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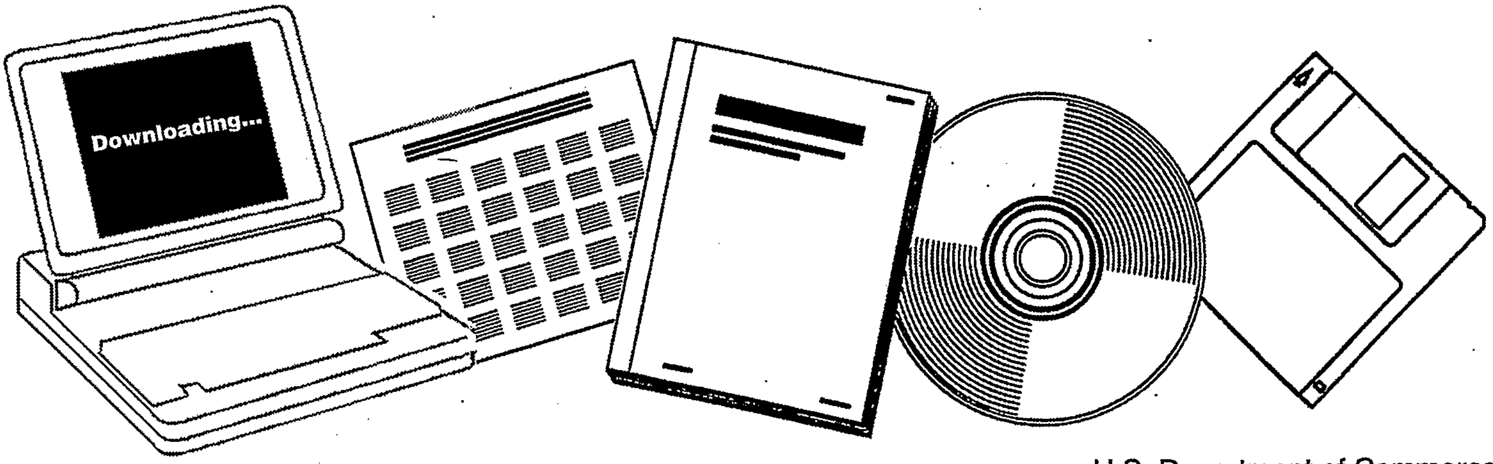
PROBE MOLECULE STUDIES: ACTIVE SPECIES IN ALCOHOL SYNTHESIS. 7TH QUARTERLY REPORT, APRIL 1992--JUNE 1992

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

JUL 1992



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DOE/PC/90305--T8
DE93 001274

PROBE MOLECULE STUDIES:
ACTIVE SPECIES IN ALCOHOL SYNTHESIS

7th Quarterly Report
April 1992 - June 1992

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July 1992

Prepared for the U.S. Department of Energy
under Grant No. DE-FG22-90PC-90305

DISCLAIMER

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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.

A reaction and analysis system capable of carrying out the experiments for this study was set up, modified, and tested[1].

CO hydrogenation reactions are being carried out in both the presence and the absence of the probe molecule under conditions which favor the formation of oxygenated products. Nitromethane, acetylenic compounds, alcohols are possible choices as probe molecules for this study. The effectiveness of these probe molecules for the study of mechanisms of alcohol synthesis has to be determined experimentally based on different catalyst systems and reaction conditions.

One of 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[2].

2. SUMMARY OF PROGRESS

(A) $Co(5\%)/Cu/ZnO/Al_2O_3$ was prepared in order to obtain high rates of ethanol and propanol formation from CO hydrogenation.

(B) The effect of CH_3NO_2 addition to the steady state CO hydrogenation over this $Co(5\%)/Cu/ZnO/Al_2O_3$ was investigated at 500 psi, 290 °C, H_2:CO=2, and 7600 hr^{-1}. A simultaneous suppression of CH_3OH, C_2H_5OH, and 1-C_3H_7OH upon CH_3NO_2 addition was observed along with the formation of $(CH_3)_3N$.

(C) C_2H_4 was also added as a probe molecule to the steady state CO hydrogenation over the same catalyst at the same condition. A significant increase in 1-propanol was observed upon C_2H_4 addition along with an equivalent decrease in methanol and dimethylether.

3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

As reported previously[3], the formation rates of ethanol and 1-Propanol over the $Co(1\%)/Cu/ZnO/Al_2O_3$ catalyst was very low. In order to obtain higher ethanol and propanol formation rates within shorter stablization time, another batch of catalyst was prepared with higher Co loading.

(A) Catalyst Preparation and Pretreatment

A Co(5% by weight)/$Cu/ZnO/Al_2O_3$ catalyst was prepared by incipient wetness impregnation of a commercial methanol synthesis catalyst, $CuO(55\%)/ZnO(36\%)/Al_2O_3(8\%)/SiO_2(1\%)$ [2], with $Co(NO_3)_2 \cdot 6H_2O$. The impregnated sample was dried at 90 °C overnight in air. The sample was then calcined in O_2 (2% in He, 80 cc/min) at 400 °C for 8 hours after increasing the temperature from 25 °C at 0.5 °C/min. It was followed by a reduction with H_2 at 400 °C for 8 hours after increasing temperature from 25 °C at 0.5 °C/min, and passivation with O_2 (2% in He, 80 cc/min) at room temperature for 1~2 hours after the H_2 treatment.

(B) CO Hydrogenation

Prior to CO hydrogenation reaction, the catalyst sample loaded in the reactor was re-reduced with 5% H_2 in He (80 cc/min) at 1 atm and 290 °C for 4.5 hr after ramping slowly (0.5 °C/min) from room temperature. CO hydrogenation over this $Co(5\%)/Cu/ZnO/Al_2O_3$ was carried out at 500 psi, 290 °C, H_2:CO=2, and GHSV=7600 hr^{-1}. The CO conversion and the rates of formation of alcohols and hydrocarbons, obtained 24-hr after starting the reaction, are given in both Table 1 and Figure 1. The CO conversion and the rates obtained with the $Co(1\%)/Cu/ZnO/Al_2O_3$ are also listed in Table 1 for comparision purposes. These results for Co(1%) were obtained after several days of CO hydrogenation since ethanol and 1-propanol increased very slowly over time.

(C) Effects of CH_3NO_2 Addition

The effect of CH_3NO_2 addition to the reaction of CO and H_2 over $Co(5\%)/Cu/ZnO/Al_2O_3$ was studied at 500 psi, 290 °C, with GHSV=7600 hr^{-1}. When 6~7 μmol/g-cat/min nitromethane were

Table 1. Rate of Formation of Alcohols and Hydrocarbons from CO Hydrogenation(H2:CO=2) over Co(1,5%)/Cu/ZnO/Al_2O_3 at 500psi, 290°C

PRODUCTS	RATE, (g/kg-cat/hr, µmol/g-cat/min)	
	Co(1%)	Co(5%)
CH_3OH	53.6, 27.9	91.7, 47.8
CH_3OCH_3	3.2, 1.2	4.4, 1.6
C_2H_5OH	1.6, 0.6	8.1, 2.9
C_3H_7OH	0.9, 0.2	2.9, 0.8
CH_4	3.3, 3.5	10.2, 10.6
C_2H_4+C_2H_6	2.5, 1.4	6.7, 3.8
C_3H_6+C_3H_8	1.7, 0.7	3.2, 1.2
C_4H_8+C_4H_{10}	1.6, 0.4	2.1, 0.6
	Total Conversion of CO (%)	
	1.8	6.3

added to the reaction mixture at steady state of CO hydrogenation reaction trimethylamine was formed and reached 6.6 µmol/g-cat/min at steady state. As shown in Table 2 and Figure 2, CH_3NO_2 addition suppressed CH_3OH, C_2H_5OH and C_3H_7OH to the same extend with no significant effect on hydrocarbon formation except a small increase in CH_4. Upon CH_3NO_2 addition CO_2 increased from 33 to 62 µmol/g-cat/min and H_2O increased from 11 to 21 µmol/g-cat/min.

The equal suppression of methanol, ethanol and propanol by CH_3NO_2 addition to the steady state CO hydrogenation over Co(5%)/Cu/ZnO/Al_2O_3 catalyst (shown in both Table 2 and Figure 2) suggests that the formation of C_2+ alcohols over this catalyst involves the same intermediate as in CH_3OH formation.

Table 2. Effect of CH_3NO_2 Addition on Product Distribution of CO Hydrogenation (H2:CO=2) over Co(5%)/Cu/ZnO/Al_2O_3 at 500psi, 290°C

PRODUCTS	RATE, (g/kg-cat/hr, µmol/g-cat/min)		R'/R
	R(no CH_3NO_2)	R' (add CH_3NO_2)	
CH_3OH	91.7, 47.8	56.5, 29.4	0.62
CH_3OCH_3	4.40, 1.59	0.54, 0.19	0.11
C_2H_5OH	8.11, 2.94	5.11, 1.85	0.63
C_3H_7OH	2.92, 0.81	1.69, 0.47	0.59
CH_4	10.2, 10.6	12.7, 13.3	1.2
$C_2H_4+C_2H_6$	6.69, 3.75	6.48, 3.64	1.0
$C_3H_6+C_3H_8$	3.15, 1.22	3.59, 1.40	1.1
$C_4H_8+C_4H_{10}$	2.08, 0.61	2.35, 0.69	1.1
CO_2	32.7	62.1	
H_2O	11.7	20.7	
CH_3NO_2	6~7	0.0	
$(CH_3)_3N$	-	6.6	

Based on the discussions on $(CH_3)_3N$ formation pathway over Cu/ZnO/Al_2O_3 in a previous report[2], the fact that almost 100% conversion of CH_3NO_2 to (CH3)3N over Co(5%)/Cu/ZnO at the selected reaction condition suggests that CH_3NO_2 selectively interacted with the C_1 methanol intermediate. This is consistent with the observation that CH_3NO_2 had no significant effect on hydrocarbon formation except for a small increase in CH_4 which cannot yet be explained. This result is in agreement with the proposed mechanism[4] of C_2+ alcohol formation via combination of C_mH_n (formed via hydrocarbon formation pathway) with a C_1H_xO ($x = 0$, 1 or 2) intermediate.

(D) Effect of C_2H_4 Addition

Under the same CO hydrogenation condition as above, C_2H_4 was added at 30~80 µmol/g-cat/min. As shown in Figure 3, a significant increase in 1-propanol was caused by C_2H_4 addition along with an equivalent decrease in methanol and dimethylether. There was very small increase in ethanol (Figure 3) and C_3+ hydrocarbons (Figure 4), and there were no effects on CH_4 and CO_2 (Figure 4). Most of the added C_2H_4 (88%) was hydrogenized into C_2H_6 (Figure 3&4). This result suggests that the combination of the methanol intermediate, $[C_1H_xO]$, with the C_mH_n species may give the C_2+ alcohols.

4. PLANS FOR THE NEXT REPORTING PERIOD

For the next reporting period, further experiments are going to be conducted with not only $Co/Cu/ZnO/Al_2O_3$ but also $Cu/ZnO/Al_2O_3$ and Co/SiO_2 in order to clarify the mechanism of C_2+ alcohol formation over the Co/Cu/ZnO catalyst system.

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

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[4] A Kiennemann, C. Diagne, J.P. Hindermann, P. Chaumette and P. Courty, Applied Catalysis, 53(1989) 197-216.

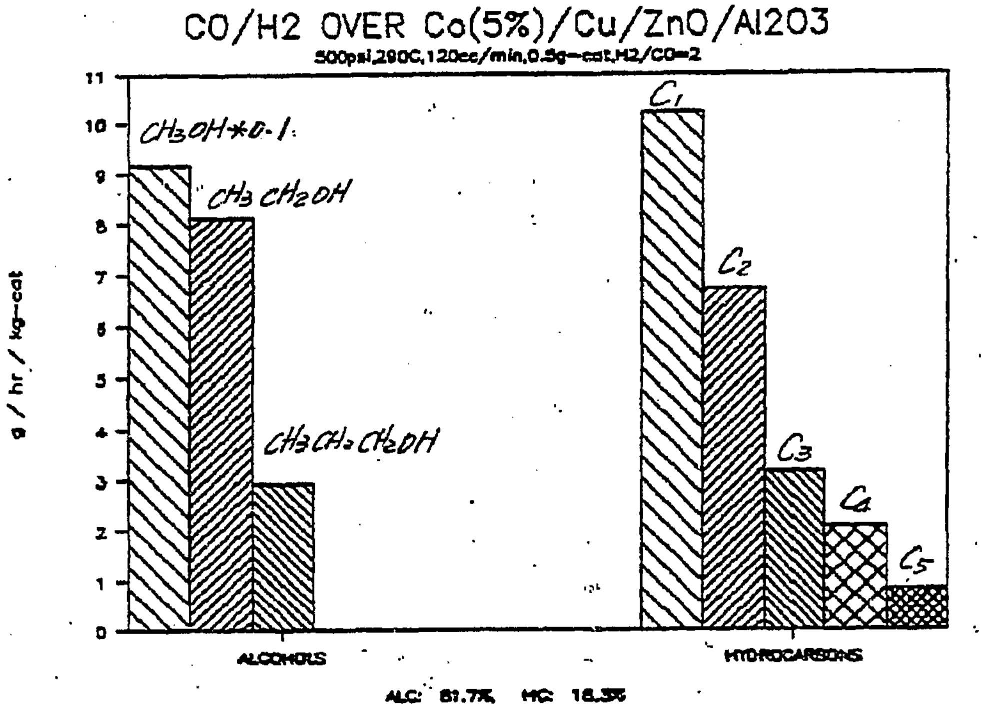

Figure 1. Formation rate of alcohols and hydrocarbons from CO hydrogenation over Co(5%)/Cu/ZnO/Al2O3 at 500 psi, 290 °C, H2/CO = 2, and GHSV = 7600 hr^{-1}.

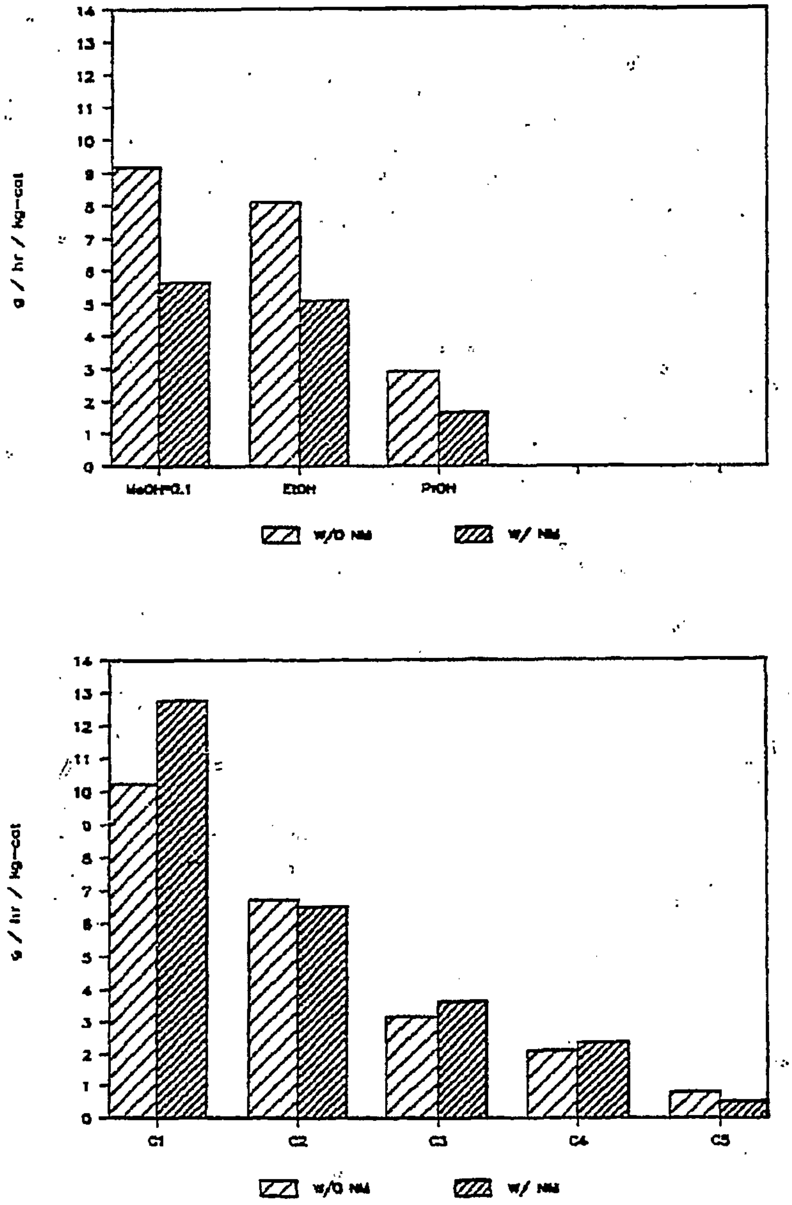

Figure 2. Effect of CH_3NO_2 addition on CO hydrogenation over Co(5%)/Cu/ZnO/ Al_2O_3 at 500 psi, 290°C, GHSV = 7600 hr^{-1}, H_2:CO=2.

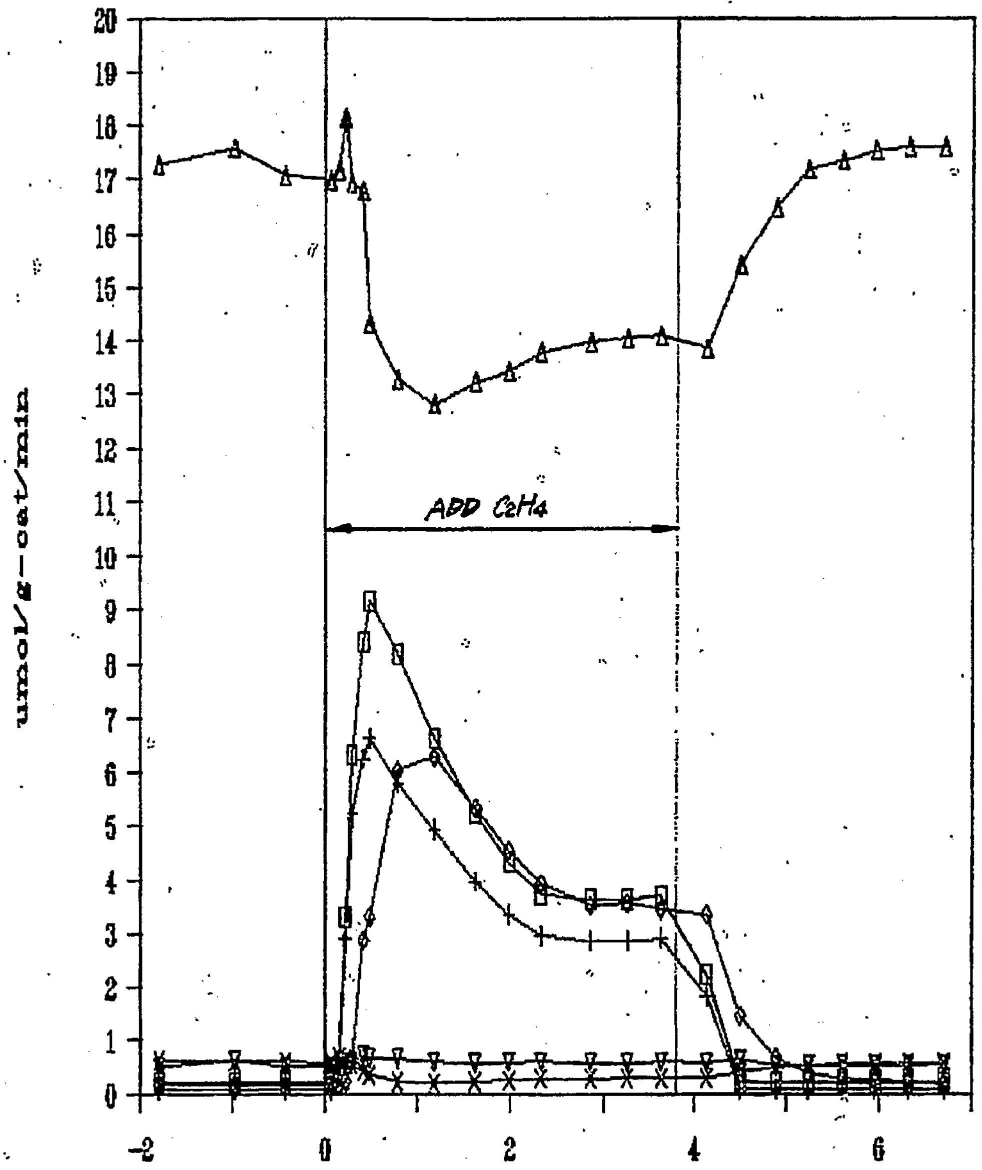

Figure 3. Effect of CH_2CH_2 addition on CO hydrogenation over Co(5%)/Cu/ZnO/Al_2O_3 at 500 psi, 290 °C, GHSV = 7600 hr^{-1}, H_2:CO = 2. □: C_2H_4, +: C_2H_6*0.1, ◊: 1-Propanol, △: Methanol, X: Dimethylether, ▽: Ethanol.

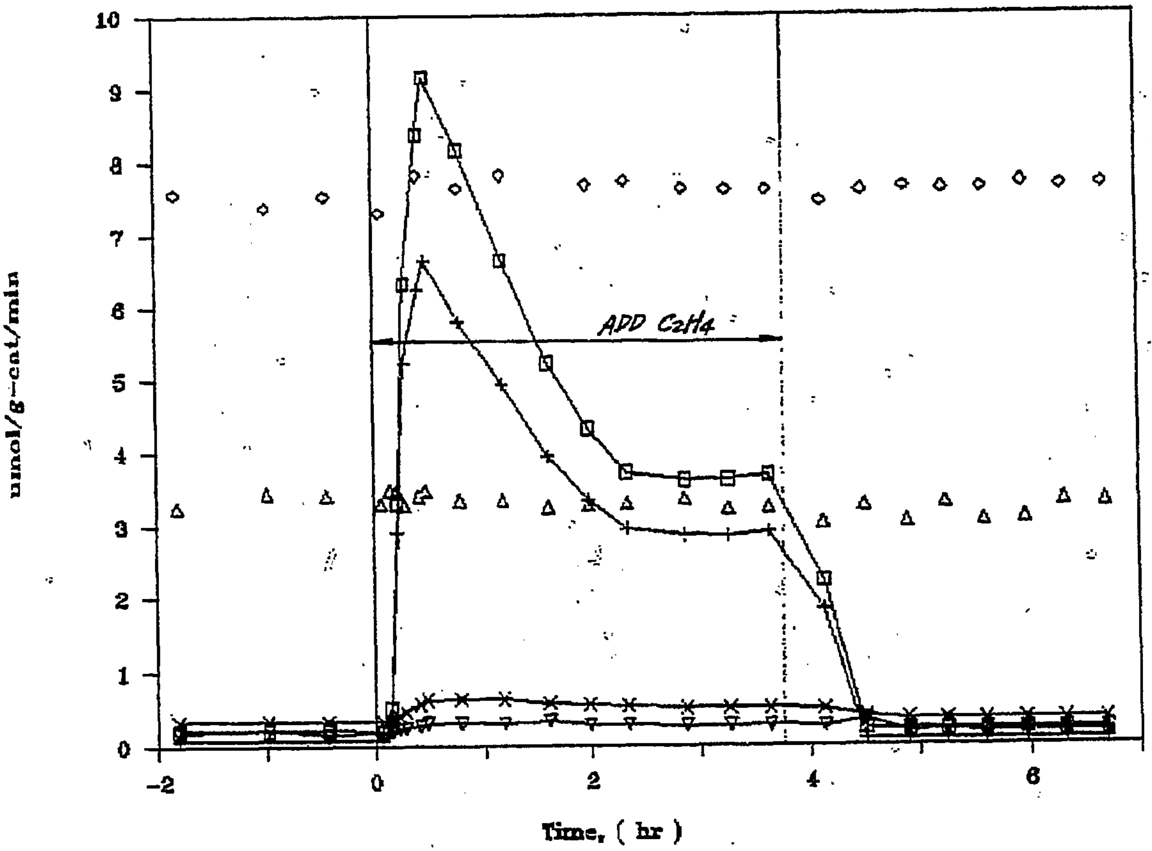

Figure 4. Effect of CH_2CH_2 addition on CO hydrogenation over Co(5%)/Cu/ZnO/ Al_2O_3 at 500 psi, 290 °C, GHSV = 7600 hr^{-1}, H_2:CO = 2. □: C_2H_4, +: C_2H_6*0.1, ◇: CO_2, Δ: CH_4, X: Total of C_3, ▽: Total of C_4& C_5.

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