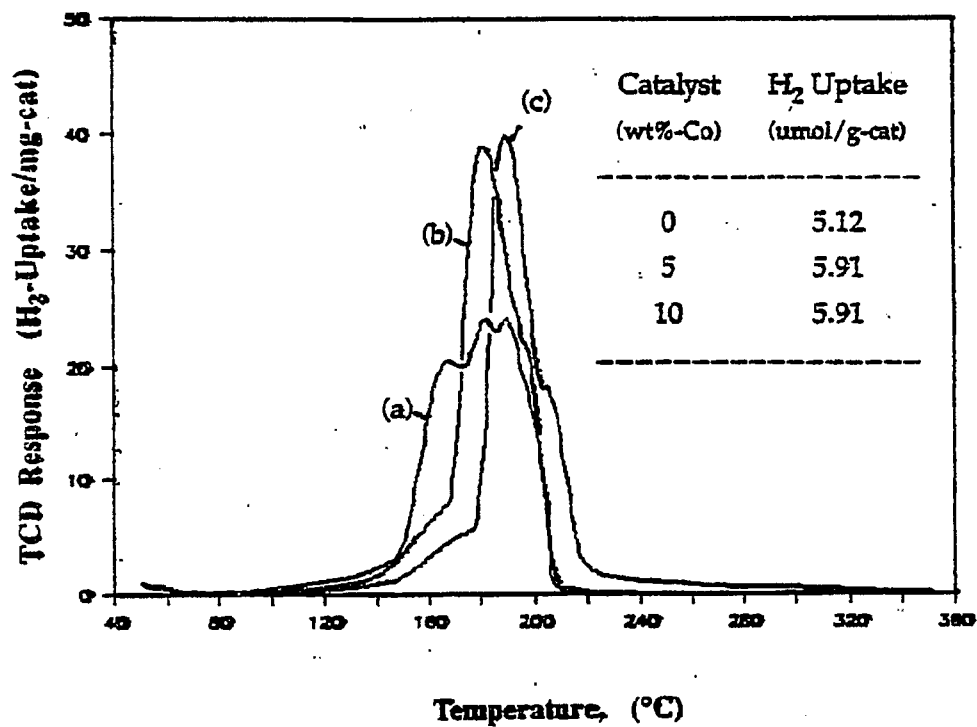


Figure 2. TPR profiles and H<sub>2</sub>-uptakes of (a) 0%-Co, (b) 5%-Co and (c) 10%-Co catalysts.

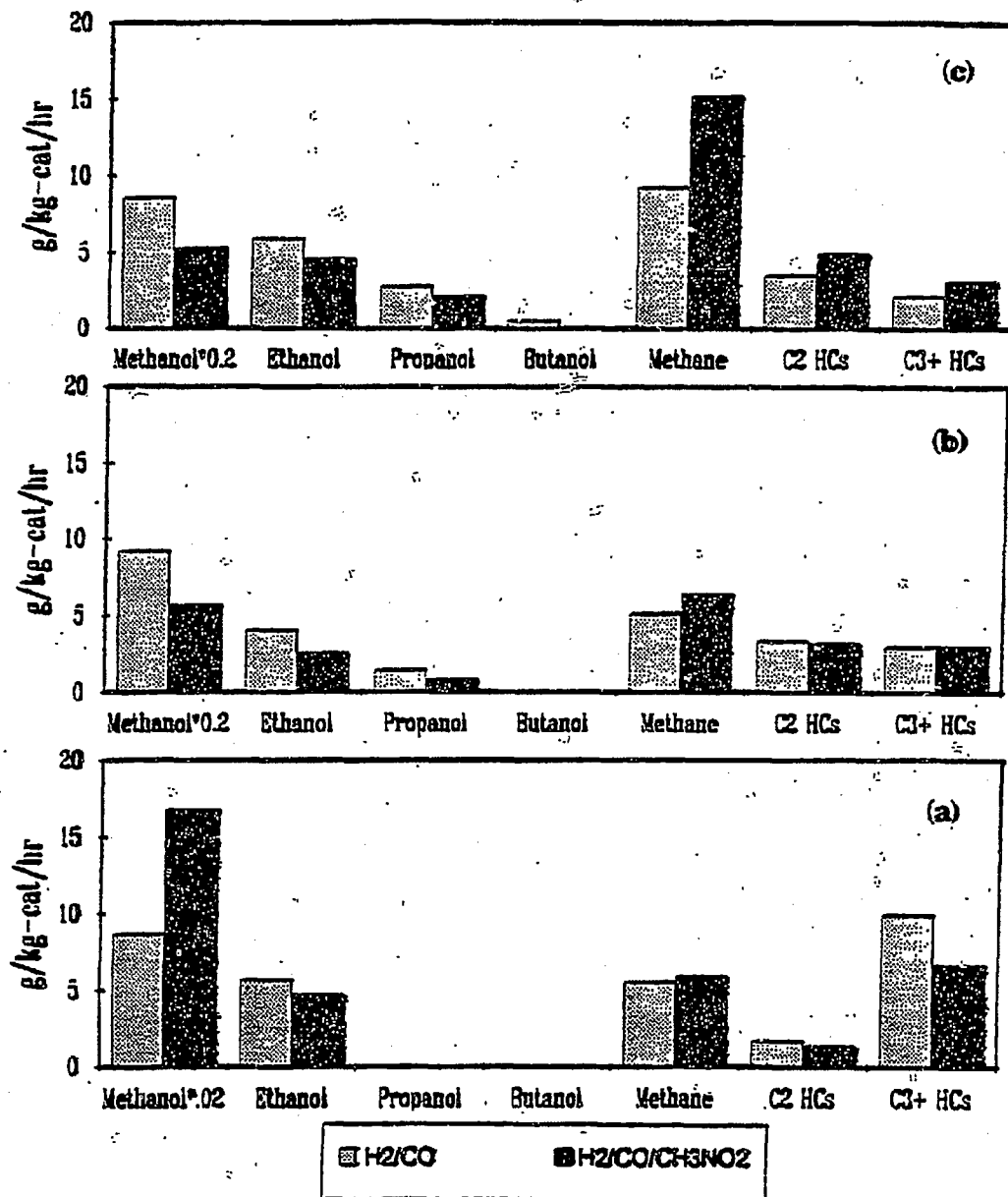


Figure 3. Effects of  $\text{CH}_3\text{NO}_2$  addition on the major products of CO hydrogenation over (a) 0%-Co, (b) 5%-Co, (c) 10%-Co catalysts.

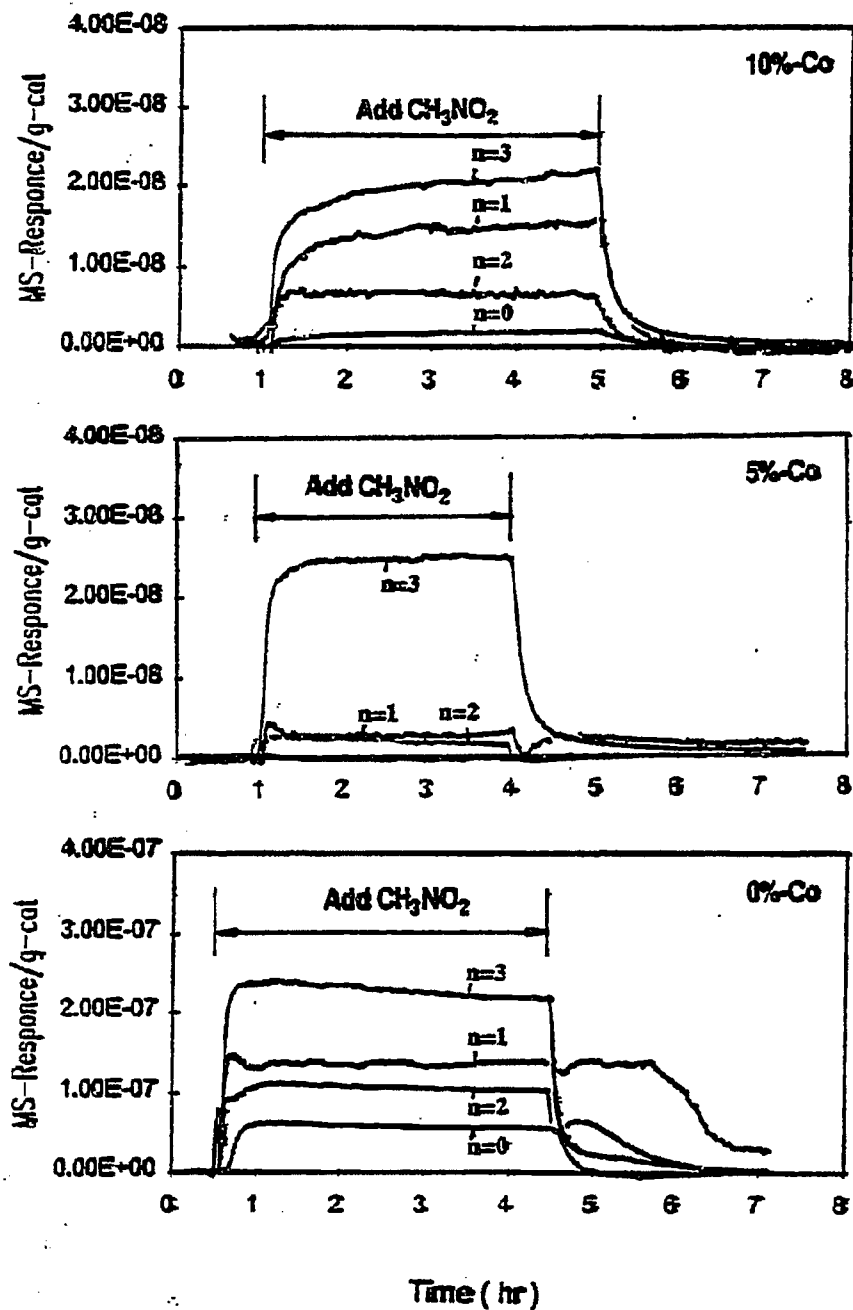


Figure 4. Formation of nitrogen compounds,  $(\text{CH}_3)_n\text{NH}_{3-n}$ ,  $n=0, 1, 2, 3$ , during the in-situ addition of  $\text{CH}_3\text{NO}_2$ .



Table 1. Steady State Data of the CO Hydrogenation over Co(0,5,10%)/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*		
	0%-Co	5%-Co	10%-Co	0%-Co	5%-Co	10%-Co
	<u>μmol/g-cat/min</u>			<u>%, μmol</u>		
<b>OXYGENATES:</b>	244.8	26.6	25.5	96.0	76.4	67.3
CH <sub>3</sub> OH	229.7	23.9	22.3	92.4	68.7	58.9
CH <sub>3</sub> OCH <sub>3</sub>	7.7	0.8	0.2	2.8	2.3	0.4
CH <sub>3</sub> CH <sub>2</sub> OH	7.4	1.5	2.1	0.8	4.2	5.6
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	0.0	0.4	0.8	0.0	1.2	2.1
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	0.0	0.0	0.1	0.0	0.0	0.3
<b>HYDROCARBONS:</b>	11.4	8.2	12.4	3.9	23.6	32.7
CH <sub>4</sub>	5.7	5.3	9.6	2.3	15.3	25.4
C <sub>2</sub> H <sub>4</sub> +C <sub>2</sub> H <sub>6</sub>	0.9	1.9	2.0	0.4	5.4	5.3
C <sub>3</sub> +HCs	4.8	1.0	0.8	1.2	2.9	2.0
<b>CO<sub>2</sub>:</b>	18.2	16.3	20.1			
<b>TOTAL:</b>	274.4	51.1	57.9			
	<u>Carbon conversion, %</u>					
	1.2	1.5	1.7			

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

Table 2. Effect of  $\text{CH}_3\text{NO}_2$  Addition on CO Hydrogenation over  $\text{Co}(0,5,10\%)/\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  at 500 psig;  $290^\circ\text{C}$ ;  $\text{H}_2/\text{CO} = 80:40$  (cc/min);  $\text{GHSV} = 6000\text{--}60000 \text{ hr}^{-1}$ .

CATALYSTS (wt%-Co):	0%-Co			5%-Co			10%-Co		
	I(I')	II	II/I	I(I')	II	II/I	I(I')	II	II/I
	$\mu\text{mol/g-cat/min}$								
$\text{CH}_3\text{NO}_2$ :	69.1			3.2			3.0		
PRODUCTS**									
$\text{CH}_3\text{OH}$	229.7(200.)	429.2	1.87	23.9(25.4)	14.7	0.62	22.3(21.4)	13.8	0.62
$\text{CH}_3\text{OCH}_3$	7.7 ( 6.1)	5.5	0.71	0.8( 0.9)	0.10	0.12	0.15(0.25)	0.02	0.12
$\text{CH}_3\text{CH}_2\text{OH}$	7.4 ( 0.7)	1.3	0.18	1.5( 1.4)	0.93	0.63	2.13(2.05)	1.66	0.78
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	0.0 ( 0.0)	0.0	-	0.4( 0.4)	0.23	0.56	0.78(0.70)	0.60	0.78
$\text{CH}_4$	5.7 ( 5.7)	6.1	1.07	5.3( 5.2)	6.63	1.25	9.62(10.6)	15.9	1.65
$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$	0.9 ( 1.0)	0.7	0.78	1.9( 1.8)	1.82	0.97	1.99(2.00)	2.79	1.40
$\text{C}_3 + \text{HCs}$	4.8 ( 1.0)	1.7	0.35	1.0( 1.0)	1.05	1.03	0.77(0.87)	1.13	1.47
$\text{CO}_2$	18.2(27.3)	274.	-	16.3(16.2)	31.0	-	20.1(20.8)	37.8	-
$(\text{CH}_3)_3\text{N}$	-	43.7	-	-	3.3	-	-	2.0	-

\* I: before  $\text{CH}_3\text{NO}_2$  addition; I': after  $\text{CH}_3\text{NO}_2$  addition ended; II: with  $\text{CH}_3\text{NO}_2$  addition.

\*\*  $(\text{CH}_3)_2\text{NH}$ ,  $\text{CH}_3\text{NH}_2$  and  $\text{NH}_3$  were formed but was hard to be quantified.

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