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January 18, 1996

Mr James Huemmrich
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**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 17. 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.

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

Regards,

Terry L. Marker
Terry L. Marker
Sr. Development Specialist

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

The effects of temperature, pressure and methanol/ethanol molar feed ratio on the performance of the 2% Pt on Zn/Mn/Zr Oxide catalyst has been evaluated in a series of pilot plant tests. Temperature has been varied from 325°C to 375°C, pressure from 30 psig to 300 psig and MeOH/EtOH ratio from 10/1 to 1/1. Raising temperature increases alcohol conversion, but reduces selectivity and productivity to the desired branched C₄ oxygenates. The higher pressure operation shifts the product ratio from isobutyraldehyde to isobutanol. Decreasing the feed ratio from 10/1 to 7/1 increases methanol conversion as well as selectivity to each of the iC₄ oxygenates. However, further reduction of the feed ratio to 4/1 does not give additional improvement. Based on these findings a pilot plant test at optimized conditions is planned using the 2% Pt on Zn/Mn/Zr oxide catalyst.

The effects of H₂, CO and CO₂ co-feeds on the performance of the have also been evaluated using the reference catalyst. Co-feeding H₂ has very little effect, whereas CO has a deleterious effect. CO₂ addition results in higher CO formation, but no substantial change in CO₂ selectivity. Therefore, it appears that the use of a CO₂ recycle would not be effective for reducing the formation of carbon oxide products.

A copper-lined reactor has been constructed that gives acceptable blank activity at temperatures up to 450°C and used to evaluate the activity of the 2% Pt on Zn/Mn/Zr oxide catalyst for methanol-only conversion. At temperatures greater than 350°C, minimal branched C₄ oxygenates are formed. Instead, the primary products are CO and CO₂. Therefore, this catalyst system does not appear to be promising for the conversion of methanol alone to higher alcohols.

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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.⁵ Upon successful testing of this sample, a 200 g portion of the support was impregnated with 2% Pt, dried and calcined. This material has been used for the process variable studies described in this report.

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. A listing of the pilot plant runs included in this report is given in Table 1. H₂, CO and CO₂ co-feeds were added using independent feed systems that are manifolded with the N₂ and methanol/ethanol feed systems immediately before the reactor inlet. In all cases, the co-feed was established with the N₂ purge for 2 hours prior to the addition of the methanol/ethanol blend.

Previous attempts to evaluate catalysts for alcohol conversion at temperatures greater than 400°C have been unsuccessful due to high decomposition of the feed to CO, CO₂ and light hydrocarbons. In order to prevent these side-reactions, a copper-lined reactor was fabricated by silver soldering a 5/8" ID copper tube inside a 3/4" ID stainless steel reactor. Blank tests in this reactor before and after methanol conversion testing show only minimal methanol decomposition. The testing procedure for methanol-only conversion was similar to that described above, except that a pure methanol feed was used in place of the 10/1 methanol/ethanol blend. A single run with C₂⁺ co-feed was accomplished by replacing the CO₂ cylinder described above with C₂⁺. The C₂⁺ feed was cut-in with the N₂, prior to alcohol addition.

RESULTS AND DISCUSSION

Large-Scale Preparation of 2% Pt on Zn/Mn/Zr (60/20/20) Oxide Catalyst

Catalysts consisting of Pt impregnated on a Zn/Mn/Zr mixed metal oxide support have been identified as promising for the synthesis of higher branched alcohols, particularly isobutanol, from lower alcohols in previous work in this program.¹⁻⁵ The optimization of the catalyst formulation (Task 2.0 of the program) was described in the previous Quarterly Reports^{4,5}. A catalyst composition of 2% Pt on a 60/20/20 (molar) Zn/Mn/Zr oxide support was found to give the best performance for higher oxygenate production. A scaled-up preparation of this material (from 30 g to 200 g) has been completed. Pilot plant testing of this material has shown comparable performance to previous samples with the same nominal composition (Table 2). This large supply of catalyst has been used for the process variable studies described in this report.

Process Variable Studies for Methanol/Ethanol Conversion

The effects of temperature, pressure and methanol/ethanol molar feed ratio on the performance of the 2% Pt on Zn/Mn/Zr Oxide catalyst has been evaluated in a series of pilot plant tests. Temperature has been varied from 325°C to 375°C, pressure from 30 psig to 300 psig and MeOH/EtOH ratio from 10/1 to 1/1. Table 3 summarizes the average conversions, selectivities and productivities obtained from 9-16 hours on stream at each of the conditions employed.

Raising temperature increases alcohol conversion, but reduces selectivity and productivity to the desired branched C₄ oxygenates. CO and light hydrocarbons production is substantially higher 375°C compared with 325°C, while CO₂ and methyl acetate (presumably from Cannizzaro condensation) are lower. Higher temperature also shifts the C₄ oxygenates product ratio toward isobutyraldehyde from isobutanol and methyl isobutyrate. Based on these results, it appears that lower temperature, with the use of lower space velocity to maintain conversion, is the preferred operating condition.

The major effect of higher pressure operation is to shift the product ratio from isobutyraldehyde to isobutanol. CO selectivity is also increased, which is surprising considering the thermodynamics of methanol decomposition to CO and H₂ should be disfavored by raising pressure. Operation at 300 psig affords the highest productivities of isobutanol and to iC₄ oxygenates observed with a 10/1 methanol ethanol feed. With the combination of higher pressure and lower temperature it may be possible to obtain these better oxygenate selectivities and productivities while reducing the amount of CO produced.

Variation of the methanol/ethanol feed ratio has been used to gain a understanding of the mechanism of alcohol coupling. Decreasing the feed ratio from 1.0/1 to 7/1 increases methanol conversion as well as selectivity to each of the iC_4 oxygenates. CO_x selectivities are also slightly reduced. However, further reduction of the methanol/ethanol feed ratio to 4/1 does not give additional improvement as light esters, presumably arising from base-catalyzed Cannizzaro reactions, and unidentified heavy by-products increase. At a 1/1 feed ratio branched higher alcohol products are substantially reduced and light ester products dominant the observed product. The highest $i-C_4$ oxygenates productivity has been obtained at a 7/1 methanol/ethanol feed ratio. This indicates that an excess of ethanol is required to prevent other base catalyzed coupling reactions (such as the Cannizzaro reaction) from occurring over this catalyst.

Based on these findings a pilot plant test at optimized conditions is planned using the 2% Pt on Zn/Mn/Zr oxide catalyst. The conditions to be used will be 325°C, 300 psig, 1 hr⁻¹ MeOH WHSV and 7/1/2 MeOH/EtOH/N₂ molar feed ratio.

Co-feeding H₂ at a 2/1 H₂/MeOH feed ratio had very little effect on the performance of the Pt on Zn/Mn/Zr oxide catalyst (Table 4). Methanol conversion is higher and selectivity shifts from isobutyraldehyde to isobutanol with H₂ giving an overall slightly higher productivity for isobutanol. It has been speculated that the dehydrogenation of methanol and ethanol to the corresponding aldehydes is a key first step in the coupling mechanism. The presence of an H₂ co-feed might be expected to inhibit the formation of these intermediates and hinder the formation of higher alcohols. However, it appears that this is not a problem to the low H₂ feed ratio used in this experiment. Future work will include a pilot plant test at a high H₂/MeOH feed ratio, similar to that observed in the product effluent of a commercial methanol synthesis process. The H₂ co-feed does appear effect the hydrogenation/dehydrogenation equilibrium between alcohol and aldehyde and, therefore, can be a factor in determining product selectivity.

Table 4 also shows that co-feeding CO has a deleterious effect on catalyst performance. Alcohol conversions and isobutanol selectivities are decreased. A large increase in other oxygenates and unidentified heavy products suggests that side-reaction such as carbonylation may be occurring. Due to the unattractiveness of this result further characterization of the reaction products has not been pursued.

The coupling of methanol and ethanol to isobutanol produces two equivalents of water as a co-product. At the conditions used for this process, the water gas shift equilibrium greatly favors the conversion of H₂O and CO to CO₂, which a major product observed in the pilot plant tests. Therefore, this water co-product results in a substantial loss in carbon efficiency. One approach to overcome this loss is to recycle CO₂ to the process, thus forcing the production of H₂O. Two levels of CO₂ co-feed (1.5 and 2.8 CO₂/MeOH) have been evaluated in order to determine whether

this approach has merit with the Pt on Zn/Mn/Zr catalyst system. Table 4 summarizes the results of this testing. CO₂ addition has a minimal effect on conversion levels, but results in lower selectivities to the desired iC₄ oxygenates due to higher CO formation. CO₂ selectivity is not substantially reduced. Therefore, it appears that the use of a CO₂ recycle would not be effective for reducing the formation of carbon oxide products with this catalyst.

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

The previous quarterly report in this project described the evaluation of three 2% Pt on Zn/Mn/Zr oxide catalyst formulations for the conversion of methanol only to higher branched oxygenates at 350°C⁵. Test conditions were identical to those employed with the 10/1 methanol/ethanol blend, except that a pure methanol feedstock was used. For all of these catalysts, the products containing C-C bonds were virtually eliminated when a methanol only feed is used. Selectivities to total C₄₊ products were less than 3%. The major products observed were due to other reactions including methanol decomposition (CO, CO₂, H₂), hydrogenation (methane), etherification (DME) and Cannizzaro condensation (methyl formate). Attempts to test these catalysts at temperatures greater than 350 °C were unsuccessful due to substantial methanol decomposition to CO, CO₂ and H₂. A blank reactor test using the standard 316 stainless steel reactor loaded with glass beads at 250 °C to 500 °C showed excessive methanol decomposition at 450 °C (35%) and 500 °C (68%)⁵. A copper-lined stainless steel reactor has been fabricated to allow catalyst testing at temperatures greater than 350°C. Table 5 shows the results of a blank test in this reactor at 350, 400 and 450°C. Methanol decomposition is less than 10% at all temperatures. At 350°C, C₂ oxygenates (DME and methyl formate) are the major products, while carbon oxides, particularly CO become more predominant at higher temperatures.

The performance of the reference 2% Pt on Zn/Mn/Zr oxide catalyst for the conversion of methanol only to higher oxygenates has been evaluated using the copper-lined reactor at 350, 400 and 450°C. Table 5 shows that minimal branched C₄ oxygenates are formed. Instead, the primary products are CO and CO₂. Therefore, the performance of this catalyst system for methanol only conversion is not improved by operation at higher temperatures.

Based on the results obtained with to date with Pt on Zn/Mn/Zr oxide catalysts with methanol only feed, this catalyst systems does not appear to be promising for the conversion of methanol alone to higher alcohols. It appears that this catalyst is active only for the aldol condensation step, in which a C₂ aldehyde intermediate is condensed with C₁ species, in the overall mechanism. Therefore, the final pilot plant demonstration runs and the economic evaluation of this catalyst system will be directed at the conversion of methanol with ethanol to higher alcohols.

CONCLUSIONS

The effects of temperature, pressure and methanol/ethanol molar feed ratio on the performance of the 2% Pt on Zn/Mn/Zr Oxide catalyst has been evaluated in a series of pilot plant tests. Temperature has been varied from 325°C to 375°C, pressure from 30 psig to 300 psig and MeOH/EtOH ratio from 10/1 to 1/1. Raising temperature increases alcohol conversion, but reduces selectivity and productivity to the desired branched C₄ oxygenates. The major effect of higher pressure operation is to shift the product ratio from isobutyraldehyde to isobutanol. Decreasing the feed ratio from 10/1 to 7/1 increases methanol conversion as well as selectivity to each of the iC₄ oxygenates. CO_x selectivities are also slightly reduced. However, further reduction of the methanol/ethanol feed ratio to 4/1 does not give additional improvement. Based on these findings a pilot plant test at optimized conditions is planned using the 2% Pt on Zn/Mn/Zr oxide catalyst. The conditions to be used will be 325°C, 300 psig, 1 hr⁻¹ MeOH WHSV and 7/1/2 MeOH/EtOH/N₂ molar feed ratio.

The effects of H₂, CO and CO₂ co-feeds on the performance of the have also been evaluated using the reference catalyst. Co-feeding H₂ at a 2/1 H₂/MeOH feed ratio has very little effect, whereas CO at a similar level has a deleterious effect as it reduces alcohol conversions and isobutanol selectivity. CO₂ addition has a minimal effect on conversion levels, but results in lower selectivities to the desired iC₄ oxygenates due to higher CO formation. CO₂ selectivity is not substantially reduced. Therefore, it appears that the use of a CO₂ recycle would not be effective for reducing the formation of carbon oxide products with this catalyst.

A copper-lined reactor has been constructed that gives acceptable blank activity at temperatures up to 450°C. Using this reactor, the activity of the 2% Pt on Zn/Mn/Zr oxide catalyst for methanol conversion has been evaluated at temperatures up to 450°C. At these higher temperatures minimal branched C₄ oxygenates are formed. Instead, the primary products are CO and CO₂. Therefore, this catalyst system does not appear to be promising for the conversion of methanol alone to higher alcohols.

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 and P. R. Kurek, DOE Quarterly Report No. 16. (1995).....

Table 1. Run List

RUN	CATALYST		CATALYST DESCRIPTION	LOADING g	TEMP (C) INLET	CONDITIONS			FEED RATIO MeOH/EtOH/N ₂ /Others
	A Book #	B Book #				TOTAL PSIG	MeOH WHSV	MAX	
304	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	30	2	1/0.14/2 N2	
305	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	30	2	1/0.25/2 N2	
306	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	30	2	1/1.00/2 N2	
307	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	30	2	1/0.25/2 N2	
308	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	30	2	1/0.10/2 N2	
309	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	325	30	2	1/0.10/2 N2	
310	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	375	30	2	1/0.10/2 N2	
311	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	100	2	1/0.10/2 N2	
312	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	300	2	1/0.10/2 N2	
313	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	30	2	1/0.10/2 N2 / 2 H2	
314	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	30	2	1/0.10/2 N2 / 2 CO	
315	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	30	2	1/0.10/2 N2 / (CO2)	
316	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	30	2	1/0.2 N2 / 2 C2=	
317	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	30	2	1/0.10/2 N2 / No CO2	
318	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	30	2	1/0.10/2 N2 / 1.5 CO2	
319	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	30	2	1/0.10/2 N2 / 2.8 CO2	
320	None		Glass Beads in Copper-Lined Reactor		500	30	2	1/0/2 N2	
					450	30	2	1/0/2 N2	
					400	30	2	1/0/2 N2	
					350	30	2	1/0/2 N2	
					300	30	2	1/0/2 N2	
321	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	450	30	2	1/0/2 N2	
322	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	350	30	2	1/0/2 N2	
323	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	5	450	300	2	1/0/2 N2	
					350	300	2	1/0/2 N2	
					400	300	2	1/0/2 N2	
					450	300	2	1/0/2 N2	
324	None		Glass Beads in Copper-Lined Reactor		350	300	2	1/0/2 N2	
					400	300	2	1/0/2 N2	
					450	300	2	1/0/2 N2	

Table 2. Pilot Plant Performance of Pt on Zn/Mn/Zr Oxide

Catalyst	8265-76	8265-95	8265-98
	2% Pt on Zn/Mn/Zr (60/20/20) Oxide		
	Initial Prep (g)	Certification (g)	Large Prep (g)
Plant 700 Run Number	272	297	308
Conditions	350°C, 30 psig, 2 hr ⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N ₂ (molar)		
Conversion (%)			
MeOH	58.7	50.2	53.4
EtOH	100.0	99.0	99.1
Selectivities (mole %)			
nC ₃ OH	0.0	0.5	0.4
nC ₄ OH	0.0	0.1	0.1
iC ₄ OH	11.1	13.0	11.6
iC ₄ Aldehyde	17.7	16.2	18.0
Me iButyrate	5.3	5.4	4.3
Other Oxygenates	2.0	3.2	1.5
Others (No ID)	5.3	5.7	7.3
C ₁ -C ₂ Oxygenates	5.4	4.5	4.1
C ₁ -C ₄ Hydrocarbons	1.9	2.2	1.4
CO	25.4	23.2	22.3
CO ₂	26.0	25.9	28.0
Productivities (mole/kg/hr)			
iC ₄ OH	5.2	5.5	5.1
iC ₄ Oxygenates			

Table 3. Effect of Process Variables on Performance of Pt on Zn/Mn/Zr Oxide Catalyst for Methanol/Ethanol Conversion

Catalyst	8265-98 2% Pt on Zn/Mn/Zr (60/20/20) Oxide									
	309	308	310	308	311	312	308	304	307	306
Run Number										
Conditions	2 hr ⁻¹ MeOH WHSV, 2/1 N ₂ /MeOH (molar)									
Temperature (°C)	325	350	375	350	350	350	350	350	350	350
Pressure (psig)	30	30	30	30	100	300	30	30	30	30
MeOH/EtOH (molar)	10/1	10/1	10/1	10/1	10/1	10/1	10/1	7/1	4/1	1/1
Conversion (%)										
MeOH	39.7	53.4	64.2	53.4	46.0	56.4	53.4	57.4	58.8	65.5
EtOH	96.6	99.1	98.1	99.1	95.7	97.6	99.1	97.4	93.4	82.8
Selectivities (mole %)										
nC ₃ OH	1.2	0.4	1.1	0.4	0.3	0.8	0.4	1.0	2.9	2.0
nC ₄ OH	0.1	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.5	1.2
iC ₄ OH	15.6	11.6	5.7	11.6	14.4	20.7	11.6	15.3	9.1	0.3
iC ₄ Aldehyde	16.6	18.0	13.4	18.0	11.2	7.2	18.0	19.0	12.9	1.0
Me iButyrate	4.9	4.3	2.1	4.3	5.1	5.6	4.3	5.4	4.9	0.2
Other Oxygenates	3.4	1.5	4.4	1.5	1.8	1.4	1.5	3.9	9.7	3.1
Others (No ID)	8.5	7.3	8.1	7.3	5.8	2.1	7.3	5.5	13.4	14.1
C ₁ -C ₂ Oxygenates	7.2	4.1	2.2	4.1	3.3	3.0	4.1	4.1	6.9	66.9
C ₁ -C ₄ Hydrocarbons	0.7	1.4	3.5	1.4	2.7	2.6	1.4	1.3	0.9	0.7
CO	14.5	22.3	33.9	22.3	26.2	31.2	22.3	18.1	13.0	5.1
CO ₂	27.5	28.0	25.5	28.0	29.2	25.2	28.0	26.2	25.8	5.6
Productivities (mole/kg/hr)										
iC ₄ OH	5.5	5.1	2.9	5.1	5.6	9.5	5.1	8.1	5.9	0.4
iC ₄ Oxygenates	13.0	14.9	10.8	14.9	11.9	15.4	14.9	21.0	17.4	1.8

Table 4. Effect of H₂, CO and CO₂ Co-Feeds on Performance of Pt on Zn/Mn/Zr Oxide Catalyst for Methanol/Ethanol Conversion

Catalyst		8265-98 2% Pt on Zn/Mn/Zr (60/20/20) Oxide					
Run Number	308	313	314	318	319		
Conditions	325°C, 30 psig, 2 hr ⁻¹ MeOH WHSV						
MeOH/EtOH	10	10	10	10	10	10	
N ₂ /MeOH	2	2	2	2	2	2	
Other/MeOH	None	2 H ₂	2 CO	1.5 CO ₂	2.8 CO ₂		
Conversion (%)							
MeOH	53.4	58.3	29.3	53.3	55.4		
EtOH	99.1	99.5	90.5	99.6	98.9		
Selectivities (mole %)							
nC ₃ OH	0.4	0.2	2.9	0.2	0.5		
nC ₄ OH	0.1	0.0	0.2	0.0	0.0		
iC ₄ OH	11.6	14.0	1.6	9.6	7.7		
iC ₄ Aldehyde	18.0	11.6	7.5	18.0	15.9		
Me iButyrate	4.3	7.3	0.9	6.5	4.9		
Other Oxygenates	1.5	3.2	12.8	2.2	2.4		
Others (No ID)	7.3	6.4	12.5	4.4	3.3		
C ₁ -C ₂ Oxygenates	4.1	3.9	4.9	2.4	1.5		
C ₁ -C ₄ Hydrocarbons	1.4	2.6	1.6	1.1	0.6		
CO	22.3	24.4	28.1	32.6	36.1		
CO ₂	28.0	26.4	27.2	23.0	27.3		
Productivities (mole/kg/hr)							
iC ₄ OH	5.1	6.6	0.5	4.2	3.4		
iC ₄ Oxygenates	14.9	15.5	3.1	14.9	12.6		

Table 5. Methanol-Only Conversion Using 2% Pt on Zn/Mn/Zr Oxide Catalysts

Catalyst	Glass Beads (Blank)			8265-98 2% Pt on Zn/Mn/Zr Oxide						
	Run Number	9-16	324	9-16	322	323	9-16	25-32	41-48	
Hours on Stream		9-16	25-32	41-48	9-16	25-32	41-48	9-16	25-32	41-48
Conditions	2 hr ⁻¹ MeOH WHSV, 2/1 N ₂ /MeOH (molar)									
Temperature (°C)	350	400	450	450	350	400	450	350	400	450
Pressure (psig)	30	30	30	30	30	30	30	300	300	300
Conversion (%) MeOH	0.2	2.1	8.8	45.9	95.6	95.7	46.7	95.4	96.3	
Selectivities (mole %)										
nC ₃ OH	0.0	1.8	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
nC ₄ OH	0.0	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
iC ₄ OH	0.0	0.0	0.0	0.1	0.1	0.0	0.2	0.2	0.2	0.1
iC ₄ Aldehyde	0.0	0.6	0.0	0.2	0.3	0.2	0.1	0.1	0.1	0.1
Me iButyrate	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0
Other Oxygenates	7.8	1.2	0.3	0.4	0.6	0.8	0.3	0.3	0.3	0.3
Others (No ID)	4.7	1.0	0.0	0.2	1.3	0.7	0.2	0.2	0.9	0.2
C ₁ -C ₂ Oxygenates	87.5	54.6	35.0	17.6	0.1	0.1	12.4	0.0	0.1	0.1
C ₁ -C ₄ Hydrocarbons	0.0	4.2	5.0	5.2	6.9	7.6	2.4	2.6	3.4	3.4
CO	0.0	30.9	51.7	67.3	81.2	80.6	76.5	90.9	90.7	90.7
CO ₂	0.0	5.0	6.8	9.0	9.6	9.9	7.9	5.1	5.1	5.1
Productivities (mole/kg/hr) iC ₄ OH	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.1	0.1	0.0