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January 18, 1996

Mr James Huemmrich
U. S. Department of Energy
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P.O. Box 10940, MS 921-143
Pittsburgh, PA 15236

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MAR 19 1996

OSTI

SUBJECT: OXYGENATED OCTANE ENHANCERS:
SYNGAS TO ISOBUTYLENE
Contract Number: DE-AC22-91PC90042

Dear James:

Enclosed find copies of the final version of Technical Progress Report No 16.
This report has been approved by Dr Arun Bose. This report contains
patentable material which was disclosed in an earlier patent disclosure.
Therefore it is marked "patent hold" on the appropriate pages. cleared by CPP

If you have any questions concerning this report, please contact me at (708)
391-2038.

Regards,

[Signature]

Terry L. Marker
Sr. Development Specialist

TLM/bls

Enclosures

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MASTER

RC/PF: NVD-Syngas to Isobutylene (DOE)

CC: JBaptist, PTBarger, BVVora, TLMarker

CONTRACT TITLE AND NUMBER:
Development of a Catalyst for Conversion
of Syngas-Derived Materials to Isobutylene
DE-AC22-91PC90042

Date:
Quarterly Report No. 16
Reporting Period:
1/1/95-3/31/95

Contractor:
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Des Plaines, IL 60017-5016

Author:
Paul T. Barger and Paul R. Kurek

Contract Period: March 15, 1991 to September 14, 1995

QUARTERLY TECHNICAL REPORT

The goals of this project are to develop a catalyst and process for the conversion of syngas to isobutanol. The research will identify and optimize key catalyst and process characteristics. In addition, the commercial potential of the new process will be evaluated by an economic analysis.

Previous work identified Pt or Pd on Zn/Mn/Zr co-precipitated metal oxides as promising catalysts for the conversion of a 10/1 methanol/ethanol blend to higher oxygenates.¹⁻⁴ Supports with high Zn (>45%) and low Zr (<33%) have afforded the best selectivities for the desired branched C₄ products in the standard pilot plant test after impregnation with 2% Pt.⁴ In this report the analytical characterization of this series of materials is summarized. A large scale preparation of Zn/Mn/Zr oxide support has been completed for use in future process variable studies.

The effect of noble metal loading on the Zn/Mn/Zr oxide support has been investigated. Previous comparisons were clouded by the different activity levels of the various Pt level catalysts.⁴ Therefore, varying space velocities have been used to determine the selectivity versus conversion relationships for 2% Pt and 0.5% Pt on Zn/Mn/Zr (60/20/20) oxide. This comparison shows that Pt level has a minimal affect on catalyst activity, but that the higher Pt loading gives better selectivity to the desired C₄ oxygenates.

Three 2% Pt on Zn/Mn/Zr oxide catalysts have been tested for the conversion of methanol only to higher alcohols in order to determine their activity for the condensation of C₁ species. While MeOH conversions of 40-50% have been observed, selectivities to the desired higher branched oxygenates is negligible. Instead, CO and methyl formate (from the Cannizzaro reaction) are the major products observed. These results indicates that this catalyst system has limited activity of C₁-C₁ coupling at the conditions tested. Future work will investigate the use of more severe conditions including higher temperature and pressure.

EXPERIMENTAL

Catalysts

Pt on Zn/Mn/Zr Oxide Catalysts. The preparation of these catalysts by co-precipitation of an aqueous solution of metal nitrates with KOH at pH 11, followed by impregnation of the calcined support with an aqueous Pt chloride solution has been described previously.⁴ A large-scale batch of the Zn/Mn/Zr (60/20/20) support was prepared by combining the products from 2 separate precipitations prior to calcination. A small portion of the calcined support was impregnated with 2% Pt, dried and calcined using the standard procedure⁴ to afford a sample to certify the support.

Pt on TiO₂. A commercial sample of TiO₂ from Harshaw (TI 0720) was impregnated with 2% Pt using the same procedure employed for the Pt on Zn/Mn/Zr oxide catalysts.⁴

Catalytic Testing Procedure

The pilot plant testing of catalysts for the conversion of a methanol/ethanol blend to isoalcohols was accomplished as follows. The catalyst, as 20-40 mesh granules, was loaded into a 1/2" I.D. stainless steel reactor. The reactor was purged N₂ at 250 °C, 10 psig, 0.5 scf/hr for 1 hour then pressure tested with N₂ at 250 °C, 500 psig for 1 hour. After restarting the N₂ purge, temperature and pressure were adjusted to the desired conditions. After 2 hours, the methanol/ethanol blend (10/1 molar) was cut into the plant at the desired rate and continued for 16 hours. Product analyses were obtained using two on-line GCs to analyze the total hydrocarbon/oxygenate product and the overhead gas. Conversions, selectivities and productivities (including CO and CO₂) are based on moles of carbon. For all of the tests described in this report, the averages of results obtained between 8 and 16 hours on stream are reported. A listing of the pilot plant runs included in this report is given in Table 1.

The pilot plant testing for methanol-only conversion was done in a similar manner, except that a pure methanol feed was used in place of the 10/1 methanol/ethanol blend. The blank reactor test at various temperatures (250-500 °C) was conducted using a glass bead filled, 7/8" ID, porcelain-lined stainless steel reactor to try to reduce methanol decomposition on the reactor walls at temperatures greater than 400 °C.

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RESULTS AND DISCUSSION

Noble Metal on Zn/Mn/Zr Mixed Metal Oxide Catalysts

Noble metal on basic mixed metal oxide supports have been identified as promising catalysts for the synthesis of higher branched alcohols from methanol and methanol/ethanol in previous work in this program.¹⁻⁴ Pt on Zn/Mn/Zr oxide has been identified as a promising catalyst for this application. The beginning of research directed at the optimization of the catalyst formulation (Task 2.0 of the program) was described in the previous Quarterly Report⁴ and is completed in the current report. Key compositional variables that have been investigated are metal oxide support composition and noble metal loading. The catalytic testing of various metal oxide support compositions has been described.⁴ This report summarizes the analytical characterization of these materials and the effect of noble metal loading.

Characterization of Noble Metal on Zn/Mn/Zr Oxide Catalysts. Table 2 summarizes analytical data that has been obtained to date on the various Pt and Pd and Zn/Mn/Zr oxide catalysts that have been prepared in this program. Elemental compositions, densities (ABD) and surface areas, pore volumes and average pore diameters from N₂ BET are included.

Effect of Pt Loading on Catalytic Performance. A previous attempt to compare the performances of Pt on Zn/Mn/Zr (60/20/20) oxide catalysts with various Pt loadings was clouded by the different activity levels of the catalysts. Although the 2% Pt catalyst afforded the highest selectivities to the desired C₄ oxygenates, it also gave the lowest conversion at the conditions tested.⁴ Therefore, it is possible that the improved selectivity may be due only to the lower catalyst activity. In order to obtain a better comparison, a more thorough testing procedure has been utilized in which MeOH WHSV is varied from 2 hr⁻¹ to 3 hr⁻¹ to 4 hr⁻¹ and back to 2 hr⁻¹ over 16 hour intervals to obtain data at a range of conversion levels. In contrast to the preliminary results⁴, the 0.5% and 2% Pt catalysts show little difference in activity in these tests. Figure 1 shows that the plots of methanol, ethanol and overall conversions versus space time are similar. Both samples show lower activity on return to the initial conditions indicating that some catalyst deactivation occurred over the test. However, the loss in activity is less than that seen on the space velocity changes. Figure 2 shows that the 2% catalyst affords higher selectivity to the desired iC₄ oxygenated products (isobutanol, isobutyraldehyde and methyl isobutyrate). Overall selectivities are summarized in Table 3 which indicates that the improved performance of the 2% Pt catalyst is due to a reduction in the amount of methyl formate, CO and other C₄₊ by-products. In contrast with methyl formate, the C₁-C₂ Cannizzaro reaction product, methyl acetate, increases with higher Pt.

The observed shift in oxygenate selectivity from methyl formate to methyl acetate and iso-C₄ oxygenates with increased Pt loading suggests that the extent of dehydrogenation affects the relative rates of C₁-C₁ and C₁-C₂ condensation. Aldol condensations (Reaction 1) are required for the production of the desired iso-C₄ oxygenates, while Cannizzaro condensations (Reactions 2 and 3) give rise to light ester products. In each of these reactions, aldehydes formed by alcohol dehydrogenation are key intermediates. At the high methanol/ethanol feed ratio used in the pilot plant testing, a high dehydrogenation activity catalyst (i.e. high Pt) would be expected to afford an increased acetaldehyde concentration and, therefore, favor Reactions 1 and 2 over Reaction 3.

Methanol-Only Conversion over Pt on Zn/Mn/Zr Oxide Catalysts

The coupling of two C₁ oxygenates to a C₂ species is known to be the slow step in the production of isobutanol from either syngas or methanol. In the case of C₂-C₁ coupling, an aldol condensation mechanism involving deprotonation from the resonance-stabilized α carbon of an acetaldehyde intermediate can be proposed. For C₁-C₁ coupling, the deprotonation of a formaldehyde intermediate, which less acidic than acetaldehyde is required for an aldol-type condensation. Therefore, this mechanism appears less likely for the coupling of C₁ species. However, previous tests using a 10/1 methanol/ethanol blend at various space velocities has suggested that Pt on Zn/Mn/Zr oxide may be capable of promoting this reaction.⁴ Yields of higher oxygenates are observed to increase at contact times where ethanol conversion is greater than 90%. In contrast, a Cu/Zn/Al oxide catalyst does not show any increase in higher oxygenates yield at high ethanol conversion¹ and also gives negligible methanol conversion in the absence of ethanol co-feed.⁶

Three 2% Pt on Zn/Mn/Zr oxide catalyst formulations have been evaluated for the conversion of methanol only to higher branched oxygenates. Test conditions are identical to those employed with the 10/1 methanol/ethanol blend, except that a pure methanol feedstock has been used. Table 4 summarizes the overall results (conversions and selectivities) while Figures 3 and 4 show MeOH conversions and isobutanol selectivities versus time on stream, respectively. For all of these catalysts, the products containing C-C bonds are virtually eliminated when a methanol only feed is used. Selectivities to total C₄₊ products are less than 3%. The major products arise from other reactions including methanol decomposition (CO, CO₂, H₂), hydrogenation (methane), etherification (DME) and Cannizzaro condensation (methyl

formate). These results clearly indicate the requirement for a C_2 intermediate for the aldol condensation to higher alcohols and the formation of such an intermediate from C_1 species is very slow over the Pt on Zn/Mn/Zr oxide catalyst system at the conditions used. Future work will investigate the use of more severe conditions (high temperature and pressure) to try to force the C_1 - C_1 coupling step.

An improved reactor is required for catalyst testing at temperatures greater than 350 °C to prevent substantial methanol decomposition to CO, CO₂ and H₂. A blank reactor test has been conducted in which methanol/N₂ were fed thru a 316 stainless steel reactor loading with glass beads at 250 °C to 500 °C. While methanol decomposition was acceptable at 250 °C and 350 °C (0.2% and 5.9%), it became excessive at 350 °C (35%) and 500 °C (68%). CO and H₂ were the primary products although CH₄ also grew in at the highest temperatures. A copper-lined reactor is being constructed to allow the testing of the Pt on Zn/Mn/Zr oxide catalyst at higher temperatures.

Screening of Other Potential Catalysts for Higher Alcohol Synthesis

A catalyst consisting of 2 wt.% Pt on TiO₂ has been evaluated using the standard methanol/ethanol pilot plant test. This catalyst gave minimal selectivity to the desired isobutanol (0.1%) and isobutyraldehyde (0.04%). Instead, CO, CO₂, and light hydrocarbons were the major products observed.

CONCLUSIONS

Previous work identified Pt or Pd on Zn/Mn/Zr co-precipitated metal oxides as promising catalysts for the conversion of a 10/1 methanol/ethanol blend to higher oxygenates.¹⁻⁴ Supports with high Zn (>45%) and low Zr (<33%) have afforded the best selectivities for the desired branched C₄ products in the standard pilot plant test after impregnation with 2% Pt.⁴ In this report the analytical characterization of this series of materials is summarized. A large scale preparation of Zn/Mn/Zr oxide support has been completed for use in future process variable studies.

The effect of noble metal loading on the Zn/Mn/Zr oxide support has been investigated. Previous comparisons were clouded by the different activity levels of the various Pt level catalysts.⁴ Therefore, varying space velocities have been used to determine the selectivity versus conversion relationships for 2% Pt and 0.5% Pt on Zn/Mn/Zr (60/20/20) oxide. This comparison shows that Pt level has a minimal affect on catalyst activity, but that the higher Pt loading gives better selectivity to the desired C₄ oxygenates.

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Three 2% Pt on Zn/Mn/Zr oxide catalysts have been tested for the conversion of methanol only to higher alcohols in order to determine their activity for the condensation of C₁ species. While MeOH conversions of 40-50% have been observed, selectivities to the desired higher branched oxygenates is negligible. Instead, CO and methyl formate (from the Cannizzaro reaction) are the major products observed. These results indicates that this catalyst system has limited activity of C₁-C₁ coupling at the conditions tested. Future work will investigate the use of more severe conditions including higher temperature and pressure.

REFERENCES

- 1) P. T. Barger, DOE Quarterly Report No. 12, (1994).
- 2) P. T. Barger, DOE Quarterly Report No. 13, (1994).
- 3) P. T. Barger and P. R. Kurek, DOE Quarterly Report No. 14, (1994).
- 4) P. T. Barger and P. R. Kurek, DOE Quarterly Report No. 15, (1995).
- 5) P. T. Barger, DOE Quarterly Report No. 11, (1994).

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Table 1. Run List

RUN	HOS	CATALYST A Book #	CATALYST B Book #	CATALYST A	CATALYST DESCRIPTION CATALYST B	SIZE	LOADING g	CONDITIONS			
								TEMP (C) INLET	MAX	TOTAL PSIG	MeOH WHSV
289	0-16	8265-50		2.0%Pt / Zn/Mn/Zr (33/33/33) Oxide	20-40M	5		350	30	2	1/0.1/2 N2
	24-40						350	30	2	1/0/2 N2	
	48-64						350	30	1	1/0/2 N2	
	72-88						350	75	1	1/0/2 N2	
	98-112						350	30	2	1/0.1/2 N2	
290		8265-82		2.0%Pt / Zn/Mn/Zr (10/45/45) Oxide	20-40M	5	350	30	2	1/0/2 N2	
291		8265-76		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2	1/0/2 N2	
292		8265-82		2.0%Pt / Zn/Mn/Zr (10/45/45) Oxide	20-40M	5	350	30	2	1/0/2 N2	
293		8265-50		2.0%Pt / Zn/Mn/Zr (33/33/33) Oxide	20-40M	5	350	30	2	1/0/2 N2	
294		8265-92		2.0%Pt / TiO2	20-40M	5	350	30	2	1/0.1/2 N2	
295	0-16	8265-94		0.5%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
	16-32						350	30	3	1/0.1/2 N2	
	32-48						350	30	4	1/0.1/2 N2	
	48-64						350	30	2	1/0.1/2 N2	
296	0-16	8265-95		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
	16-32						350	30	3	1/0.1/2 N2	
	32-48						350	30	4	1/0.1/2 N2	
	48-64						350	30	2	1/0.1/2 N2	
297	0-16	8265-95		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
	16-32						350	30	3	1/0.1/2 N2	
	32-48						350	30	4	1/0.1/2 N2	
	48-64						350	30	2	1/0.1/2 N2	
298	32-40			None (Glass Beads)	20-40M	5	250	30	2	1/0/2 N2	
	40-48						350	30	2	1/0/2 N2	
	48-56						450	30	2	1/0/2 N2	
	56-64						500	30	2	1/0/2 N2	
299		8265-95		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
300		8265-95		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	2.5	350	30	4	1/0.1/2 N2	
301		8265-97		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	

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Table 2. Analytical Characterization of 2% Pt on Zn/Mn/Zr Oxide Supports and Catalysts

CATALYST NUMBER	DESCRIPTION OF CATALYST/SUPPORT (Targets)	ELEMENTAL ANALYSES (Wt.%)							ABD g/cc	N ₂ BET ANALYSIS			Plant 700 RUN NUMBERS
		Pt	Pd	Zn	Mn	Zr	Na, ppm	K, ppm		SA (m ² /g)	PV (cc/g)	PD (Å)	
8265-72	60/20/20 Zn/Mn/Zr Oxide Support			42.2	10.2	19.9							
8265-76	Impregnated with 2% Pt	1.9		41.2	10.0	19.5	90	2100	1.31	59	0.16	112	272/274/275/276/277/291
8265-86	Impregnated with 0.5% Pt	0.6							0.33	88	0.15	68	284
8265-87	Impregnated with 2% Pt	2.0							0.33	45	0.15	136	285/286
8265-88	Impregnated with 5% Pt	6.4								48	0.16	134	
8265-94	Impregnated with 2% Pt	2.0							0.33	42	0.16	150	295
8265-95	Impregnated with 0.5% Pt	0.5					125	2100	0.33	73	0.15	86	296/297/299/300
8265-96	60/20/20 Zn/Mn/Zr Oxide Support			41.3	9.8	19.4				100	0.22	86	
8265-97	Impregnated with 2% Pt	1.8					44	5300	0.33	79	0.20	102	301
8265-98	Impregnated with 2% Pt	1.9		40.6	9.8	19.4	100	8800	0.33	58	0.17	118	
8265-28	45/45/10 Zn/Mn/Zr Oxide Support			18.1	13.1	5.7				44	0.15	134	
8295-38	Impregnated with 2% Pt	1.9		33.7	26.2	11.1			0.73	36	0.13	144	252
8265-34	Impregnated with 2% Pd		2.0						0.73	39	0.13	132	251
8265-30	45/10/45 Zn/Mn/Zr Oxide Support			27.2	5.6	39.1				96	0.17	70	
8265-77	Impregnated with 2% Pt	1.9		27.2	5.6	39.4			1.28	84	0.17	84	273
8265-56	Impregnated with 2% Pd		1.9						0.73	65	0.14	86	263
8265-20	33/33/33 Zn/Mn/Zr Oxide Support			21.8	18.2	28.7				129	0.20	62	
8265-50	Impregnated with 2% Pt	2.0		21.3	17.6	28.5			0.71	84	0.21	98	258
8265-22	Impregnated with 2% Pd		2.1						0.73	116	0.19	62	247
8265-78	20/20/60 Zn/Mn/Zr Oxide Support			11.3	8.1	48.6				152	0.35	92	283
8265-80	Impregnated with 2% Pt	2.0							0.67	167	0.32	76	
8265-81	Impregnated with 2% Pd		2.1										
8265-62	20/60/20 Zn/Mn/Zr Oxide Support			17.1	29.1	24.0				107	0.25	96	
8265-90	Impregnated with 2% Pt	1.9		16.6	28.4	23.2			0.33	87	0.25	114	288
8265-85	Impregnated with 2% Pd		1.9						1.04	77	0.15	78	282
8265-58B	10/45/45 Zn/Mn/Zr Oxide Support			6.2	16.2	43.3				185	0.37	80	
8265-82	Impregnated with 2% Pt	1.8							0.63				278/279/290/292
8265-83	Impregnated with 2% Pd		2.0						0.55	178	0.36	82	280

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Table 3. Effect of Pt Loading on Catalyst Performance

Catalyst Number	8265-94			8265-95		
Description	0.5% Pt on Zn/Mn/Zr Oxide (60/20/20)			2.0% Pt on Zn/Mn/Zr Oxide (60/20/20)		
Run	295			297		
Conditions	350 C, 30 psig, 10/0.1/2/ MeOH/EtOH/N2					
MeOH WHSV (hr-1)	2	3	4	2	3	4
Conversion (%)						
MeOH	51.8	35.0	25.6	50.2	41.0	31.0
EtOH	99.9	93.7	86.6	99.0	94.3	90.7
Selectivity (C%)						
nC3OH	0.1	2.5	4.1	0.5	2.1	3.1
nC4OH	0.1	0.2	0.2	0.1	0.2	0.3
iC4OH	11.8	8.0	3.7	13.0	12.0	8.0
iC4 Aldehyde	17.8	16.5	11.1	16.2	18.6	18.1
Me iButyrate	4.8	1.6	0.9	5.4	3.9	2.9
MeiBu Ether	0.0	0.1	0.0	0.0	0.0	0.0
C5+OH	0.7	0.8	0.8	1.2	1.2	1.4
Other Ald/Ketone	0.7	6.0	11.4	1.8	5.0	7.5
Other Esters	0.3	0.1	0.1	0.1	0.0	0.0
Others	5.6	8.8	10.9	5.7	5.8	8.0
DiME Ether	0.9	0.4	0.4	1.2	0.8	0.6
MeEt Ether	0.0	0.0	0.0	0.1	0.1	0.1
Me Formate	2.6	2.3	3.7	0.8	0.7	0.7
Me Acetate	1.9	3.2	3.2	2.4	4.0	4.5
Hydrocarbons	1.7	1.1	1.1	2.2	1.9	1.7
CO	24.5	25.0	27.3	23.2	21.6	22.3
CO2	26.5	23.4	21.2	25.9	22.1	20.8

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Table 4. Methanol-Only Conversion Using 2% Pt on Zn/Mn/Zr Oxide Catalysts

Catalyst Number	8265-76		8265-50		8265-82	
Description	2.0% Pt on Zn/Mn/Zr Oxide (60/20/20)		2.0% Pt on Zn/Mn/Zr Oxide (33/33/33)		2.0% Pt on Zn/Mn/Zr Oxide (10/45/45)	
Run	272	291	258	293	278	292
Feed	MeOH/EtOH	MeOH	MeOH/EtOH	MeOH	MeOH/EtOH	MeOH
Conditions	350 C, 30 psig, 2 hr-1 MeOH WHSV, N2 Inert					
Conversion (%)						
MeOH	58.7	49.6	57.3	49.1	73.3	60.1
EtOH	100.0	-	99.8	-	100.0	-
Selectivity (C%)						
nC3OH	0.0	0.0	0.2	0.0	0.4	0.0
nC4OH	0.0	0.0	0.0	0.0	0.0	0.0
iC4OH	11.1	0.2	10.8	0.2	8.9	0.2
iC4 Aldehyde	17.7	0.3	15.6	0.3	12.0	0.2
Me iButyrate	5.3	0.1	4.9	0.1	7.3	0.1
MeiBu Ether	0.0	0.0	0.0	0.0	0.1	0.0
C5+OH	0.9	0.2	1.1	0.3	1.0	0.1
Other Ald/Ketone	0.8	0.3	0.9	0.3	0.8	0.1
Other Esters	0.3	0.2	0.4	0.2	0.9	0.2
Others	5.3	0.9	9.8	0.8	4.9	0.8
DiME Ether	1.1	7.9	1.3	8.4	1.0	8.9
MeEt Ether	0.0	0.0	0.0	0.0	0.0	0.0
Me Formate	2.5	10.3	2.7	7.3	0.6	3.3
Me Acetate	1.8	0.0	2.2	0.0	0.2	0.0
C1	0.8	6.6	0.9	6.9	0.6	3.1
C2+s	1.1	0.7	2.1	1.2	0.8	0.4
CO	25.4	61.3	21.0	63.6	38.6	72.9
CO2	26.0	11.0	26.2	11.3	22.3	10.0
PATENT HOLD						

Figure 1.

Effect of Pt Loading on Catalyst Performance

Conditions: 350 C, 30 psig, 1 hr-1 MeOH WHSV, 1/0.1/2 MeOH/EtOH/N2

—□— 0.5% Pt on Zn/Mn/Zr

—◇— 2.0% Pt on Zn/Mn/Zr

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Figure 2.

Effect of Pt Loading on Catalyst Performance

Conditions: 350 C, 30 psig, 1 hr-1 MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

$\square$ 0.5% Pt on Zn/Mn/Zr

$\diamond$ 2.0% Pt on Zn/Mn/Zr

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Figure 3.

Comparison of MeOH/EtOH and MeOH-only Feeds

Conditions: 350 C, 30 psig, 2 hr-1 MeOH WHSV, 1/0.1/2 or 1/0/2 MeOH/EtOH/N2 (molar)

—□— 2XPt on Zn/Mn/Zr (60/20/20)

—◇— 2XPt on Zn/Mn/Zr (33/33/33)

—△— 2XPt on Zn/Mn/Zr (10/45/45)

—×— 2XPt on Zn/Mn/Zr (60/20/20)

—+— 2XPt on Zn/Mn/Zr (33/33/33)

—*— 2XPt on Zn/Mn/Zr (10/45/45)

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Figure 4.