PROBE MOLECULE STUDIES: ACTIVE SPECIES IN ALCOHOL SYNTHESIS. ELEVENTH QUARTERLY REPORT, APRIL 1993--JUNE 1993

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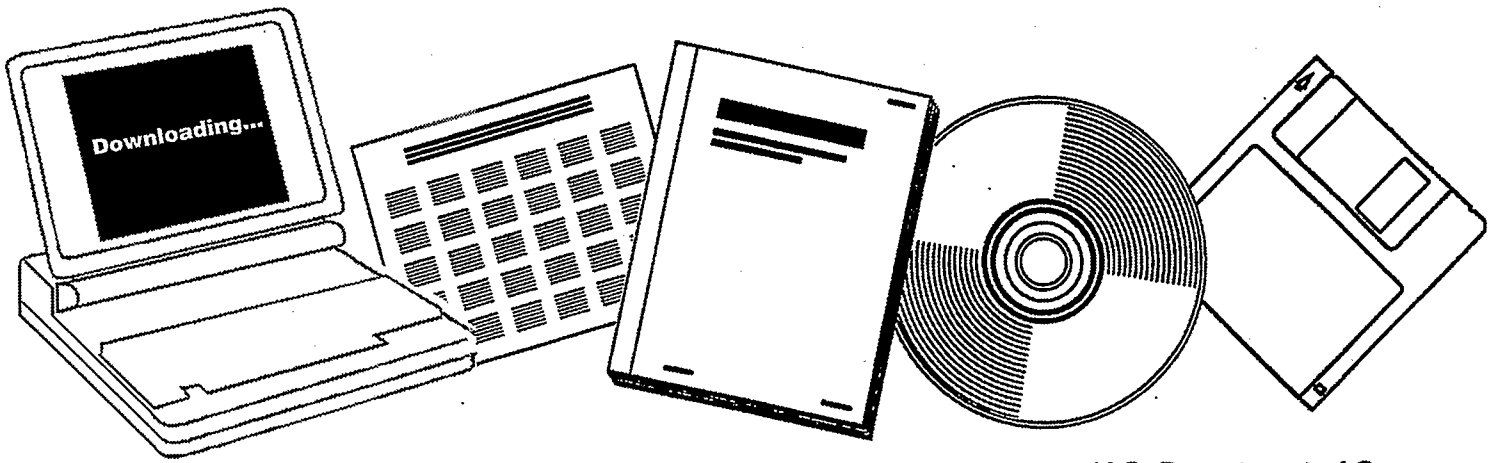

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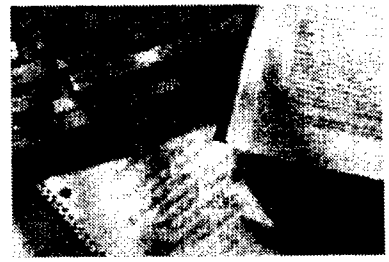

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PROBE MOLECULE STUDIES: ACTIVE SPECIES IN ALCOHOL SYNTHESIS

11th Quarterly Report
April 1993 - June 1993

Donna G. Blackmond (PI)
Irving Wender (Co-PI)
Rachid Oukaci
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Prepared for the U.S. Department of Energy
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TABLE OF CONTENT

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) CO hydrogenation reactions were carried out over a series of Cu/Co/Cr catalysts prepared by coprecipitation method by Murty's group[2]. The results were compared with the data obtained with ZC45 catalyst[3] as well as the $Co(0, 5, 10\%)/Cu/ZnO/Al_2O_3$ catalysts[4].

(B) High pressure reduction found to enhance both activity and selectivity of the Co-Cu catalysts for C_1-C_6 alcohol synthesis was used to retest some of the catalysts which had already been studied.

(C) Experiments of nitromethane addition to the CO hydrogenation over ZC45 with both the conventional and the new reduction treatment and over the $Co(10\%)/Cu/ZnO/Al_2O_3$ catalyst reduced at high pressure have been carried out to study the reaction mechanism.

3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

(A) CO hydrogenation over the Cu/Co/Cr catalysts.

Four catalyst samples from Murty's group have been tested with CO hydrogenation reaction at 500 psig, 290°C, GHSV≈7000 hr^{-1}, $H_2/CO=2$ for 2~4 hours. The composition of the catalysts are listed in Table 1[2]. The steady state data obtained over these four catalysts around 3 hours after the reactions were started are given in Table 2 and compared with the data obtained with ZC45 and the Co(0, 5, 10%)/Cu/ZnO/Al_2O_3 catalysts also 2~4 hours after the reactions were started. It is shown in Table 2 that:

(a) #1, #3 and #4 of the Co/Cu/Cr samples had much lower activities and higher selectivities towards hydrocarbons than the Co(5, 10%)/Cu/ZnO/Al_2O_3 samples;

(b) only sample #2 of the Co/Cu/Cr catalysts had similar activity and selectivity to those of the Co(5, 10%)/Cu/ZnO/Al_2O_3 catalysts;

(c) none of the catalysts prepared by coprecipitation, including ZC45, demonstrated significantly higher activities for C_2^+ alcohols than those obtained with the catalysts prepared by impregnation of CuO/ZnO/Al_2O_3 with cobalt nitrate (Co(5,10%)/Cu/ZnO/Al_2O_3 catalysts), at least when they were reduced at atmospheric pressure;

(d) all the catalysts containing Co had much lower activities for methanol formation;

(e) the Co containing catalysts, except for #1, #3 and #4 of Co/Cu/Cr , had higher activities of C_{3+} alcohols than the the Co(0%)/Cu/ZnO/Al_2O_3 catalyst.

(B) Enhancement of both activity and selectivity of the Co-Cu catalysts for C_1-C_6 alcohol synthesis using a new reduction procedure.

It has been found that reducing the catalyst at the reaction pressure, 500

psig, rather than at atmospheric pressure enhanced both the activity and selectivity of ZC45 and Co(10%)/Cu/ZnO/Al_2O_3 catalysts for C_1-C_6 alcohol formation. The steady state data of CO hydrogenation over these two catalysts which received the new reduction treatment are listed in Table 3 and compared with the data over the same samples reduced at atmospheric pressure. It is shown that:

(a) the activities and selectivities for C_1-C_6 alcohol formation over both ZC45 and Co(10%)/Cu/ZnO/Al_2O_3 catalysts were enhanced by high pressure reduction;

(b) on ZC45 the selectivity was shifted to higher alcohols;

(c) the activities for hydrocarbons over ZC45 were enhanced by high pressure reduction, while they were hardly affected on Co(10%)/Cu/ZnO/Al_2O_3;

(C) CH_3NO_2 addition to CO hydrogenation over catalyst samples with the two different reduction treatments.

CH_3NO_2 was added as probe molecule to the CO hydrogenation over the catalyst samples of ZC45 reduced at both atmospheric and high pressure and over the Co(10%)/Cu/ZnO/Al_2O_3 catalyst reduced at high pressure. Figure 1 and 2 show the reaction results obtained with the samples of ZC45 and Co(10%)/Cu/ZnO/Al_2O_3, respectively, reduced at (a) low pressure, and (b) high pressure. The data for the Co(10%)/Cu/ZnO/Al_2O_3 catalyst reduced at low pressure were reported in previous report[5]. The followings are the observations from the experimental results.

(a) With all these four catalyst samples:

- methanol was suppressed and trimethylamine was detected during the addition of nitromethane;
- the ratios of the formation rates with CH_3NO_2 addition to those without CH_3NO_2 addition, R, for C_2-C_6 alcohols increased with carbon number with the R values for C_4-C_6 alcohols being all greater than 1;

- the effects of nitromethane addition on the formation rates of hydrocarbons, or the R values of hydrocarbons, did not follow the same trend as those of alcohols.

(b) With the samples of ZC45 reduced at both low and high pressures, nitromethane addition suppressed the formation of C_1-C_6 hydrocarbons, while it enhanced the formation rates of C_1-C_6 hydrocarbons over $Co(10\%)/Cu/ZnO/Al_2O_3$.

4. PLANS FOR THE NEXT REPORTING PERIOD

The following studies are planned for the next reporting period:

a) Nitromethane addition to the CO hydrogenation over ZC45 samples reduced at high and low pressures with detection of N_2 to assist in the understanding of the reaction pathways.

b) Nitromethane addition to the CO hydrogenation over $Co(0\%)/Cu/ZnO/Al_2O_3$ and $Co(5\%)/Al_2O_3$ reduced differently to assist in the understanding of both the reaction pathway(s) and the active site(s).

c) XRD experiments with the catalyst samples which received different reduction treatments to assist in the understanding of the active sites as well as the effect of reduction pressure.

d) Experiments of temperature programmed reduction at high pressure to generate information on the effect of the reduction pressure.

5. REFERENCES

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

[2] U. A. Donatto, Tess L. Hoard, and A. N. Murty, 1992, (unpublished).

[3] DOE Quarterly Report, No. 10, 1993, under Grant No. DE-FG22-90PC-90305.

[4] DOE Quarterly Report, No. 7&8&9, 1992, under Grant No. DE-FG22-90PC-90305.

[5] DOE Quarterly Report, No. 9, 1992, under Grant No. DE-FG22-90PC-90305.

[6] DOE Quarterly Report, No. 5&6&7, 1992, under Grant No. DE-FG22-90PC-90305.

[7] F. A. P. Cavalcanti, R. Oukaci, I. Wneder, D. G. Blackmond, j. Catal. 123, 270-274 (1990).

Table 1. Cu/Co/Cr Catalyst Composition (from Ref. 2).

Sample (#)	Cu/Co (atomic ratio)	Cu/Co/Cr
1	1.3	40/30/30
2	1.7	50/30/20
3	3.3	50/15/35
4	4.6	70/15/15

Table 2. Formation Rates[a] of the Products of CO Hydrogenation at 500 psig; 290°C; H_2:CO = 2.

CATALYSTS:	Co/Cu/Cr				Co/Cu/Zn/Al			
	#1	#2	#3	#4	ZC45	10%-Co	5%-Co	0%-Co
	ACTIVITY, μmol-C/g-cat/min							
OXYs + HCs:	**12.9**	**53.7**	**3.0**	**7.6**	**25.1**	**57.3**	**58.7**	**320.1**
OXYGENATES:	**2.0**	**17.5**	**0.2**	**0.1**	**9.6**	**28.1**	**25.5**	**290.4**
CH_3OH	1.4	7.6	0.2	0.1	2.3	15.2	16.0	248.6
CH_3OCH_3	0.0	0.0	0.0	0.0	0.0	0.4	0.4	18.6
CH_3CH_2OH	0.4	7.0	0.0	0.0	3.3	7.9	6.4	23.2
$CH_3CH_2CH_2OH$	0.2	2.9	0.0	0.0	2.0	3.7	2.2	0.0
$CH_3CH_2CH_2CH_2OH$	0.0	0.0	0.0	0.0	2.0	0.9	0.5	0.0
HYDROCARBONS:	**10.9**	**36.2**	**2.8**	**7.5**	**15.5**	**29.2**	**33.2**	**29.7**
CH_4	6.4	9.8	32.2	6.7	6.0	15.7	12.7	5.5
$C_2H_4+C_2H_6$	1.3	4.4	0.2	0.4	2.7	6.4	8.0	1.8
C_{3+} HCs	3.2	22.0	0.4	0.4	6.8	7.1	12.5	22.4
CO_2:	10.0	34.2	7.4	6.0	28.8	27.7	31.5	18.5
	SELECTIVITY[b], mol-C %							
OXYGENATES:	**15.5**	**32.6**	**6.7**	**1.3**	**38.2**	**49.0**	**43.5**	**90.7**
CH_3OH	10.9	14.2	6.7	1.3	9.1	26.5	27.3	77.7
CH_3OCH_3	0.0	0.0	0.0	0.0	0.0	0.7	0.7	5.8
CH_3CH_2OH	3.1	13.0	0.0	0.0	13.1	13.8	10.9	7.2
$CH_3CH_2CH_2OH$	1.5	5.4	0.0	0.0	8.0	6.4	3.7	0.0
$CH_3CH_2CH_2CH_2OH$	0.0	0.0	0.0	0.0	8.0	1.6	0.9	0.0
HYDROCARBONS:	**84.5**	**67.4**	**93.3**	**98.7**	**61.8**	**51.0**	**56.5**	**9.3**
CH_4	49.6	18.2	73.3	88.2	23.9	27.4	21.6	1.7
$C_2H_4+C_2H_6$	10.1	8.2	6.7	5.3	10.8	11.2	13.6	0.6
C_{3+} HCs	24.8	41.0	13.3	5.3	27.1	12.4	21.3	7.0
	CO CONVERSION, %							
	0.6	2.2	0.3	0.3	1.4	2.2	2.2	1.3

a: 2~3 hours after the CO hydrogenation reaction was started.

b: CO_2 is not included.

Table 3. Effect of Reduction Pressure on the Activity and Selectivity of CO Hydrogenation[a] over ZC45 and Co(10%)/Cu/ZnO/Al_2O_3 at 500 psig; 290°C; H_2:CO = 2.

	ACTIVITY μmol-C/g-cat/min				SELECTIVITY[b] %, mol-C			
Catalyst:	ZC45		10%-Co		ZC45		10%-Co	
Reduction Condition[c]:	LPR	HPR	LPR	HPR	LPR	HPR	LPR	HPR
OXYs + HCs:	**29.0**	**97.5**	**45.9**	**58.7**				
OXYGENATES:	**14.5**	**60.7**	**29.6**	**42.0**	**50.0**	**62.2**	**64.5**	**71.6**
Methanol	4.6	7.9	22.3	28.9	15.9	8.1	48.5	49.2
Dimethylether	0.0	0.0	0.3	0.1	0.0	0.0	0.7	0.2
Ethanol	5.2	12.8	4.3	5.9	17.9	13.1	9.4	10.1
n-Propanol	2.7	7.2	2.3	4.7	9.3	7.4	5.0	8.0
n-Butanol	2.0	9.6	0.4	1.6	6.9	9.8	0.9	2.7
n-Pentanol	0.0	10.0	0.0	0.8	0.0	10.3	0.0	1.4
n-Hexanol	0.0	13.2	0.0	0.0	0.0	13.5	0.0	0.0
HYDROCARBONS:	**14.5**	**36.8**	**16.3**	**16.7**	**50.0**	**37.8**	**35.5**	**28.4**
Methane	4.5	11.4	9.6	9.5	15.5	11.7	20.9	16.2
C_2	2.6	7.2	4.2	4.0	9.0	7.4	9.2	6.8
C_{3+}	7.4	18.2	2.5	3.2	25.5	18.7	5.4	5.4
CO_2:	**31.9**	**128.**	**20.1**	**64.0**				
	CO CONVERSION, %							
	1.6	6.5	1.7	2.6				

a: 24 hours after the reaction was started.

b: CO_2 is not included.

c: LPR represents low-pressure-reduction, and HPR represents high-pressure-reduction.

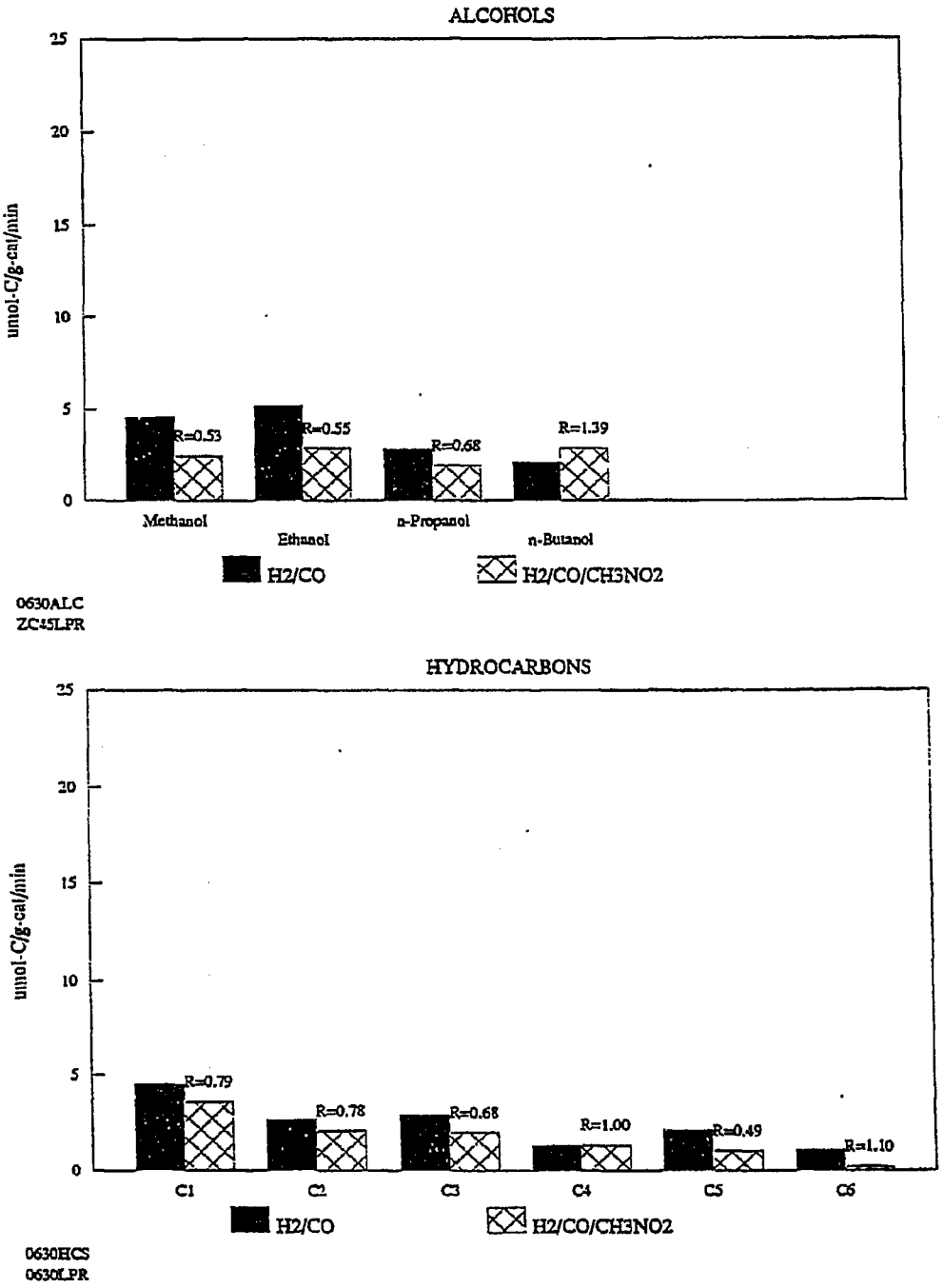
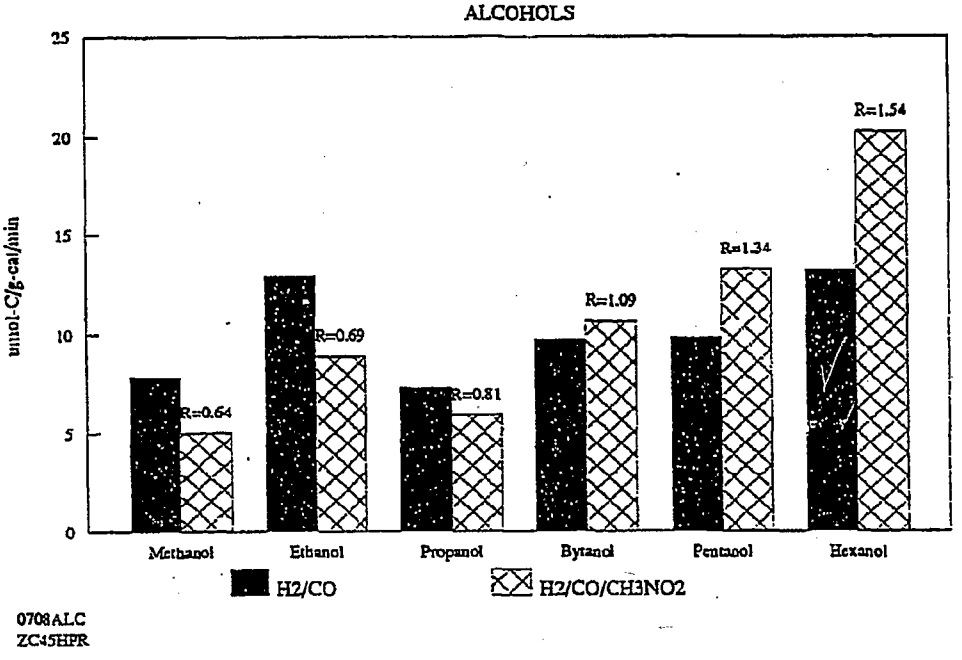


Figure 1(a). Effect of CH_3NO_2 addition on the products of the CO hydrogenation over the sample of ZC45 reduced at low pressure. R is the ratio of the rate with CH_3NO_2 addition to the rate without CH_3NO_2 addition.



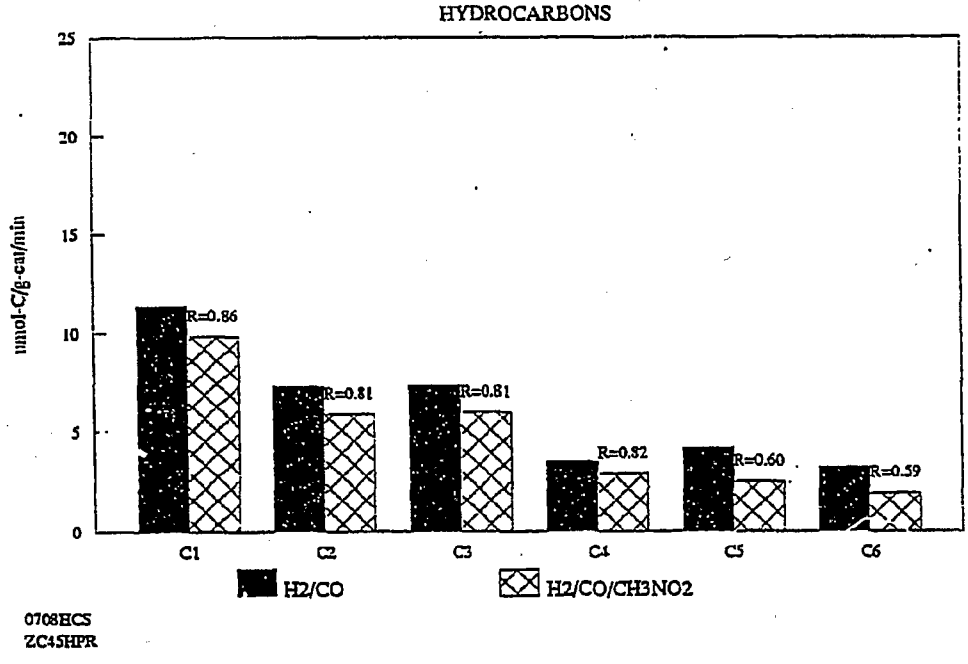
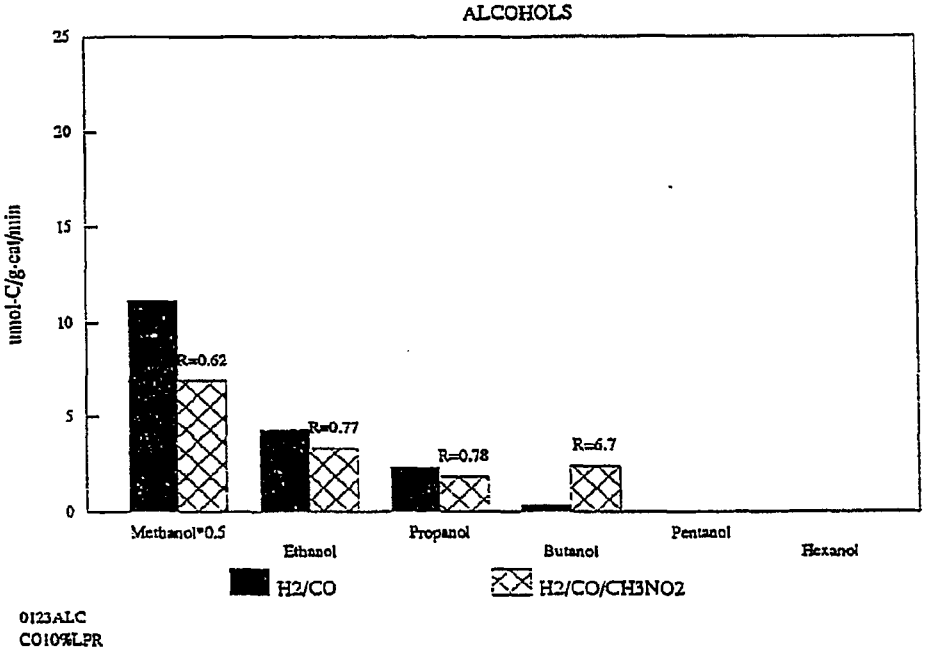


Figure 1(b). Effect of CH_3NO_2 addition on the products of the CO hydrogenation over the sample of ZC45 reduced at high pressure. R is the ratio of the rate with CH_3NO_2 addition to the rate without CH_3NO_2 addition.



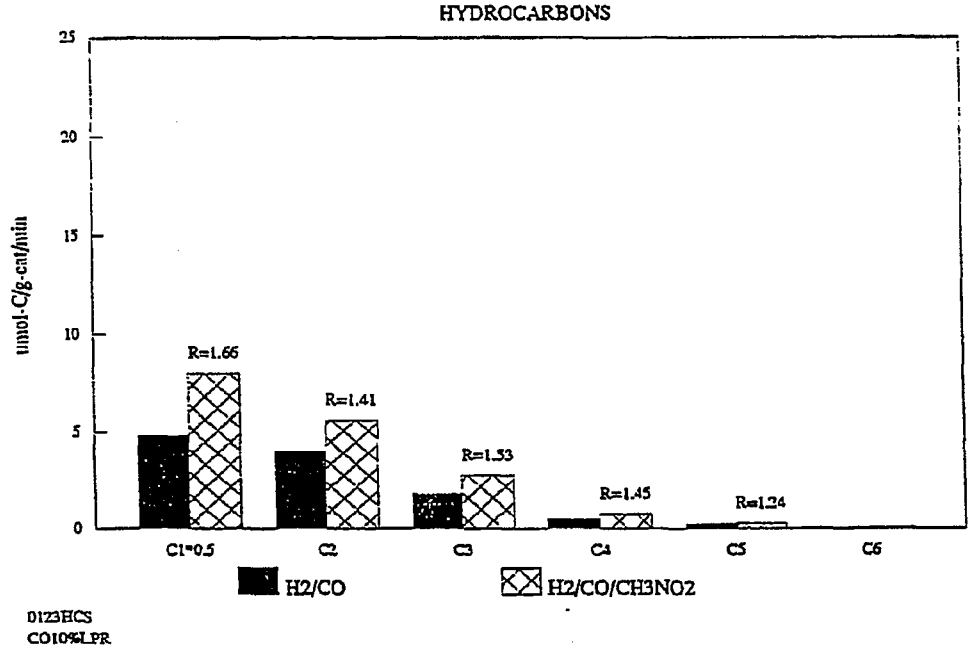
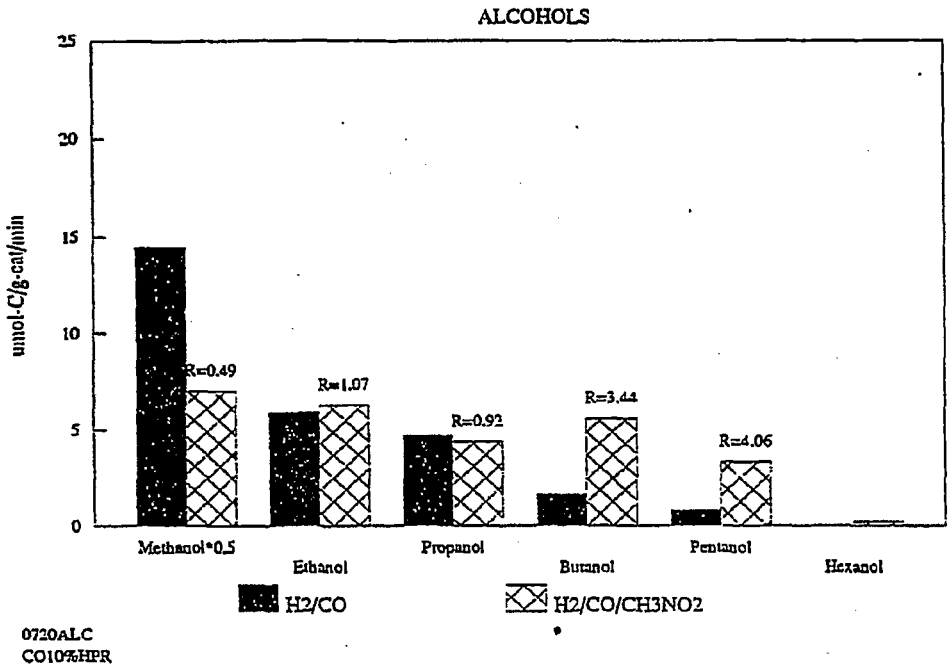
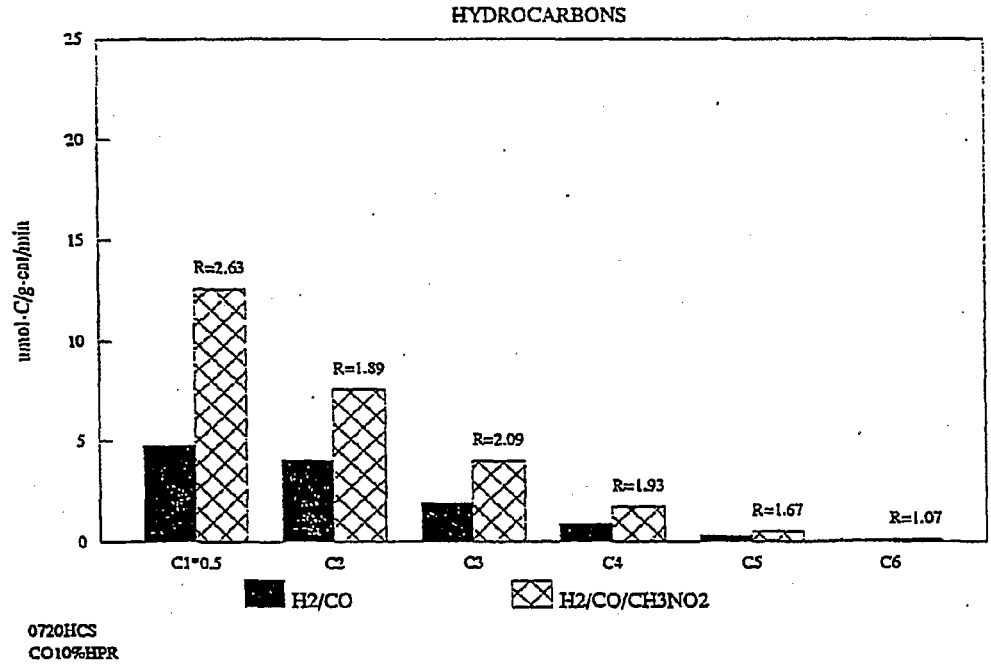


Figure 2(a). Effect of CH_3NO_2 addition on the products of the CO hydrogenation over the sample of Co(10%)/Cu/ZnO/Al_2O_3 reduced at low pressure. R is the ratio of the rate with CH_3NO_2 addition to the rate without CH_3NO_2 addition.





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