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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 $Co/Cu/ZnO/Al_2O_3$. Detailed motivations for studying this system as well as using CH_3NO_2 as the probe molecule were given in a previous report[1].

2. SUMMARY OF PROGRESS

(A) Pretreatment of a $Co(0\%)/Cu/ZnO/Al_2O_3$ 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 $Co(0\%)/Cu/ZnO/Al_2O_3$ catalyst.

(E) CH_3NO_2 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 $Co(0\%)/Cu/ZnO/Al_2O_3$.

A $Cu/ZnO/Al_2O_3$ catalyst with 0% loading of Co was pretreated by performing the same incipient wetness impregnation as for the 5%-Co[2] and

10%-Co samples[3] but with HNO_3 instead of $Co(NO_3)_2.6H_2O$, at the equivalent pH value. The rest of the treatments were the same as for the 5%-Co and 10%-Co samples[2, 3].

(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_3O_4 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_2 (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_2 in Ar flowing at 20 cc/min, and the temperature was increased at 1°C/min up to 500°C. The amount of H_2 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_2 in Ar (20 cc/min).

Figure 2 gives the TPR profiles and the integrated amounts of total H_2-uptake of the 0%-, 5%- and 10%-Co catalysts. It shows that the addition of Co increased the H_2-uptake. No peak (H_2-uptake) was observed at temperatures higher than 250°C (upto 500°C).

(D) CO Hydrogenation over Co(0%)/Cu/ZnO/Al_2O_3

CO hydrogenation over Co(0%)/Cu/ZnO/Al_2O_3 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_2 formation was not significantly affected by Co addition.

(E) CH_3NO_2 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_3NO_2 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_3NO_2 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_3NO_2 addition on the CO hydrogenation products is shown in Figure 3. Figure 4 shows the formation of nitrogen compounds, $(CH_3)_nNH_{3-n}$, n = 0, 1, 2, 3, during the in-situ addition of CH_3NO_2.

As reported before[2], over $Co(5\%)/Cu/ZnO/Al_2O_3$, 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_4. Methylamines were formed with almost 100% nitrogen conversion to trimethylamine, and no NH_3 was detected.

Over $Co(10\%)/Cu/ZnO/Al_2O_3$, 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_3 were formed with 73% nitrogen conversion to trimethylamine.

Over $Co(0\%)/Cu/ZnO/Al_2O_3$, the fomation of methanol was enhanced

while the formation of ethanol was suppressed and hydrocarbons were not significantly affected. Methylamines and 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 Co_3O_4. The disappearance of the Co_3O_4 phase in the reduced 10%-Co catalyst suggests that most cobalt was reduced. The increase in 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 Co[4] 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 Co°, 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 Cu°. The similar BET surface area[3] 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 $Cu/ZnO/Al_2O_3$ 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[5] 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_2^+ alcohols. However, it is still not clear whether the formation of C_{2+} 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_3NO_2 Addition to the CO Hydrogenation

It has been reported that the Cu/ZnO catalyst is also active for amine alkylation reactions[6] and that the lower substituted amines, R(R')NH, trap the methanol intermediate, CH_zO (z=1,2), to form higher substituted amines, $R(R')NCH_3$[7]. 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_3NO_2 was converted into methylamines, mainly the highest substituted methylamine, trimethylamine, i.e. CH_3NO_2 was reduced to methylamine and

the formation of higher substituted amines diverted the methanol interme-diates. 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[8].

In the previous study using probe molecule addition to CO hydroge-nation over supported Ru[9], CH_3NO_2 was found to generate the CH_x $(x \leq 3)$ surface species via C-N bond cleavage. The CH_x $(x \leq 3)$ surface species was found to be the chain growth intermediate in the formation of C_{2+} hydrocar-bons as it incorporated into the C_{2+} hydrocarbons randomly. The fact that the addition of CH_3NO_2 to the CO hydrogenation over the 5%-Co catalyst did not promote the formation of C_{2+} hydrocarbons suggests that the CH_x $(x \leq 3)$ surface species were not generated from the added CH_3NO_2 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_x $(x \leq 3)$ 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_3 was detected might be the evidence that some CH_x species were generated from CH_3NO_2 and that they were involved also in the formation of higher alcohols. Although it is not clear how the CH_x 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_3NO_2 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_3NO_2

added based on per gram catalyst was much higher. The increase in methanol with the addition of CH_3NO_2 over this catalyst seems to be caused by the excessive addition of CH_3NO_2 which significantly increased CO_2. CO_2 is known to have a promotion effect on methanol formation over Cu/ZnO catalysts. It is interesting to notice that with CH_3NO_2 addition over this catalyst ethanol was suppressed and methylamines, mainly trimethylamine, as well as small amount of 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) CH_3NO_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 CH_x species was not generated from CH_3NO_2 over Cu°.

5. PLANS FOR THE NEXT REPORTING PERIOD

The following experiments are planned for the next reporting periods:

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

b) Characterization, CO hydrogenation and probe molecule (CH_3NO_2, C_2H_4) addition over $Co(5\%)/Al_2O_3$ and a $Co/Cu/ZnO/Al_2O_3$ catalyst prepared by coprecipitation from a research group in Argentina.

c) XPS experiments with selected catalyst samples.

6. REFERENCES

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

[2] DOE Quarterly Report, No.7, 1992, under Grant No. DE-FG22-90PC-90305.

[3] DOE Quarterly Report, No.8, 1992, under Grant No. DE-FG22-90PC-90305.

[4] A. lapidus, a. Krylova, V. Kazanskii, V. Borovkov and A. Zaitsev, Appl. Catal., 73, 65-82(1991)

[5] P.Courty, D. Durand, E. Freund, and A. Sugier, C1-C6 Alcohols from Synthesis Gas on Copper-Cobalt Catalysts, J. Mol. Catal., 17, 241-254(1982).

A. Sugier, E. Freund and J-F. Le Page, US Patent 4 346 179, (1982).

P.Chaumette, P. Courty, D.Durand, P. Grandvallet, and C. Travers, UK Patent, GB 2 158 730A, (1985).

P. Courty, D. Durand, A. Sugier, and E. Freund, US Patent 4 659 742, (19).

J.A Dalmon, P. Chaumette and C. Mirodatos, Higher Alcohols Synthesis on Cobalt Based Model Catalysts, Catalysis Today, 15, 101-127(1992).

[6] A. Baiker, Ind. Eng. Chem., Prod. Res. Dev., Vol. 20, 615-618(1981).

[7] G. A. Vedage, R. G. Herman, and K. Klier, J. Catal. 95, 423-43491985).

[8] J. G. Nunan, C. E. Bogdan, K. Klier, K. J. Smith, C-W Young, and R. G. Herman, J. Catal., 116, 195-221(1989)

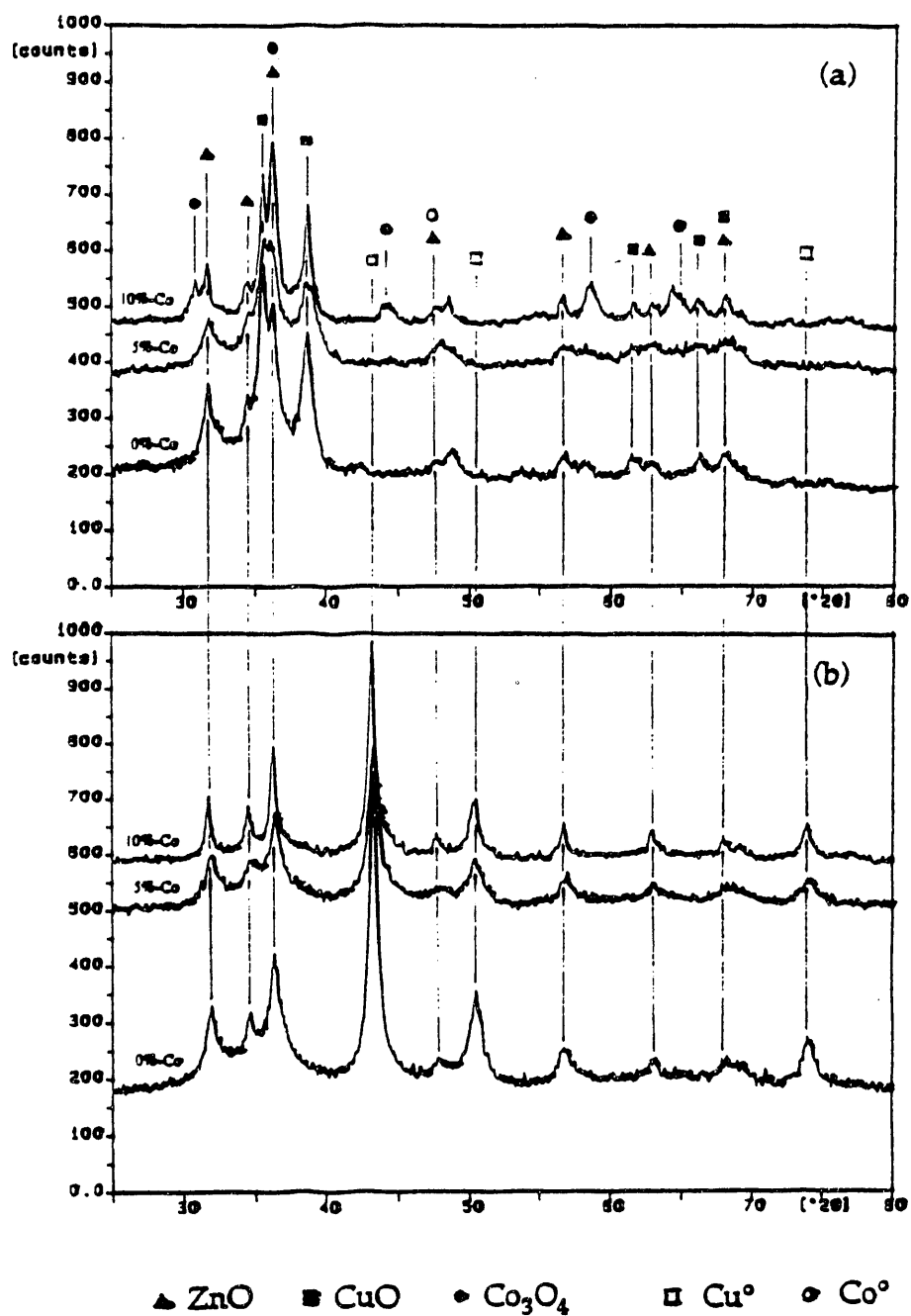[9] F. A. P. Cavalcanti, R. Oukaci, I. Wender, and D. G. Blackmond, J. Catal. 123, 260-274(1990).

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

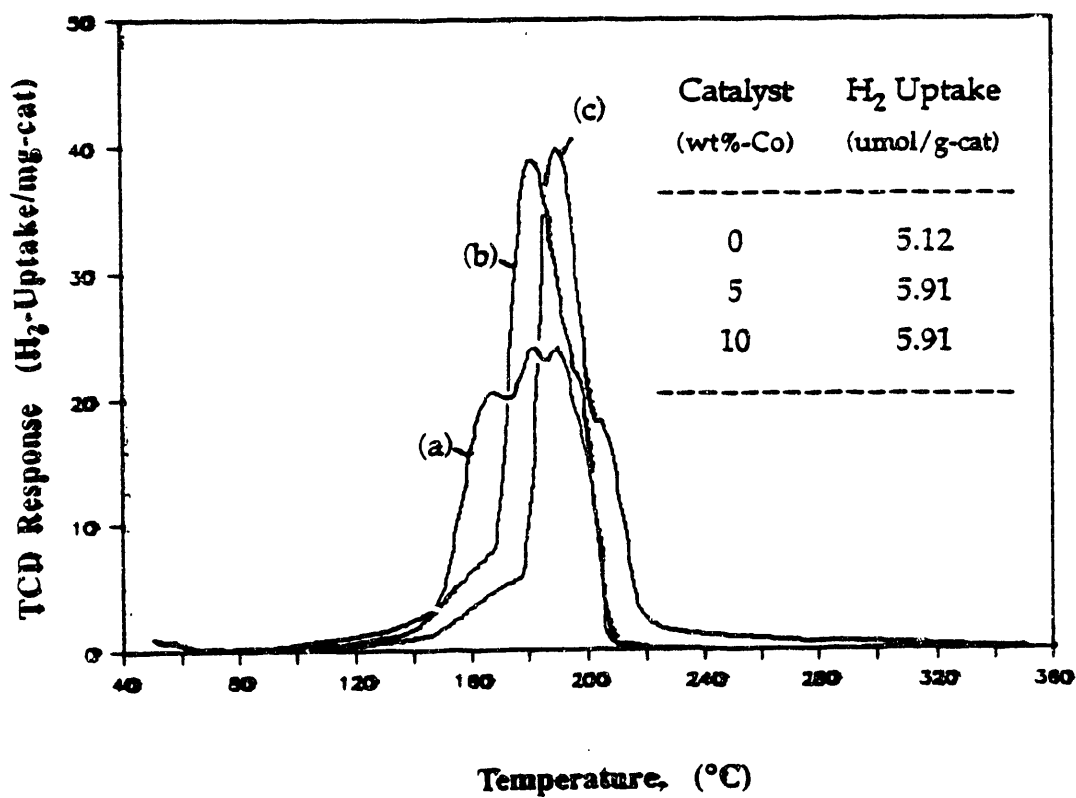| Catalyst	H_2 Uptake
(wt%-Co)	(umol/g-cat)
0	5.12
5	5.91
10	5.91

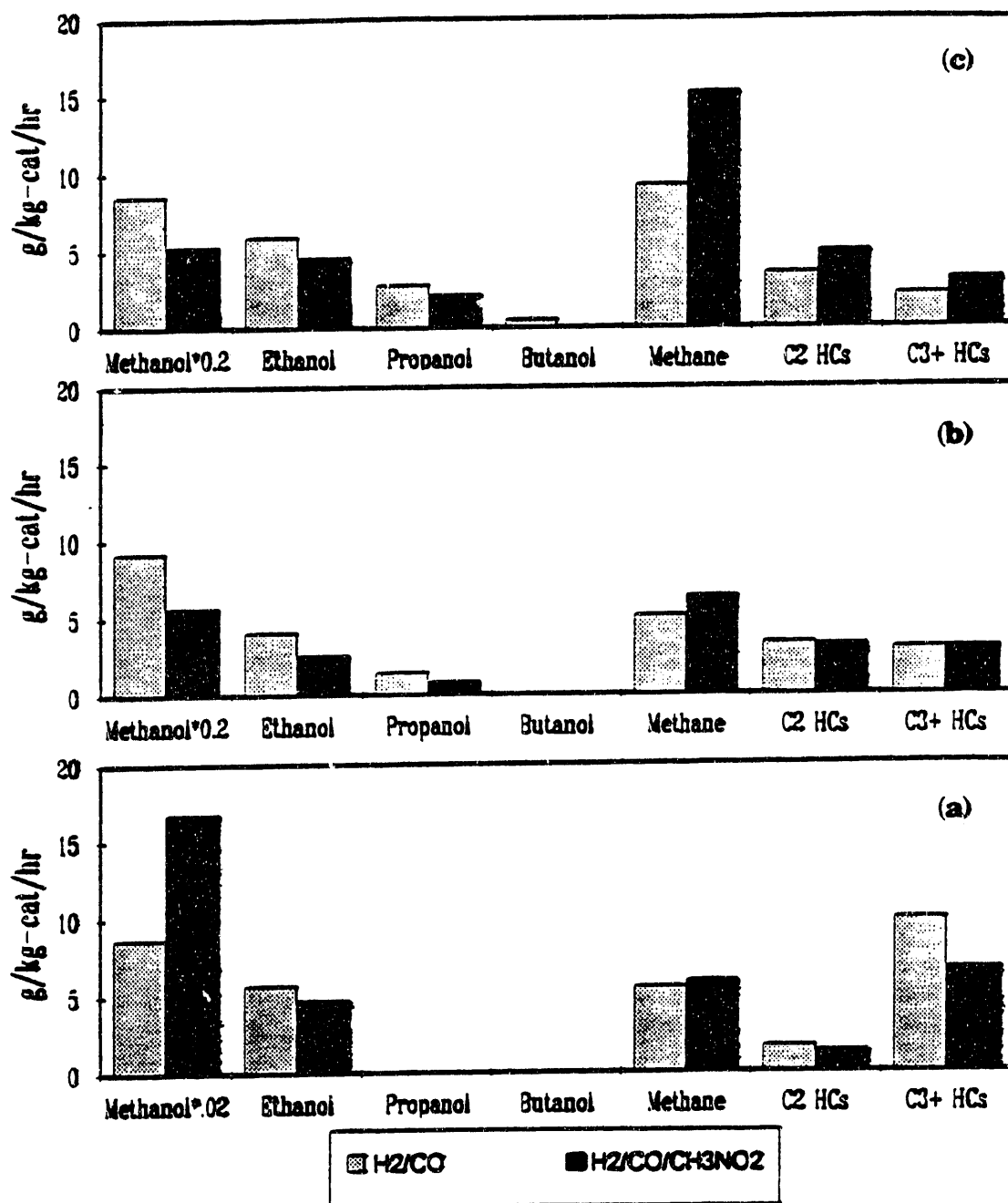Figure 2. TPR profiles and H_2-uptakes of (a) 0%-Co, (b) 5%-Co and (c) 10%-Co catalysts.

Figure 3. Effects of CH_3NO_2 addition on the major products of CO
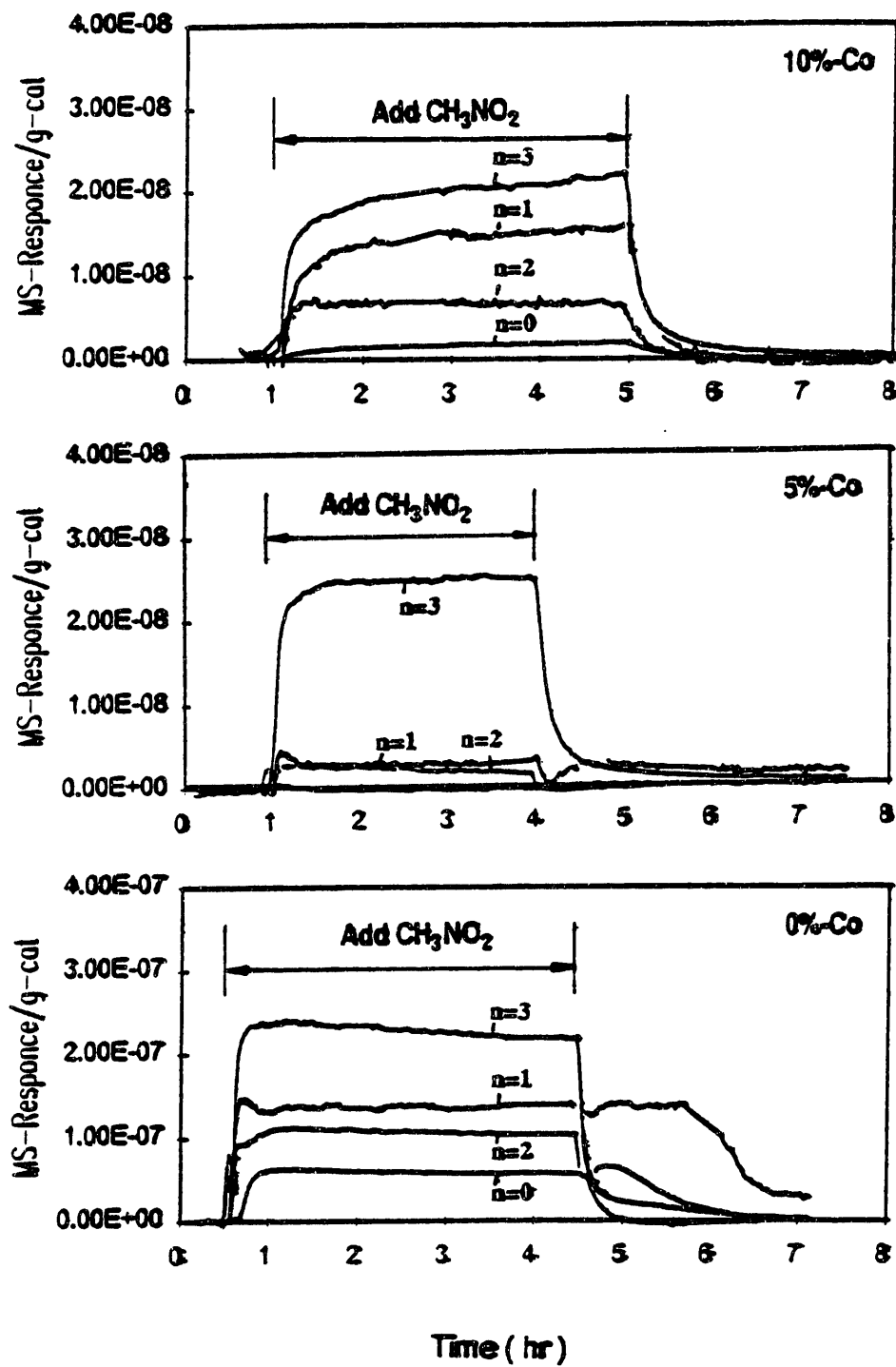hydrogenation over (a) 0%-Co, (b) 5%-Co, (c) 10%-Co catalysts.

Time (hr)

Figure 4. Formation of nitrogen compounds, $(CH_3)_nNH_{3-n}$, n=0, 1, 2, 3, during the in-situ addition of CH_3NO_2.

Table 1. Steady State Data of the CO Hydrogenation over Co(0,5,10%)/Cu/ZnO/Al$_2$O$_3$ at 500 psig; 290°C; H$_2$:CO = 80:40 (cc/min); GHSV = 6000~60000 hr^{-1}.

PRODUCTS	ACTIVITY			SELECTIVITY*		
	0%-Co	5%-Co	10%-Co	0%-Co	5%-Co	10%-Co
	μmol/g-cat/min			%, μmol		
OXYGENATES:	244.8	26.6	25.5	96.0	76.4	67.3
CH$_3$OH	229.7	23.9	22.3	92.4	68.7	58.9
CH$_3$OCH$_3$	7.7	0.8	0.2	2.8	2.3	0.4
CH$_3$CH$_2$OH	7.4	1.5	2.1	0.8	4.2	5.6
CH$_3$CH$_2$CH$_2$OH	0.0	0.4	0.8	0.0	1.2	2.1
CH$_3$CH$_2$CH$_2$CH$_2$OH	0.0	0.0	0.1	0.0	0.0	0.3
HYDROCARBONS:	11.4	8.2	12.4	3.9	23.6	32.7
CH$_4$	5.7	5.3	9.6	2.3	15.3	25.4
C$_2$H$_4$+C$_2$H$_6$	0.9	1.9	2.0	0.4	5.4	5.3
C$_3$+HCs	4.8	1.0	0.8	1.2	2.9	2.0
CO$_2$:	18.2	16.3	20.1			
TOTAL:	274.4	51.1	57.9			
	Carbon conversion, %					
	1.2	1.5	1.7			

*CO$_2$ is not included.

Table 2. Effect of CH_3NO_2 Addition on CO Hydrogenation over Co(0,5,10%)/Cu/ZnO/Al$_2$O$_3$ at 500 psig; 290°C; H$_2$:CO= 80:40 (cc/min); GHSV=6000~60000 hr^{-1}.

CATALYSTS (wt%-Co):	0%-Co			5%-Co			10%-Co		
STEADY STATES[*]:	I(I')	II	II/I	I(I')	II	II/I	I(I')	II	II/I
					μmol/g-cat/min				
CH_3NO_2:		69.1			3.2			3.0	
PRODUCTS[**]									
CH_3OH	229.7(200.)	429.2	1.87	23.9(25.4)	14.7	0.62	22.3(21.4)	13.8	0.62
CH_3OCH_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
CH_3CH_2OH	7.4 (0.7)	1.3	0.18	1.5(1.4)	0.93	0.63	2.13(2.05)	1.66	0.78
$CH_3CH_2CH_2OH$	0.0 (0.0)	0.0	-	0.4(0.4)	0.23	0.56	0.78(0.70)	0.60	0.78
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
$C_2H_4+C_2H_6$	0.9 (1.0)	0.7	0.78	1.9(1.8)	1.82	0.97	1.99(2.00)	2.79	1.40
C_3+ 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
CO_2	18.2(27.3)	274.	-	16.3(16.2)	31.0	-	20.1(20.8)	37.8	-
$(CH_3)_3N$	-	43.7	-	-	3.3	-	-	2.0	-

[*] I: before CH_3NO_2 addition; I': after CH_3NO_2 addition ended; II: with CH_3NO_2 addition.

[**] $(CH_3)_2NH$, CH_3NH_2 and NH_3 were formed but was hard to be quantified.

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