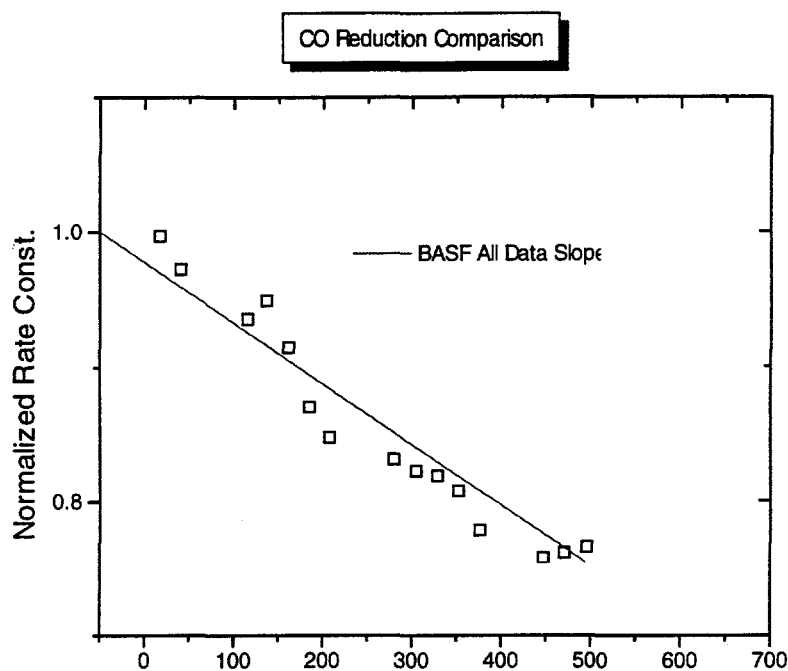**Figure 1.4.13. CO Reduction Comparison**

CO Reduction Comparison

TASK 2: AFDU SHAKEDOWN AND OPERATIONS

2.1 Liquid Phase Hydrodynamic Run'

Nothing operationally to report this quarter. See Task 1.4 for run preparations.

TASK 3: RESEARCH AND DEVELOPMENT

3.1 New Processes for DME

The work this quarter focused on particular aspects of LPDME activity maintenance.

Dehydration Catalyst Screening Runs

In the previous quarterly we reported that an interaction between BASF S3-86 methanol catalyst and Catapal B γ-alumina is the cause of catalyst deactivation under LPDME conditions. This finding resulted in our active screening for alternative dehydration catalysts. In this quarter, nine more dehydration catalysts were examined, including two silica alumina, two modified Catapal B γ-alumina, a fumed alumina, two metal phosphate, and two ZrO_2-based samples. However, none exhibited better performance than γ-alumina.

Silica Alumina

Silica based materials are the preferred dehydration catalysts, since a previous experiment (14045-31) showed that a high surface area silica gel, while inert toward methanol dehydration, did not cause premature aging of the BASF S3-86 methanol catalyst. Two silica-aluminas of high silica content, i.e., Siral 85 (85% silica and 15% alumina) and Siral 95 from Condea, were

tested. The results for these two samples are shown in Table 3.1.1 and Figure 3.1.1 below, along with the results from a run using our standard catalyst system (S3-86 plus Catapal B γ-alumina). The methanol equivalent productivity of the systems containing Siral 85 and 95 is very low, e.g., at 20 hours onstream, 12.9 and 15.0 mol/kg-hr, respectively, compared to 30.7 mol/kg-hr for the standard catalyst system. This is due to both an extremely low dehydration activity and low methanol synthesis activity. The rate constants in Table 3.1.1 quantitate this observation. The results from these two experiments indicate that silica alumina is not a better dehydration catalyst than γ-alumina for our application.

Table 3.1.1. Kinetic Results from the Runs using S3-86 along with Siral 85 (14191-43), Siral 95 (13465-100), and Catapal B γ-alumina (11782-3), respectively

Run	Catalyst S3-86:Al2O3	Time on Stream (hr)	Productivity (mol/kg-hr)			Rate Constant	
			MEOH	DME	Equiv.	$k_m{}^a$	$k_d{}^b$
14191-43	80:20	20	8.5	2.2	12.9	1.0	1.2
13465-100	80:20	20	13.3	0.9	15.0	1.8	0.4
11782-3	82:18	20	2.1	14.3	30.7	2.6	17.0

a: Methanol synthesis rate constant calculated from $R_m = k_m f_{H_2}^{2/3} f_{CO}^{1/3} (1 - appr.)$, based on methanol catalyst weight.

b: Methanol dehydration rate constant calculated from $R_d = k_d f_{CO_2}^{-0.33} f_{MEOH}^{0.11} f_{CO}^{0.70} (1 - appr.)$, based on dehydration catalyst weight.

Figure 3.1.1 Catalyst screening using Siral 85 and Siral 95 plus S3-86
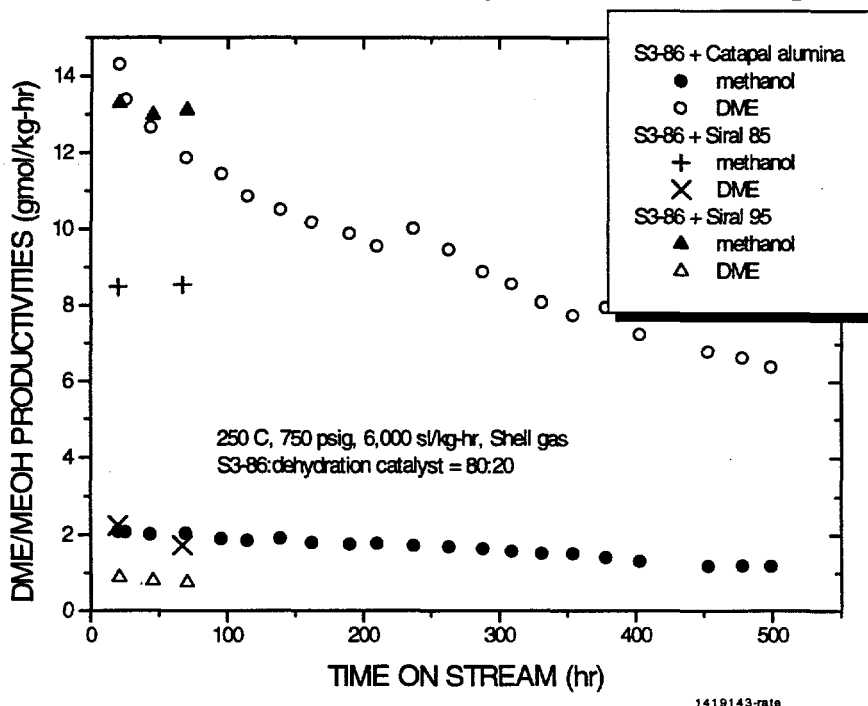
Two important observations should be noted, especially since they appear frequently in the series screening runs: First, different dehydration catalysts have different impacts on the methanol catalyst. The lower initial activity of the methanol catalyst in the catalyst systems containing silica alumina (see Table 3.1.1) indicates faster deactivation of the methanol catalyst in the presence of silica alumina than in the presence of γ-alumina. It is likely that this deactivation started during catalyst reduction. This occurs during the activation procedure for the methanol catalyst which runs 24 hr from room temperature to 240°C under diluted hydrogen before syngas is introduced into the system.

Second, different dehydration catalysts deactivate differently. The low dehydration activity from the silica alumina samples was unexpected, since silica alumina is normally more acidic than γ-alumina, and therefore should be more active toward dehydration. This low activity is attributed to the fast deactivation of silica alumina based on the following observation. We monitored the exit gas flow rate in the early hours of the run using Siral 85. Since the synthesis reaction is molecule-reducing, lower flow rate means greater activity. Judging by the flow rate shown in Table 3.1.2, the activity of the Siral 85 system at 1.2 hr on stream is fairly high, i.e., corresponding to a methanol equivalent productivity near 30 mol/kg-hr. Thus, we infer that the silica alumina had an initial dehydration activity at least comparable to the γ-alumina. However, this activity dropped considerably in the first 20 hr on stream as can be seen from the increasing flow rate. Again, it is likely that the activity of the silica alumina already started to drop during the reduction.

Table 3.1.2. Exit Gas Flow Rate as a Function of Time On Stream for the Run using Siral 85

Time on stream (hr)	Normalized exit flow rate[a]
1.2	0.79
4.3	0.85
20	0.89

a: Normalized by the inlet flowrate. For the run using S3-86 and Catapal γ-alumina, the normalized exit flowrate at 20 hr on stream is 0.77, corresponding to a methanol equivalent productivity of 30.7 mol/kg-hr.

Modified Catapal B γ-Alumina

One of our hypotheses about the interaction between the methanol and dehydration catalysts is that ZnO from the methanol catalyst might migrate onto alumina under the reaction conditions. The effect of this migration could be twofold: ZnO may deactivate the dehydration catalyst by reacting with the acid sites, and/or the methanol catalyst may lose its activity by losing its active component. If this is true, one would expect that:

1) the activity of the alumina would drop considerably if it is doped with ZnO; and
2) the doped Catapal B would result in a better stability of the methanol catalyst due to the smaller driving force for the migration.

Based on these considerations, a ZnO-doped Catapal B sample (14191-65) was prepared by impregnating the alumina with zinc nitrate, followed by calcination at 560°C for 4 hr to convert $Zn(NO_3)_2$ into ZnO and disperse ZnO on the alumina surface. The loading of ZnO is 40 wt%. According to the literature [Xie, et al., in: Adv. Catal., V37 (1990) p1], this corresponds to the highest loading of ZnO on alumina in atomically dispersed form. Further loading will result in ZnO crystallite formation.

Figures 3.1.2 and 3.1.3 display the activity of the catalyst system consisting of BASF S3-86 methanol catalyst and ZnO-Catapal B in comparison with that of the standard catalyst system (S3-86 plus virgin Catapal B). The reaction was run at the standard conditions (250°C, 750 psig, 6,000 GHSV, methanol:dehydration catalyst =80:20) using Shell gas. As expected, the ZnO-doped Catapal B has a lower dehydration activity than the virgin Catapal B. However, it shows little improvement in the stability of the methanol catalyst.

A WO_3-modified Catapal B γ-alumina was prepared by impregnating Catapal B γ-alumina with an aqueous solution of ammonium meta tungstate, followed by calcination at 700°C. Tungsten oxide has been reported in the literature to have dehydration activity at least as high as γ-alumina. This sample was tested along with BASF S3-86 methanol catalyst under the standard conditions using Shell gas (13465-58). Figures 3.1.2 and 3.1.3 show that the catalyst system does not exhibit better activity or stability than the standard catalyst system (S3-86 plus virgin Catapal B γ-alumina).

Figure 3.1.2. Methanol Synthesis Rate Constant as a Function of Time On Stream for Different Catalyst Systems
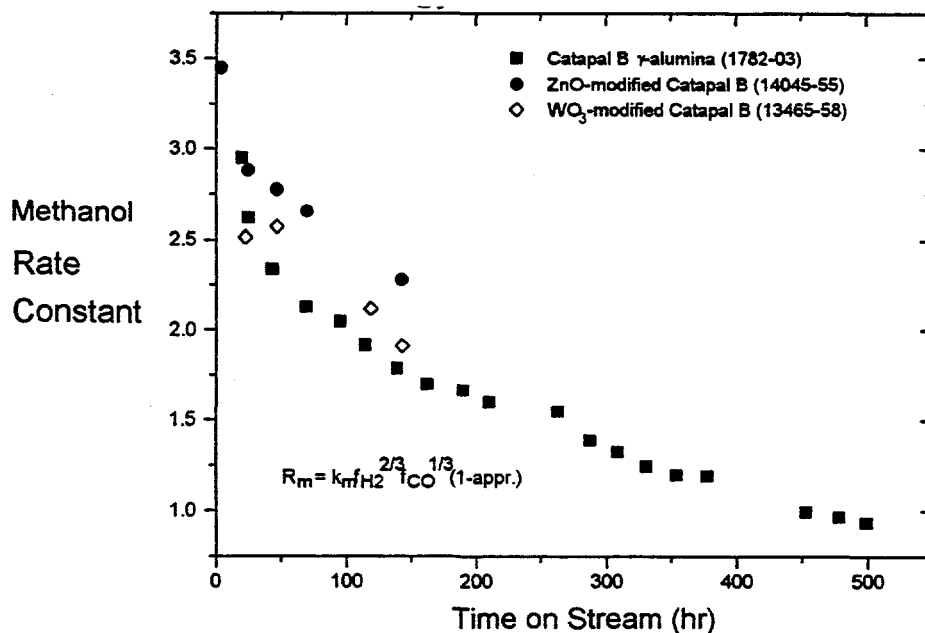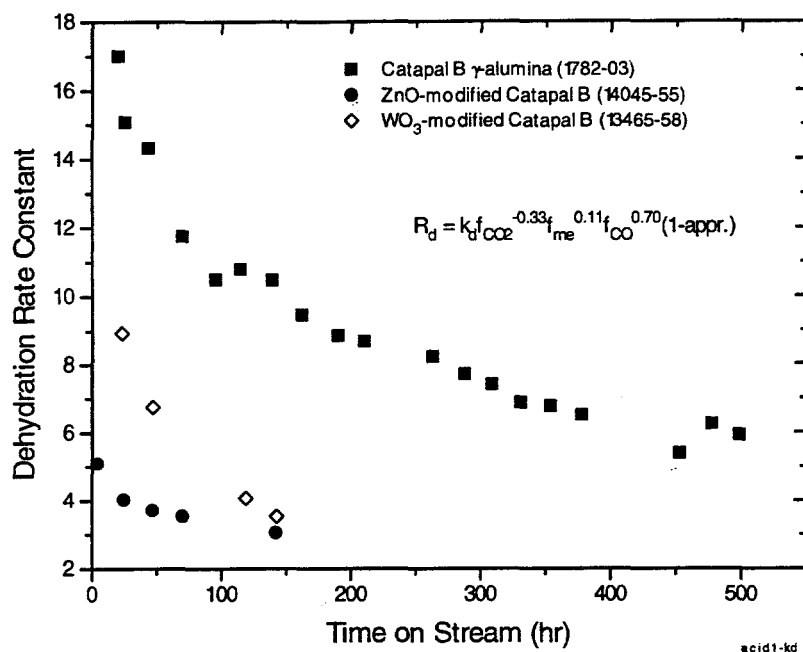
Figure 3.1.3. Dehydration Rate Constant as a Function of Time On Stream for Different Catalysts

Legend:
- ■ Catapal B γ-alumina (1782-03)
- ● ZnO-modified Catapal B (14045-55)
- ◇ WO₃-modified Catapal B (13465-58)

$$R_d = k_d f_{CO2}^{-0.33} f_{me}^{0.11} f_{CO}^{0.70}(1\text{-appr.})$$

acid1-kd

Fumed Alumina

Fumed alumina from Degussa (aluminum oxide C, average particle size = 13 nm) was tested along with BASF S3-86 methanol catalyst as an alternative dehydration catalyst (13465-91). Figure 3.1.4 shows that both initial methanol synthesis and methanol dehydration activities, in terms of rate constant, are low for this catalyst system as compared to the standard one, followed by continuous drop in both activities.

Figure 3.1.4. Activity of the Catalyst System Consisting of S3-86 and Fumed Alumina (13465-91)
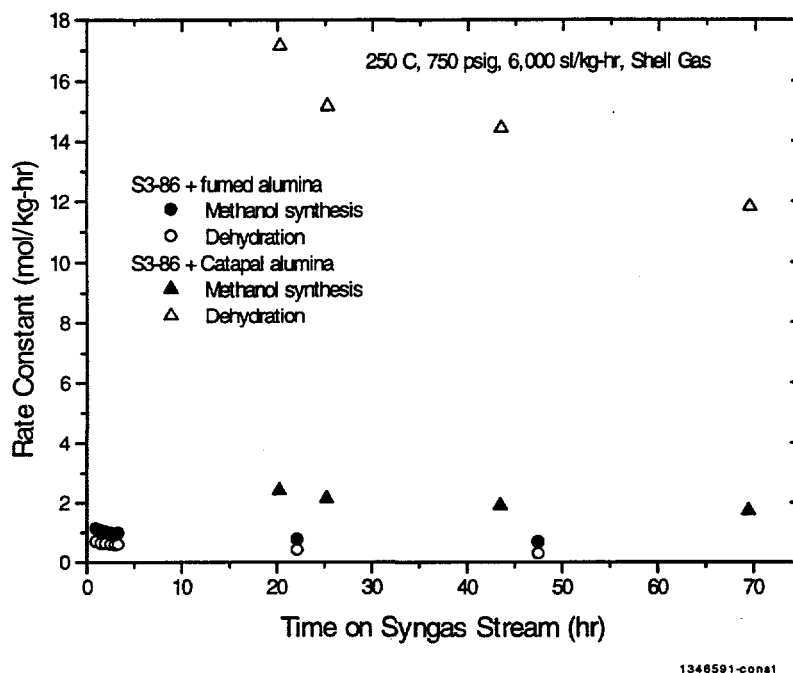
The interpretation of the poor activity and stability of this system is complicated by the following two factors. First, when the slurry was discharged from the reactor, clumps of the catalyst mixture were observed on the stirring rod and the walls of the reactor. This is due to low sedimentation of the very fine powders in the oil. If the sediment was also formed under the reaction conditions, it could lead to poor catalyst performance. The second complication is the fact that the fumed alumina contains a small amount of HCl (<0.5% by specification). The uncertainty is that Cl⁻ may migrate onto the methanol catalyst under the reaction conditions, leading to methanol catalyst deactivation, since Cl⁻ is a known methanol catalyst poison.

Metal Phosphates

Metal salts such as phosphates, sulfates, and chlorides have been used as industrial dehydration catalysts. Therefore, two phosphate samples were examined this month: one calcium phosphate, called hydroxyapatite, sample (Ca:P = 1.58), and a silica doped with 34% phosphorous acid. Owing to the high acid loading, the acid-doped silica contains some free H_3PO_4. Therefore, we would also like to use this sample to probe the possibility of using homogeneous acids as dehydration catalysts for LPDME. The runs were conducted under the standard LPDME conditions (250°C, 750 psig, 6,000 GHSV, 80:20 catalyst ratio). As shown in Figure 3.1.5, both samples have almost nil dehydration activity. This lack of activity could be due to the reaction temperature (dehydration using metal phosphates usually takes place at higher temperatures, e.g., > 300°C), the low water level in our system (high water level is needed to prevent H_3PO_4 from being dehydrated, therefore losing its acidity, above 200°C), or incompatibility with the methanol catalyst.

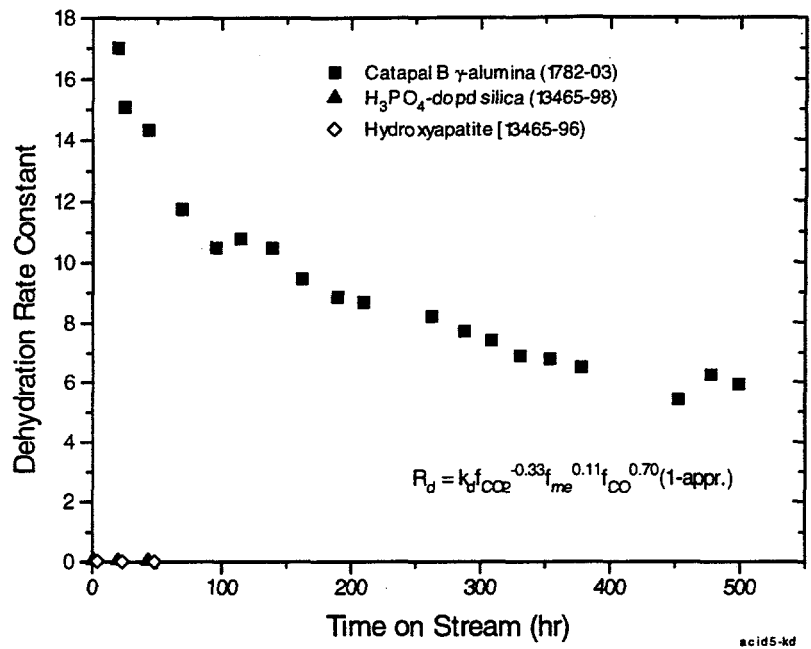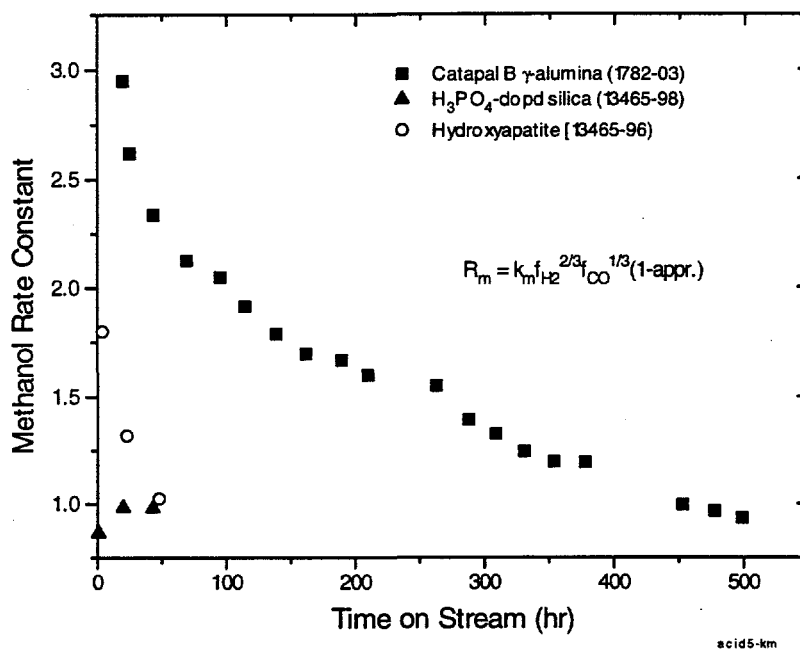**Figure 3.1.5. Dehydration Rate Constant as a Function of Time On Stream for Different Catalyst Systems**

Figure 3.1.6. Methanol Synthesis Rate Constant as a Function of Time On Stream for Different Catalyst Systems

Legend:
- ■ Catapal B γ-alumina (1782-03)
- ▲ H_3PO_4-dopd silica (13465-98)
- O Hydroxyapatite (13465-96)

$$R_m = k_m f_{H2}^{2/3} f_{CO}^{1/3} (1\text{-appr.})$$

acid5-km

Both catalysts have significant impact on methanol catalyst activity, although they did not exhibit any dehydration activity. As shown in Figure 3.1.6, the methanol catalyst, when used along with the hydroxyapatite sample, deactivates at a higher rate than in the standard catalyst system. A different effect on the stability of the methanol catalyst was observed in the case of H_3PO_4-doped silica. The activity of the methanol catalyst must have been severely diminished during the reduction, as indicated by the low initial activity of the catalyst. The long-term impact of this sample on the methanol catalyst is not clear since the run was terminated at 43 hr on stream.

ZrO_2, and ZrO_2-Modified Silica Gel

Two ZrO_2-based materials were tested because dehydration of alcohols using ZrO_2 has been reported in the literature. A bulk ZrO_2 sample was obtained by calcining $Zr(OH)_4$ at 600°C for 6 hr. The surface area of the calcined sample was 38.1 m^2/g. The second sample, ZrO_2-modified silica, was prepared by impregnating a silica gel (Davison grade 55) with zirconium ethoxide, followed by calcination. Both test runs, conducted under the standard conditions (13465-88 and 14191-33), show that the ZrO_2 samples had essentially zero dehydration activity. While the bulk zirconia sample had little impact on the activity of the methanol catalyst, the ZrO_2-modified silica gel caused a continuous drop in the methanol catalyst activity.

Experiments using Robinson-Mahoney Basket Internals and Pelletized Catalysts

Robinson-Mahoney basket internals were purchased for our 300 cc autoclave from Autoclave Engineers Group. Figure 3.1.7 shows the assembly of this system. An annular basket, which sits

stationary inside the autoclave reactor, is used to hold pelletized catalyst samples. An agitator, connected to the shaft of our current reactor system, provides the necessary agitation. Baffles are built inside and outside the basket to prevent vortexing. This setup is designed to help understand the mechanism of catalyst deactivation under LPDME conditions. First, it enables us to separate spent methanol and dehydration catalysts for characterization. Second, it creates a physical environment different from the slurry such as pellets vs. powders, and there is an absence of collisions between catalyst particles. Whether this results in a different deactivation pattern will provide insight into the mechanism of catalyst deactivation.

Reactor Shakedown

A shakedown run of this reactor system was conducted using the BASF S3-86 methanol catalyst (#ZU 553-5072) alone. The catalyst pellets were between 1 and 3.35 mm. Before the run, the reactor system was passivated using flowing syngas at 300 C and 1,200 psig for 20 hr. The catalyst was reduced using the standard procedure. As shown in Figure 3.1.8, the standard heating ramp was too fast for methanol catalyst pellets in this setup, resulting in incomplete reduction; the total H_2 uptake during this reduction was 1.7 scf/lb, 61% of the normal uptake. The system was switched to Shell gas when the reduction temperature reached 240°C.

As shown in Figure 3.1.9, the methanol productivity of this system (9 mol/kg-hr) was much lower than that of a normal slurry phase run (15 mol/kg-hr). The apparent rate constant of this system was 70% smaller. The low activity was due to a mass transfer limitation in the system. Figure 3.1.10 shows that productivity increased with stirring speed. No attempt to overcome this limitation by exceeding 2,000 rpm was made because of potential damage to the system. The activity of the system appeared to be stable except for a small initial drop. However, it should be mentioned that the apparent activity of this system will not be sensitive to catalyst deactivation because the reaction rate is mass transfer limited.

The catalysts used in the LPDME run were BASF S3-86 tablets (#ZU 553 5072) crushed into a 1.0-1.7 mm size and Catapal B 1/8"x1/8" tablets from Calsicat (02E-60A) crushed into a smaller size (about four pieces from every tablet). The S3-86 and Catapal catalyst pellets were mixed first in a 80:20 ratio and loaded into the basket. Since the shakedown run showed much slower H_2 uptake by the pellets during reduction and incomplete reduction of the catalyst using the temperature ramp designed for powder S3-86, a new reduction scheme was employed in the current run, based on the BASF activation procedures for packed bed application. The reduction results are shown in Figure 3.1.11. Again, H_2 uptake was slower compared to the powder case. However, the final H_2 uptake (2.6 scf/lb) was close to the acceptable value (2.8 - 3.0 scf/lb), which is near the stoichiometric uptake.

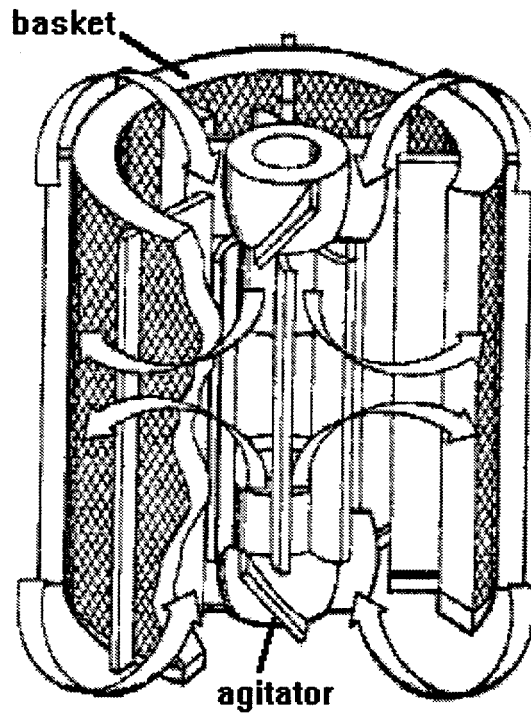**Figure 3.1.7. Schematic of Robinson-Mahoney Stationary Catalyst Basket**

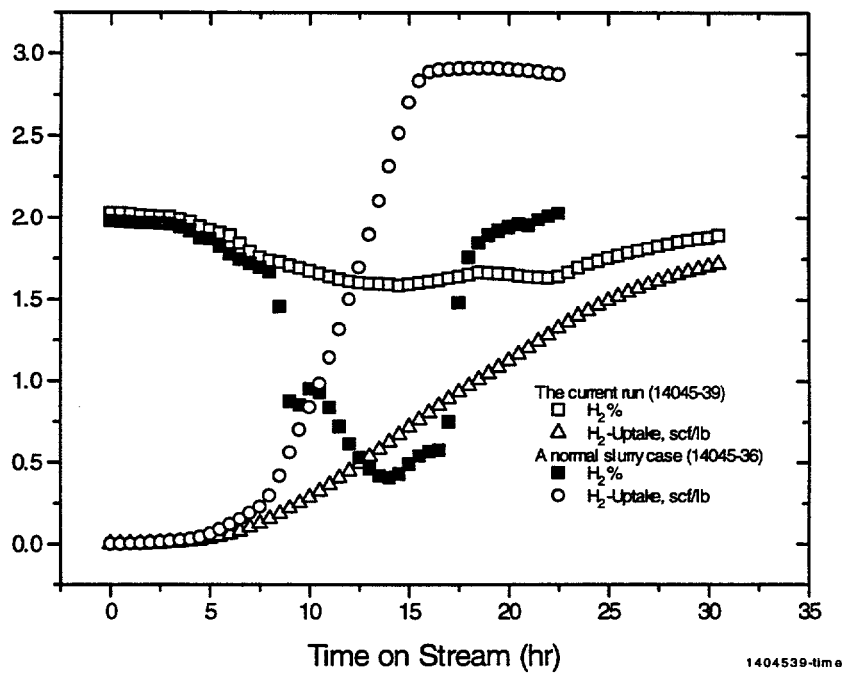**Figure 3.1.8. Profiles of Catalyst Reduction**

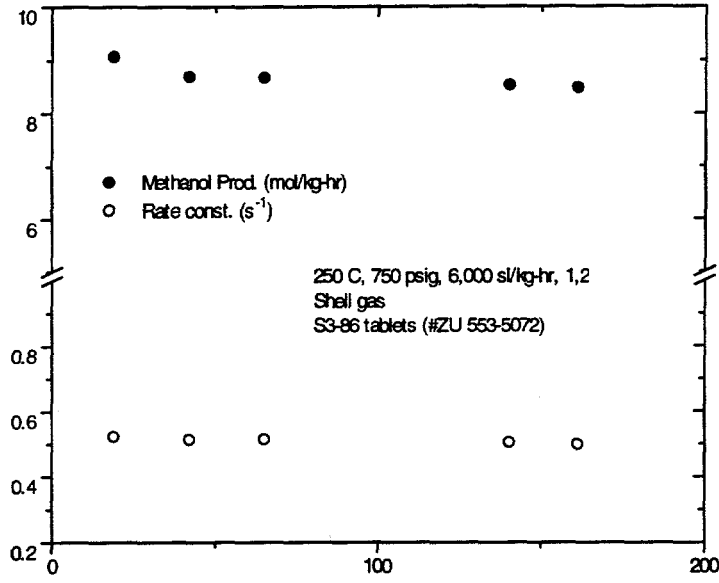**Figure 3.1.9. Shakedown Run of the 300 cc Autoclave with Robinson-Mahoney Basket Internals**

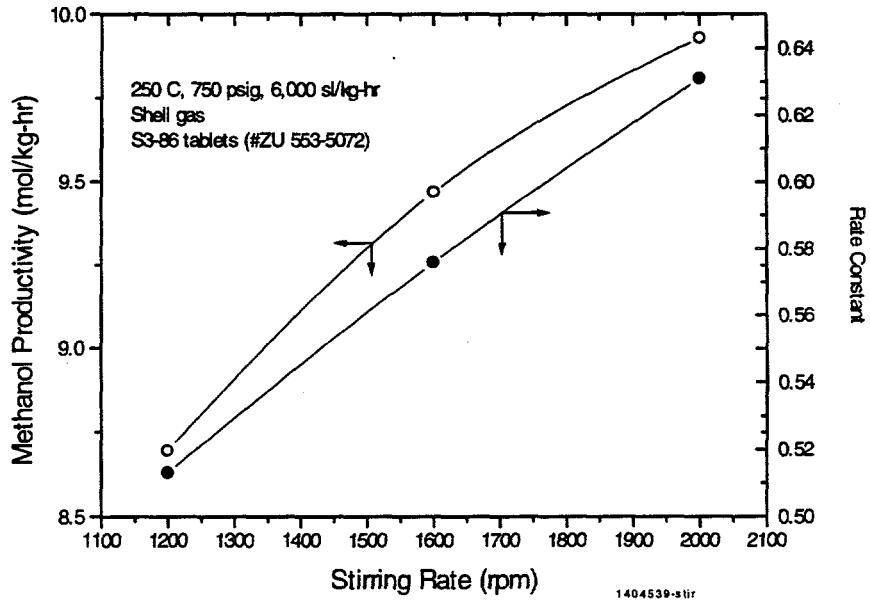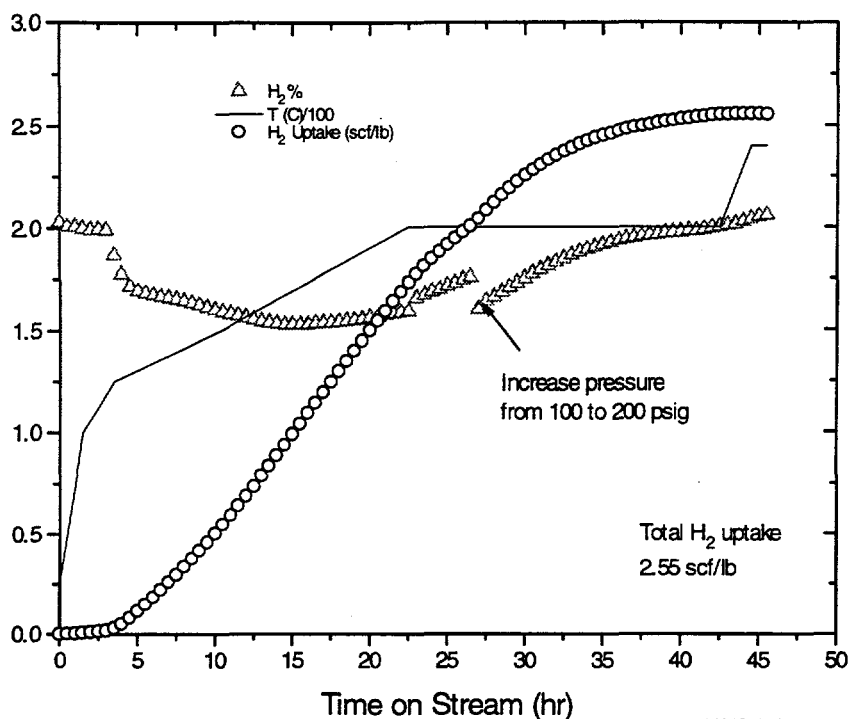**Figure 3.1.10. Activity as a Function of Stirring Speed**

Figure 3.1.11.   Reduction Profiles of the Robinson-Mahoney Run (10454-43)

LPDME Run

The first part of the LPDME run was carried out at 250°C, 750 psig and 5000 GHSV using Shell gas. The stirring rate was higher than that used in slurry phase runs (1,600 vs. 1,200 rpm) to enhance mass transfer. As shown in Figure 3.1.12, the productivity of the system (10.5 mol/kg-hr) was only one third of the initial productivity (30 mol/kg-hr) of a mixture of S3-86 and Catapal alumina powders, indicating that the reaction was mass transfer limited. However, if the catalyst system deactivated, the reaction rate would eventually be comparable to the mass transfer rate, and from then on catalyst deactivation would be observable. The run was allowed to proceed for 350 hr more than needed for the reaction rate to slow down below the mass transfer rate, but no deactivation was observed. The stirring rate was then increased to 2,000 rpm to boost mass transfer rate, and space velocity was decreased from 6,000 to 1,500 sl/kg-hr to decrease the reaction rate, giving a better chance to observe catalyst deactivation. However, still little deactivation was detected up to 500 hr on stream.

Figure 3.1.12. LPDME Run Using Robinson-Mahoney Basket Internals (14045-43)
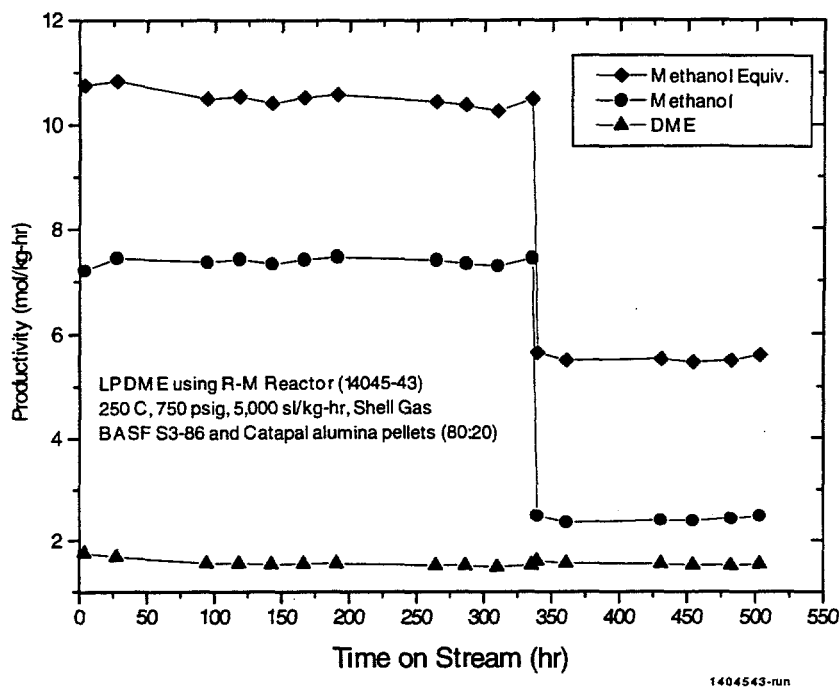
The run was stopped at this point. Part of the spent catalyst pellet mixture was preserved for analysis, and part was ground into powder in a nitrogen box and charged back in the autoclave reactor to check its activity. The reactor was operated in the slurry phase mode and free of mass transfer limitations. The powder mixture underwent the standard reduction. The minimal H_2 uptake, 0.17 scf/lb, occurred mainly between 100 and 130°C. The activity was checked under the standard conditions, and the results (14045-52) are summarized in Table 3.1.3.

Also listed in Table 3.1.3 for comparison are the activity data from two other experiments. The first one, 14045-58, was conducted using the powders prepared by crushing the *fresh* S3-86 and Catapal B pellets from the same batches used for the Robinson-Mahoney run. This measured the initial activity of the catalyst system used for the Robinson Mahoney run. The second experiment (11782-3) was a standard LPDME life run using genuine powder samples.   As shown in Table 3.1.3, the S3-86 powder prepared from the fresh S3-86 pellets had the same activity as the genuine S3-86 powder. The dehydration activity of the Catapal B powder prepared from the fresh pellets was only slightly lower (11%) than that of the genuine Catapal B powder.

Table 3.1.3. The Activity of the Catalysts used in the LPDME Run using Robinson-Mahoney Basket Internals. Reaction conditions: 250°C, 750 psig, 6,000 sl/kg-hr, Shell Gas

Run	Catalyst	Time on Stream, hr	MEOH Equiv. Prod. (mol/kg-hr)	Concentration (%) MEOH	DME	Rate Constant k_m[b]	k_d[c]
14045-52	powders from spent pellets	508	27.1	1.53	5.96	2.7	10.2
14045-58	powders from fresh pellets	20.5	30.6	0.78	7.06	2.9	15.1
11782-03	genuine powders	20	30.7	1.01	6.95	3.0	17.0
"	"	499	14.0	0.49	2.67	0.9	5.9

a: Methanol synthesis rate constant calculated from $R_m = k_m k_{co_2} f_{H_2}^{2/3} f_{CO}^{1/3} (1-appr.)$, based on methanol catalyst weight.

b: Methanol dehydration rate constant calculated from $R_d = k_d f_{CO_2}^{-0.33} f_{MEOH}^{0.11} f_{CO}^{0.70} (1-appr.)$, based on alumina weight.

The results in Table 3.1.3 indicate that 500 hours in the Robinson-Mahoney run did not cause a significant change in the methanol catalyst activity (a 7% drop). For a similar period in the normal LPDME life run in a slurry phase reactor (11782-3), a much greater drop in activity was observed (70%). In fact, the activity of the methanol catalyst pellets dropped at a rate of only 0.013% hr^{-1} in the Robinson-Mahoney run. This rate is even smaller than the S3-86 powder under LPMEOH conditions in a 300 cc autoclave (0.045% hr^{-1}).

However, deactivation in the dehydration catalyst was observed in the Robinson-Mahoney run. The Catapal B pellets lost 32% of their activity upon 508 hours on stream. From this single experiment, there is no way to tell if this deactivation occurred only in the early period of the run or throughout the run. Note that in the normal LPDME life run (11782-3), the dehydration activity dropped by 65% in a similar period.

This experiment shows two important phenomena:

1) Point contact between methanol catalyst and alumina *pellets* does not cause deactivation of the methanol catalyst.
2) The fluid phase (mineral oil) neither causes nor transports anything that causes deactivation.

This suggests that certain physical features in a slurry phase operation, such as attrition which leads to the formation of methanol catalyst and alumina fines and good mixing between two catalyst powders, may be the cause or a necessary step for methanol catalyst to deactivate. For instance, these features may provide large contact area and long contact time, which are needed to foul the methanol catalyst or to go through solid phase reactions between methanol catalyst and alumina.

In contrast, the physical features associated with a slurry phase operation are not necessary for the alumina catalyst to deactivate. If one assumes that this deactivation is caused by migration of

Cu- and/or Zn-containing species from the methanol catalyst to the alumina, then this migration is conducted either by surface diffusion through the point-contact between the pellets of the two catalysts or mass transfer through the fluid medium, or both. More severe deactivation in dehydration activity occurred in the powder case for a similar period (Table 3.1.3), indicating that either this process can be accelerated by good mixing in a slurry phase operation, or there exists an additional mechanism for alumina deactivation, e.g., a process in concert with the deactivation of the methanol catalyst. In addition to this migration hypothesis, coking could be the cause of alumina deactivation. Elemental and coke analysis of the spent alumina sample will be conducted to resolve this issue.

3.2 New Fuels from Dimethyl Ether (DME)

Overall 2QFY95 Objectives

The following set of objectives appeared in Section III of Quarterly Technical Progress Report No. 1 (Oct 94 - Dec 94).

(i) Continue to develop the concept of methanol to isobutanol over compositions of Ag, Cs/SrO with the goal of increasing oxygenate selectivity.

(ii) Prepare DME carbonylation catalyst candidates for immobilization on supports.

(iii) Initiate catalyst development work on the cracking of ethylidene diacetate to vinyl acetate and acetic acid.

(i) Chemistry and Catalyst Development

Methanol to Isobutanol
The Ag/K/SrO catalyst was retested to check reactor performance. The catalyst deactivated quickly, as in the sample tested and reported in the last quarterly. Carbon balances from the on-line GC averaged 84%. By method of preparation, the Ag and K wt % values were 6.6 and 8.2, respectively.

The Ag/Cs mol ratio was then varied as shown in Table 3.2.1. The weight % of Ag and the weight % of Cs are represented by x and y, respectively. Catalyst #1 was reported in the last quarterly and produced a mol % selectivity to C_2-C_4 oxygenates of ~23-17. Catalyst #2 was stopped after ~45 hours of testing, and the oxygenate selectivity was ~15-12 mol %. Oxygenate selectivity was lower than that for Catalyst #1, but the activity was constant. Catalyst #3 was stopped after 70 hours of testing because the oxygenate selectivity dropped from 12-5 mol %. The data suggest that when the mol ratio of Ag/Cs is ~1, or possibly less than 1, the catalyst is more selective for C_2-C_4 oxygenate and has a reasonable lifetime.

The best catalyst, catalyst #1, was prepared again to determine reproducibility of the catalyst preparation procedure. The conversion - selectivity profile is shown in Figure 3.2.1. The near constant selectivity is similar to that reported before. The only difference is the volume of

catalyst charged. At 2 ml of catalyst charged, the methanol conversion nearly doubled while the oxygenate selectivity remained nearly the same.

The Ag/Cs ratio of 0.5 on SrO, catalyst 4, was prepared and tested. The mol % selectivity to useful oxygenates was 12-15% conversion. Carbon mass balances were in the 91-109 % range. To date the best Ag/Cs ratio is ~ 1.

Table 3.2.1 x%Ag; y%Cs on SrO

| Cat.	x	y	x/y	mol % useful oxygenates*	hrs. on-stream
1	5.8	7.3	1.0	23-17	200
2	7.0	4.4	2.0	15-12	45
3	10.9	4.1	3.0	12-5	70
4	3.4	8.4	0.5	15-12	80

*Ethanol + Propionaldehyde + Isobutyraldehyde + n-Propanol + Isobutanol

Figure 3.2.1. Methanol Conversion and Ethanol + Propionaldehyde + Isobutyraldehyde + n-Butanol + Isobutanol Selectivity vs Time on Stream


Ag/Cs/SrO (from Acetate)
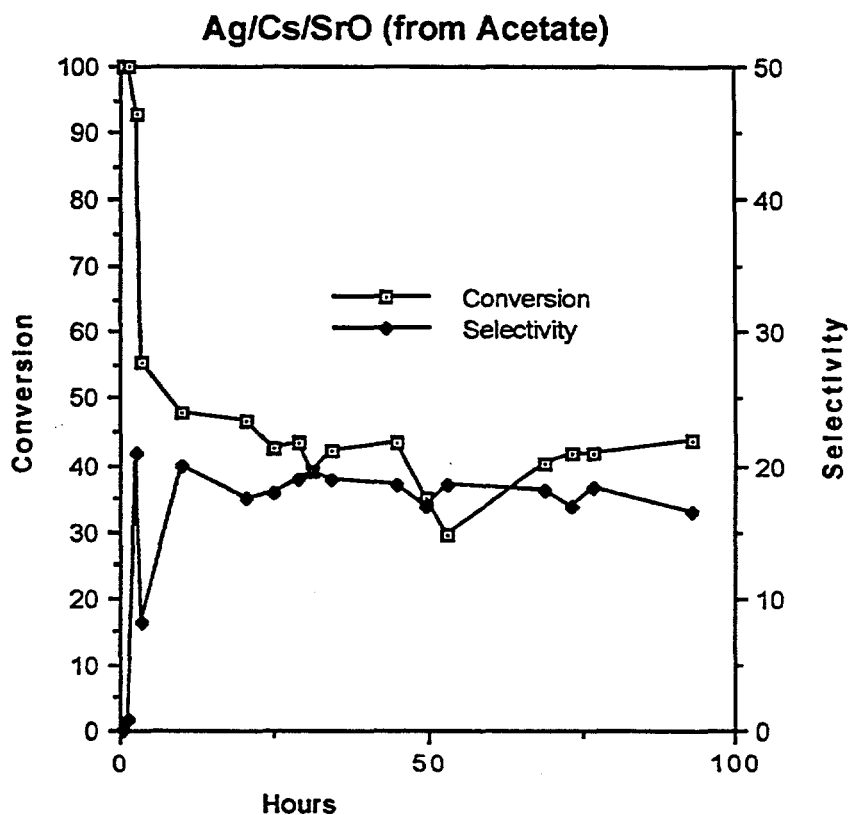
The Ag and Cs were supported on MgO with a mol ratio of 1. The wt% Ag and Cs were 5.8 and 7.3, respectively, based on method of preparation. The conversion and selectivity plot is provided in Figure 3.2.2. The mol % to useful oxygenates was 5%. Since the methanol conversion was decreasing, the run was terminated. Carbon mass balances were in the 83-87% range.

Figure 3.2.2. Methanol Conversion and Ethanol + Propionaldehyde + Isobutyraldehyde + n-Butanol + Isobutanol Selectivity vs Time on Stream


Ag/Cs/MgO (from Acetate)
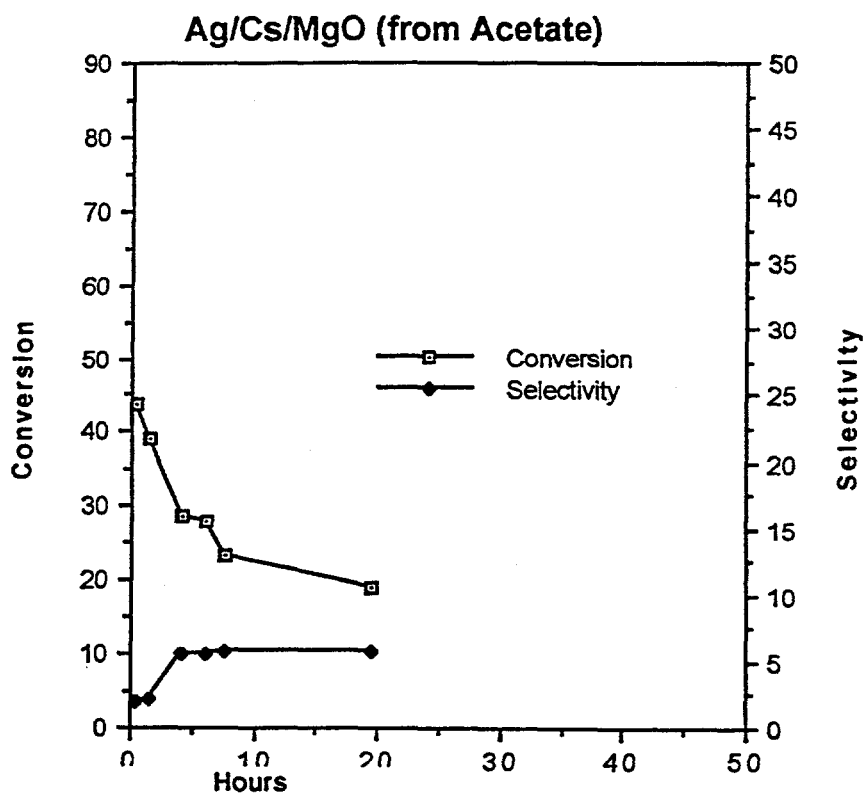
Similar results were obtained by supporting Ag and Cs on CaO when the ratio of Ag/Cs was 1. Figure 3.2.3 illustrates the steady decline in methanol conversion and oxygenate selectivity. Carbon mass balances were in the 70-91% range.

Figure 3.2.3 Methanol Conversion and Ethanol + Propionaldehyde + Isobutyraldehyde + n-Butanol + Isobutanol Selectivity vs Time on Stream
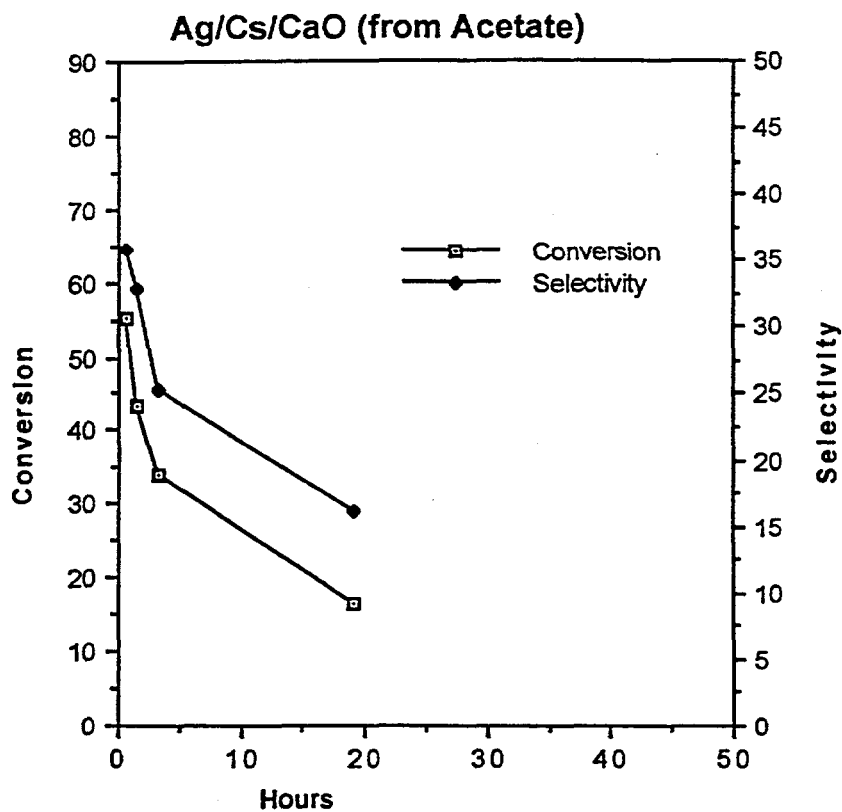
However, with a change of the Ag/Cs ratio to 0.5, the oxygenate selectivity increased with time (Figure 3.2.4). This catalyst will be re-tested. The carbon mass balances were in the 85-90% range.

Figure 3.2.4. Methanol Conversion and Ethanol + Propionaldehyde + Isobutyraldehyde + n-Butanol + Isobutanol Selectivity vs Time on Stream
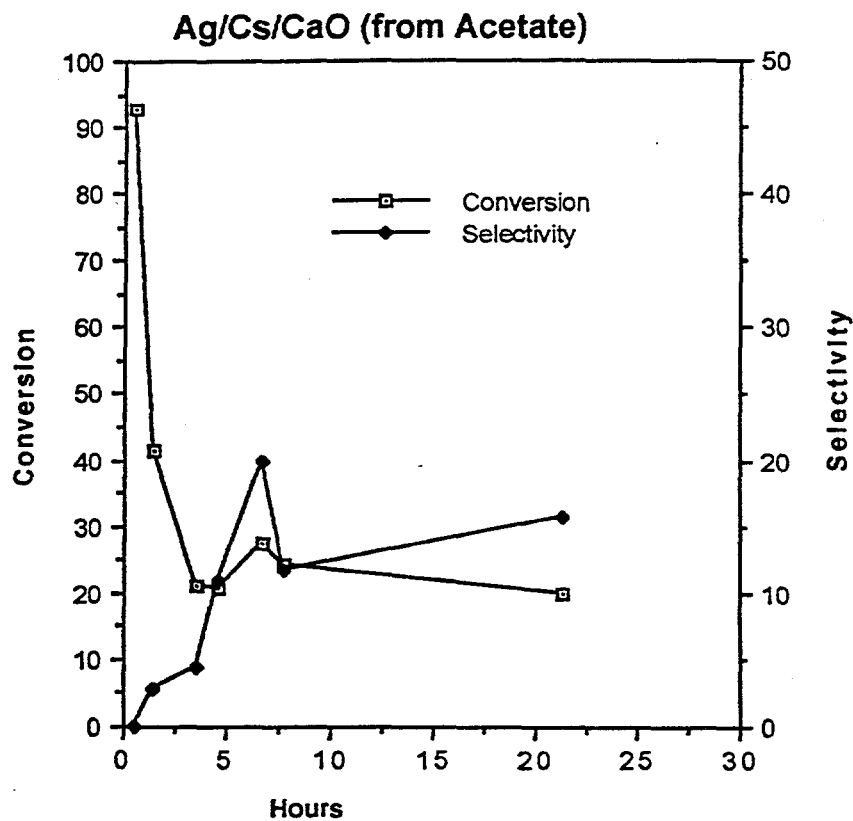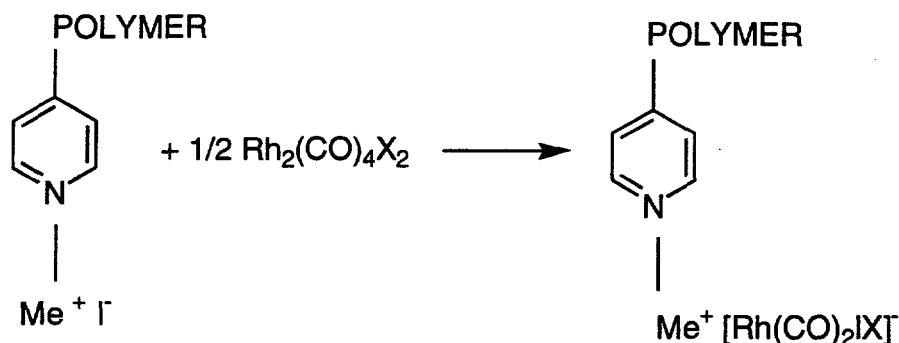
Ag and Cs are currently impregnated onto the SrO together from the same solution as the acetate salts. One synthetic variation is to impregnate the SrO first with Cs, followed by calcination treatment, and then to impregnate with Ag. This yields a catalyst that performs like the regular preparation procedure. Carbon mass balances were $90^+\%$.

(ii) DME to Ethylene Diacetate (EDA)

Literature Review

In early January, a literature search was conducted on heterogeneous carbonylation catalysts, and based on this search, a plan was generated for our goal of converting DME to EDA.

One approach is to prepare a rhodium complex supported on an anion exchange resin in order to generate the catalytically active $[Rh(CO)_2I_2]^-$ for carbonylation. The three important patents in this area are those of Drago et al. (US 4328125), Marston et al. (US 5155261), and Minami et al. (US 5364963). All of these patents deal with heterogeneous catalysts for the conversion of methanol to acetic acid. For example, Drago et al. have taught a way to prepare a rhodium catalyst supported on a polystyrene vinylpyridine copolymer via the scheme shown below.

POLYMER $\quad\quad\quad\quad\quad\quad\quad\quad\quad$ POLYMER

$$+ \; 1/2 \; Rh_2(CO)_4X_2 \longrightarrow$$

Me $^+$ I$^-$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ Me$^+$ $[Rh(CO)_2IX]^-$

This method involves first refluxing the polymer with methyl iodide, followed by a reaction with the rhodium carbonyl. The same catalyst could also be prepared in the reactor by using $RhCl_3 \cdot XH_2O$ with commercially available resins such as Amberlite IRA-400 or Dowex 1-X8 resins.

Luft et al. (Chem.-Ing. Tech., Vol. 59, 1987, pp. 485-486) have prepared cationic phosphine complexes of rhodium such as $[Rh(dpe)_2]^+BF_4^-$, dpe=diphenylphosphinoethane, which they have supported on alumina, silica and activated charcoal. These have been used for the gas phase carbonylation of methyl acetate to acetic anhydride using a feed of CO/methyl acetate/methyl iodide at a pressure of 11 bar, 185°C. The same catalyst was also observed to convert DME to acetic anhydride in the gas phase, though the conversion was much slower (lower by a factor of 4).

The most important patents for the preparation of EDA from methyl acetate by using a heterogeneous Rh catalyst are those of Park et al. (US 5371274, US 5371275). The first patent uses the catalyst $RhClCO(PPh_3)_2$ supported on a carrier like alumina, keiselguhr, or silica, together with an accelerator such as triphenylphosphine. The reactants are methyl acetate,