in the formation of low alkanes, therefore poor DME selectivity, and potentially, coke formation). The test was started at 250°C, the normal reaction temperature for LPDME. Figure 3.1.8 shows that at this temperature the chabazite is not an active dehydration catalyst, yielding, initially, 1% DME in the effluent compared to 6.8% when the Catapal B alumina is used (run 13467-11). Furthermore, this dehydration activity dropped by a factor of 5 in the next 15 hours, accompanied by an increase in the methanol effluent concentration. However, after 20 hours on stream, both the methanol synthesis and dehydration activity of the system became rather stable. The DME concentration in the effluent was about 0.17%, an order of magnitude higher than when the dehydration catalyst was not present. More oxygenates and low alkanes were detected, amounting to 0.3% in the effluent compared to 0.02% when alumina was used.

Next, we increased the reaction temperature to 270°C, the level at which the chabazite is normally used as a methyl amine synthesis catalyst. The DME production was doubled at 270°C, accompanied by a decrease in methanol concentration. The methanol equivalent productivity was lower than that at 250°C. Apparently, the increase in the dehydration activity was not enough to compensate for the increase in the equilibrium approach of the methanol synthesis reaction (from 38% at 250°C to 61% at 270°C), which slows down the reaction. Again, the noteworthy observation from this run was the stability of the catalyst system even at 270°C.

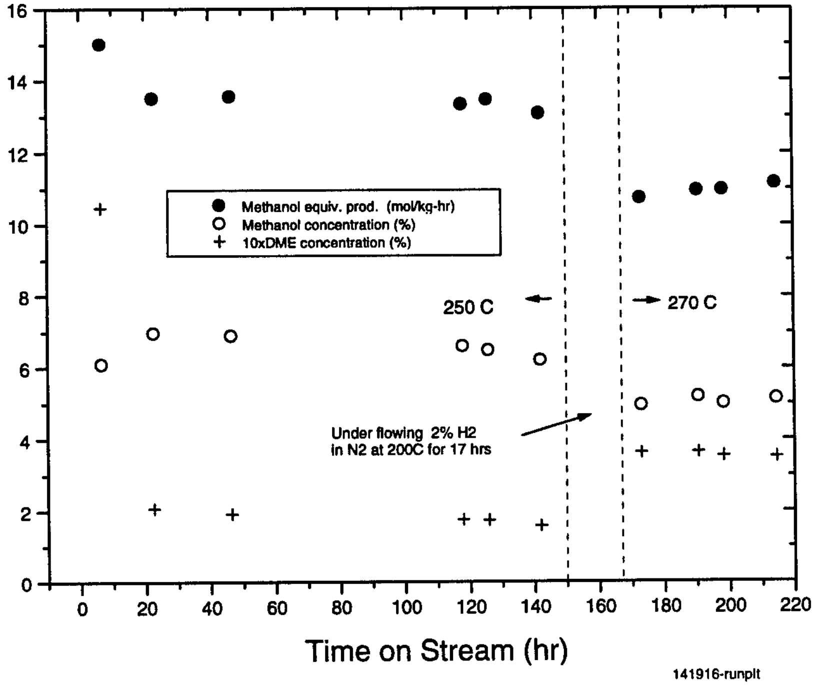


Figure 3.1.8 - Catalyst Screening Run 14191-6
BASF S3-86 plus APCI Chabazite
Dehydration Catalyst (83.3:16.7)
750 psig, 5,000 sl/kg-hr, Shell gGas

Figure 3.1.9 - The Stability of Different Catalyst Systems

250°C, 750 psig, 5,000-6,000 sl/kg-hr, Shell gas

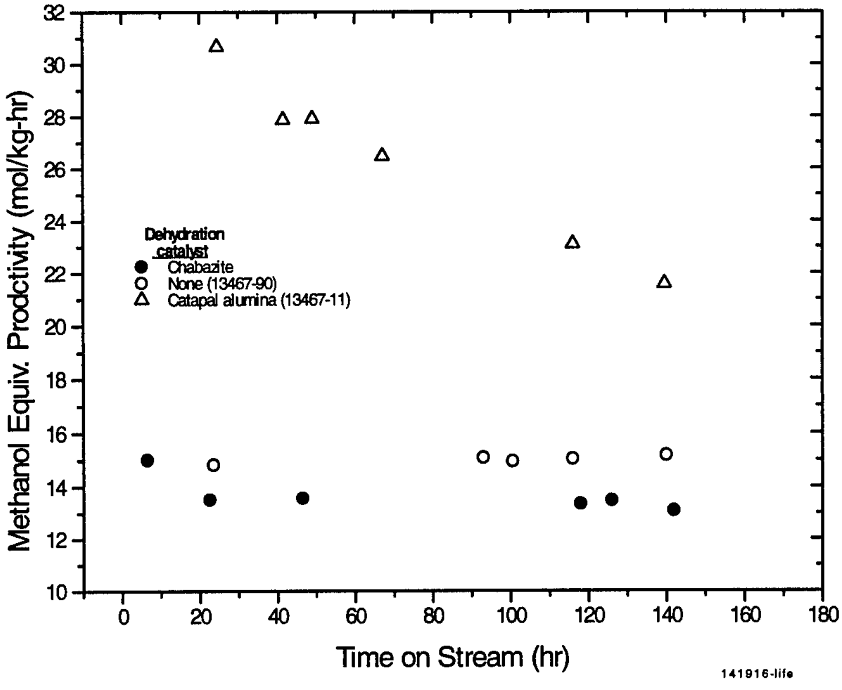


Figure 3.1.9 compares the stability of different catalyst systems at 250°C in terms of methanol equivalent productivity. It can be seen that the stability of the chabazite system is comparable to that of pure S3-86, and much better than that of the Catapal B alumina system.

Mg-Y

The second zeolitic material we tested, along with S3-86, is a magnesium ion-exchanged zeolite Y (14191-17). The reaction was conducted at 250°C, 750 psig, 6,000 sl/kg-hr in space velocity, using Shell gas. The dehydration activity of the catalyst upon 22 hour under syngas was very low, resulting in a methanol equivalent productivity of 15.3 mol/kg-hr compared to 30 when Catapal B alumina was used under similar conditions. No life test was conducted for this catalyst.

A noteworthy observation from the two runs using zeolitic materials was the very fast deactivation of dehydration catalysts at the beginning of the runs. From 6 to 22 hr under a syngas stream, the DME concentration decreased by a factor of 5 for chabazite, and 2.3 for Mg-Y. The activity in these two runs within 6 hr on stream was not monitored with GC. However, the exit gas flowrate measurement (the higher the activity, the smaller the exit gas flow) in the run using Mg-Y suggests that, within an hour under syngas, the catalyst had a dehydration activity comparable to the Catapal B alumina. In other words, Mg-Y lost 90% of its dehydration activity in the first 6 hr under syngas. It appears that both zeolite samples were much more vulnerable under LPDME conditions than the Catapal B alumina. However, in both cases, the methanol catalyst did not seem to deteriorate along with the zeolite catalysts. The stability of the

S3-86/chabazite system shown in Figures 3.1.8 and 3.1.9 corresponds to a chabazite that has lost most of its dehydration activity.

TiO_2

A commercial TiO_2 powder (anatase) from Aldrich was tested. Although it is reported in the literature that TiO_2 is a dehydration catalyst, little dehydration activity was detected in our LPDME run (14191-21) using the TiO_2 sample. A later BET measurement shows that this sample has a surface area of only 9 m^2/g.

3.1.4 Literature Review on One Step Syngas-to-DME Synthesis

A literature search on DME synthesis covering the work from 1967 to 1990 was conducted when the LPDME project was begun in the early 90's. A more recent search of Chemical Abstracts and Derwent from 1990 to the present was conducted on one step DME synthesis from syngas. Except for a novel catalyst by Eastman Kodak, the development of both catalyst and process in recent years still follows the same path, i.e., the catalyst system is some form of mixture of methanol and dehydration catalysts, and the process utilizies either a packed bed or a slurry phase reactor. However, a richer data base is now available from the new publications, providing a broader range of catalysts we can examine, many other methods we can apply to alter DME catalysts, and more information on issues of interest such as catalyst stability.

Catalysts

A 1993 patent by Eastman Kodak [G. Irick, Jr., P. N. Mercer and K. E. Simmons, US Patent 5,254,596, 19 October, 1993] discloses a novel catalyst for one step DME synthesis from syngas. The catalyst consists of "chemically mixed" titanium-zinc oxide, $Zn_xTi_yO_z$, with x ranging from 0.025 to 0.58 and z from 2.03 to 2.58 at y equal to 1. Note that this catalyst contains neither common components in traditional methanol synthesis catalysts such as Cu, Cr, Al and Pd, nor a typical acidic solid for dehydration. The test reaction was run in a packed bed reactor. Methanol was the primary product when the temperature was below 300°C, but DME selectivity increased to 60% at 325°C. The methanol equivalent productivity of the catalyst was comparable to the Air Products LPDME process when the reaction temperature was above 300°C.

Two patents by Mitsubishi Heavy Ind. Co., LTD, Japan, demonstrate how the activity and stability of a catalyst depend on the details of catalyst preparation. In a 1991 patent [Japanese patent 3,008,446, 19 January 1991], two methanol catalysts were prepared by co-precipitation of Cu, Zn, Cr, and Al nitrates. The resulting methanol catalysts of 150-250 mm were then mixed with g-alumina of the same size, and pressed into 600-1000 mm pellets. The activity and stability of the two catalysts were tested in a 2 cc fixed bed reactor, and the results are shown below. Among the differences between catalysts A and B, although both had the same elemental composition, was the order in which one nitrate was added into another during methanol catalyst preparation. No DME selectivity data were reported in the patent.

Catalyst	Initial CO %conversion	CO %conversion after 100 hr
A	61	54
B	39	21

Reaction conditions: 250°C, 50 ATM, GHSV = 8,000 hr^{-1}, H_2:CO = 2:1..

The second Mitsubishi patent [Japanese Patent 2,280,836, 16 November 1990] shows that DME catalysts of supported form have better activity and stability than a physical mixture of methanol and dehydration catalysts. Catalysts of supported form were prepared by depositing Cu, Zn, and Al on the surface of various metal oxides. The metal oxides served as both catalyst support and dehydration catalyst. The following example illustrates the difference between a catalyst in the supported form and a catalyst mixture:

Catalyst	Initial CO %conversion	CO % conv. after 1,000 hr
CuO-ZnO-Al_2O_3/Al_2O_3 (100:75:25/65), supported	65	61
CuO-ZnO-Al_2O_3 + Al_2O_3 (100:75:25/65), mixture	53	18

Reaction conditions: 250°C, 50 atm, 4,000 1/hr, H2:CO = 2.

A noteworthy point in the patent is the wide range of metal oxides that were employed as the support and dehydration component for the supported form catalysts. These included Al_2O_3, TiO_2, Fe_2O_3, SnO_3, and ZrO_2, and all exhibited similar activity.

Stable catalysts systems were observed in these two Mitsubishi patents. In a better Air Products LPDME run using Texaco gas, CO conversion dropped by 45% upon 500 hr on stream. In contrast, catalyst A in the first patent exhibited only an 11% decrease in CO conversion upon 1,000 hr on stream, while the catalyst of supported form in the second patent dropped only 6% upon 1,000 hr on stream. Stable bifunctional catalyst systems under gas phase reaction conditions were also reported by Topsoe [J. B. Hansen, and F. Joensen, in "Natural Gas Conversion Symposium Proceedings" (Ed. A. Holman) 1991, p 457]. An aging test showed only a modest activity loss during a 1,800 hr test period. No detail catalyst information and test data of aging test were presented.

A patent by Snamprogetti [G. Manara, B. Notari and V. Fattore, US Patent 4,177,167, 4 December 1979] shows how the stability of a catalyst system depends on the dehydration catalyst. When a methanol catalyst is used with a g-alumina, the system shows fast deactivation (61% decrease in CO conversion after 310 hrs at 300°C). When the methanol catalyst is mixed with a g-alumina that has been modified by silicon compounds, the system exhibits good DME productivity and exceptionally good stability at 280 - 330°C (virtually no decrease in CO conversion after 500 hours on stream in certain cases).

When a catalyst mixture is used, the intimate contact between the methanol synthesis component and dehydration component appears to play a role in the catalyst activity. NKK Corporation, Japan, issued a patent in 1994 [K. Fujimoto, T. Shikada, Y. Yamaoka, and T. Sumigama, European Patent 591,538, 13 April 1994] on the LPDME process and catalyst. Two types of catalysts were disclosed The first type involved a procedure for the preparation of a powder mixture of methanol and dehydration catalysts. First, a commercial methanol catalyst (BASF S3-85 or ICI 51-2) and g-alumina were co-pulverized into 20 mm in a ball mill, and then the powder was compressed at 300 kg/cm^2 for about 24 hr to adhere. The pressed pellets were pulverized again to < 120 mm. The final powder was used as a DME catalyst in a slurry phase autoclave reactor. The procedure of co-pulverization-compression-re-pulverization is aimed at bringing two catalysts together, therefore shortening the mass transfer distance in the sequential reactions of methanol synthesis and methanol dehydration. Comparative examples are given below:

Catalyst	CO % conversion	DME % yield
Co-pulverized, compressed, re-pulverized	41.5	30.3
Co-pulverized without compression	33.3	23.1

Reaction conditions: 280°C, 30 atm, H_2:CO = 1:1, 6,000 sl/kg-hr, 100 cc autoclave with 30 g of n-hexadecane, methanol catalyst:alumina = 2:1 by weight.

The second type of catalyst was made by co-pulverizing (no compression) a commercial methanol catalyst and CuO doped g-alumina. A very interesting observation is that methanol catalyst plus CuO-doped alumina has higher activity than methanol catalyst plus pure alumina.

Catalyst	CO % conversion	DME % yield
Methanol catalyst + CuO/g-alumina	51.0	34.4
Methanol catalyst + g-alumina	37.8	30.7

The same reaction conditions as shown above.

A study at the Institute of Coal Chemistry (ICC), China, also examined the role of intimate contact between methanol synthesis and dehydration catalysts in DME production [J. L. Tao, Y. Q. Liu and Z. H. Chen, Tianranqi Huagong 16 (1991) 17]. One catalyst tested in a 1 cc packed bed reactor was a mixture of methanol catalyst and g-alumina powders of 400-800 mm (*mixture*). The other catalyst was prepared by mixing methanol catalyst and g-alumina powders of <150 mm, followed by pressing and sieving them into 400-800 mm pellets (*pellet*). The results demonstrated that the pellet exhibited a slightly lower CO conversion, but much higher DME selectivity than the mixture, indicative of the benefit of good interaction between two catalysts.

Different dehydration catalysts were examined in a study by Sofianos and Scurrell [A. C. Sofianos and M. S. Scurrel, Ind. Eng. Chem. Res. 30 (1991) 2372)], including g-alumina, silica alumina, Y zeolite, mordenite, and ZSM-5. DME catalysts were prepared by intimate mixing of finely milled methanol catalyst and dehydration catalyst, followed by molding the powder mixture under pressure into 300-500 mm. Catalyst performance was tested in a packed bed reactor using a H_2/CO (2:1) gas mixture. As shown in the table below, of all the dehydration catalysts, g-alumina was found to be the best. Silica-alumina, with its known strong acidity, did not show significant higher activity than g-alumina when the temperature was above 250°C, yet produced twice as much CO_2 as g-alumina. Zeolitic materials exhibited CO conversion comparable to g-alumina at 275°C, but poorer DME selectivity due to higher conversion to CO_2 and low alkanes (C_1-C_4). Mordenite reportedly exhibited very poor stability.

Dehydration component	CO %conversion		
	Total	To DME	To CO_2
g-alumina	41.0	25.8	13.2
silica-alumina	47.3	17.9	27.8
H-ZSM5	28.3	17.1	9.6
H-Y zeolite	37.5	16.4	17.6
ZM 760 mordenite	32.3	11.9	16.9

Reaction conditions: 275°C, 40 atm, H_2:CO = 2:1, GHSV = 16,000 1/hr.

The same study also demonstrates that the catalyst system consisting of methanol catalyst and g-alumina deactivates rapidly. At 275°C, CO conversion drops by 38% after 120 hr on stream. Catalyst activity, however, can be restored momentarily by treating the deactivated catalyst at the same temperature with air for 2 hr.

A 1991 German patent [K. Decker, H. J. Bisinger, L. Ebner, H. Mere, G. Ohlmann, A. Seidel, K. D. Vollgraf, H. Zarmer (Akad Wissenschaffen DDR), German Patent 291,937, 18 July 1991] also examined ZSM-5 as a dehydration component in pelletized DME catalyst made of methanol and dehydration catalyst powders (a binder was used). However, in a different temperature range, a different result was obtained. As shown in the table below, ZSM-5 yielded higher DME productivity than g-alumina at 210 and 230°C.

Dehydration component	CO conversion (%)		DME productivity (g/lt-hr)	
	210°C	230°C	210°C	230°C
ZSM-5	28.4	56.6	70.2	116.9
g-alumina	37.8	56.7	57.3	97.9

Reaction conditions: 50 atm, 1,930 lt/lt-hr, H_2:CO = 85:15.

ZSM-5 with Si/Al ratio ranging from 12 to 98 were tested, showing no significant difference. No data above 230°C were reported.

Performance

Table 3.1.4 summarizes the typical performance of DME synthesis reported in the above literature, in terms of CO conversion and/or methanol equivalent productivity. Also included are typical Air Products LPDME results using different types of syngas. Deactivation factor is ignored in the table, and initial activity is used whenever possible. That is, the data in the table represent the best performance of each catalyst/process. It is impossible to make a legitimate or true comparison of these catalysts/processes verses Air Products' process, since different reaction conditions (e.g., T, P, SV, catalyst ratio, feed gas composition) are used. However, in spite of the wide range of reaction conditions, the methanol equivalent productivity from most of the runs falls between 20 and 40 mole/kg-hr. The productivity in the German case is much lower than the others. However, the reaction temperature and space velocity are also very low in that study. In brief, it appears that none of the catalysts/processes is outperforming the others by an overwhelming advantage.

Table 3.1.4 - Comparison of Different Catalysts and Processes for One Step Syngas-to-DME Synthesis

Developer	Catalyst	Process	Gas H_2:CO:CO_2	Temp (C)	Press. (atm)	SV (sl/kg-h)	CO conv. (%)	MEOH prod. (mol/kg-h)	DME prod. (mol/kg-h)	Methanol equiv. prod. (mol/kg-hr)
Eastman	$Zn_xTi_yO_z$	pkd bed	67:33:0	250	70	12,000	1	1.6	0.04	1.7
Eastman	$Zn_xTi_yO_z$	pkd bed	75:25:0	300	83	12,000	13	13.4	2.2	17.8
Eastman	$Zn_xTi_yO_z$	pkd bed	67:33:0	325	70	12,000	73	25	25.9	50.9
Mitsubishi	CuO-ZnO-Al_2O_3/g-Al_2O_3 pressed mixture	pkd bed	67:33:0	250	50	8,000	61	n.a.	n.a.	n.a.
Mitsubishi	CuO-ZnO-Al_2O_3/g-Al_2O_3 supported	pkd bed	67:33:0	250	50	8,000	65	n.a.	n.a.	n.a.
NKK Co.	methanol catalyst/g-Al_2O_3 co-pulverized, compressed re-pulverized	slurry	50:50:0	280	30	6,000	41.5	1.2	8.4	18.0
NKK Co.	methanol catalyst/CuO/ g-Al_2O_3, co-pulverized	slurry	50:50:0	280	30	6,000	51.9	1.7	12.0	25.7
ICC	methanol catalyst/g-Al_2O_3	pkd bed	67:33:0	250	20	6,150	28.3	0	10.0	20.0
ICC	methanol catalyst/g-Al_2O_3	pkd bed	67:33:0	260	20	6,150	38.6	1.1	13.0	27.1
ICC	methanol catalyst/g-Al_2O_3	pkd bed	67:33:0	275	20	6,150	45.8	0.4	16.0	32.4
Sofianos	methanol catalyst/g-Al_2O_3	pkd bed	67:33:0	275	40	16,000	41.0	4.8	30.4	65.2
Sofianos	methanol catalyst/H-ZSM5	pkd bed	67:33:0	275	40	16,000	28.3	0	21.0	21.0
Sofianos	methanol catalyst/g-Al_2O_3	pkd bed	1:1:0	250	40	6,670	34			35
German	methanol catalyst/ZSM-5	pkd bed	85:15:0	210	50	2,000	28.4	0.5	1.5	3.5
German	methanol catalyst/ZSM-5	pkd bed	85:15:0	230	50	2,000	56.6	0.7	2.5	5.7
APCI	BASF S3-86/Catapal alumina	slurry	35:51:13 (Texaco)	250	52	6,000	34.3	7.6	11.5	30.6
APCI	BASF S3-86/Catapal alumina	slurry	30:66:3 (Shell)	250	52	6,000	23.4	2.1	13.4	28.5
APCI	BASF S3-86/Catapal alumina	slurry	70:24:6 (H_2-rich)	250	52	3,600	70	10	6	22

3.2 New Fuels from Dimethyl Ether (DME)

3.2.1 Overall 1QFY95 Objectives

The following set of objectives appeared in Section III of Quarterly Technical Progress Report No. 16 written under Contract No. DE-AC22-91PC90018.

- Continue to develop the concept of methanol to isobutanol over compositions of Ag on SrO with the goal of increasing oxygenate selectivity and extending catalyst lifetime.
- Initiate catalyst development work on the cracking of ethylidene diacetate to vinyl acetate and acetic acid.
- Initiate the design and construction of small-scale continuous reactor to study DME to ethylidene diacetate conversion.

3.2.2 Chemistry and Catalyst Development

Methanol to Isobutanol

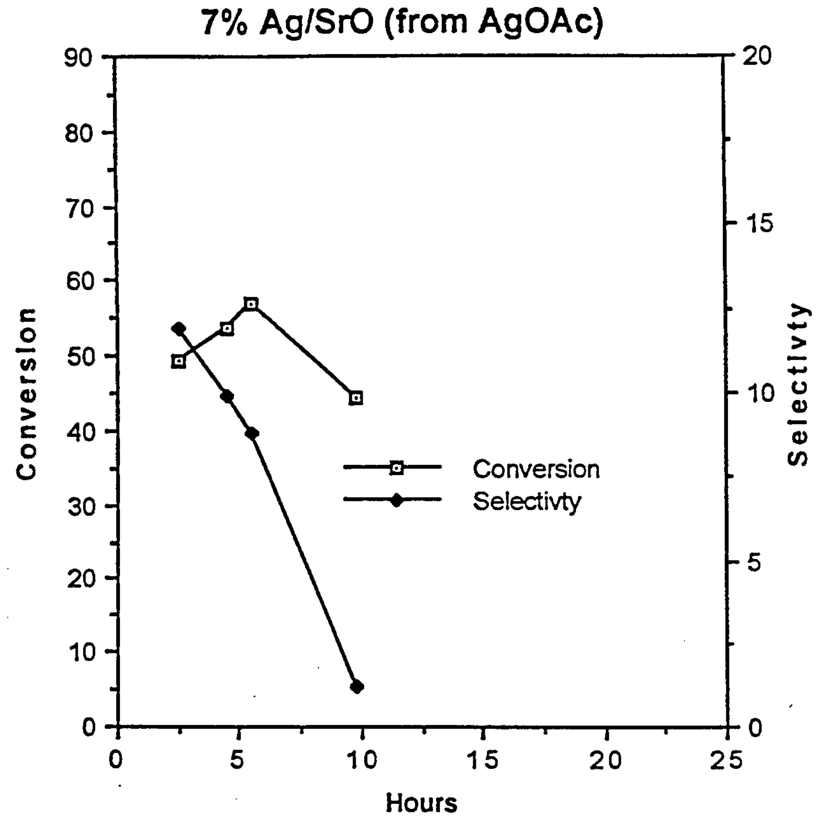
In the previous quarterly, it was mentioned that several Ag/SrO compositions were waiting to be verified by wet analysis. In one example, the expected wt % was 28-30 by method of preparation. Silver analysis put the exact value at 27.52%. Therefore calcination in an inert crucible, like Au, prevents the loss of Ag. Calcination in a quartz tube put the Ag loss at approximately 40%.

All Ag/SrO compositions prepared to date show catalytic activity for the conversion of methanol to isobutanol. Lifetime and selectivity to isobutanol and isobutylaldehyde has been a continuing problem with only slight improvements through the research effort.

A 7% Ag/SrO catalyst prepared from Ag acetate was loaded on top of a Cu screen in a Cu reactor with a Au covered thermocouple. An attempt was made to remove all sources of stainless steel from the reactor zone. With a 24.8 mol % of MeOH in N_2 feed stream, the resulting MeOH conversion and isobutanol selectivity is shown in Figure 3.2.1. The carbon balance was between 74-81 mol %, which was lower than normal, suggesting that the new capillary column must be re-calibrated with respect to molar response factors. Total isobutylaldehyde and isobutanol selectivity fell from an initial value of ~14 mol % to ~2 mol % in 10 hours.

With a fresh catalyst sample from the same batch but now with a a 49.6 mol% MeOH in N_2 feed stream, the resulting MeOH conversion and isobutanol selectivity is shown in Figure 3.2.2. The carbon balance was between 62-71 mol %. The direction of the carbon balance suggests that a non-linear response exists for the methanol. In both of these examples, the methanol conversion is nearly identical but the latter has more methanol in the feed. The total isobutylaldehyde and isobutanol selectivity fell from an initial value of ~10 mol % to 0.5 mol % in 20 hours.

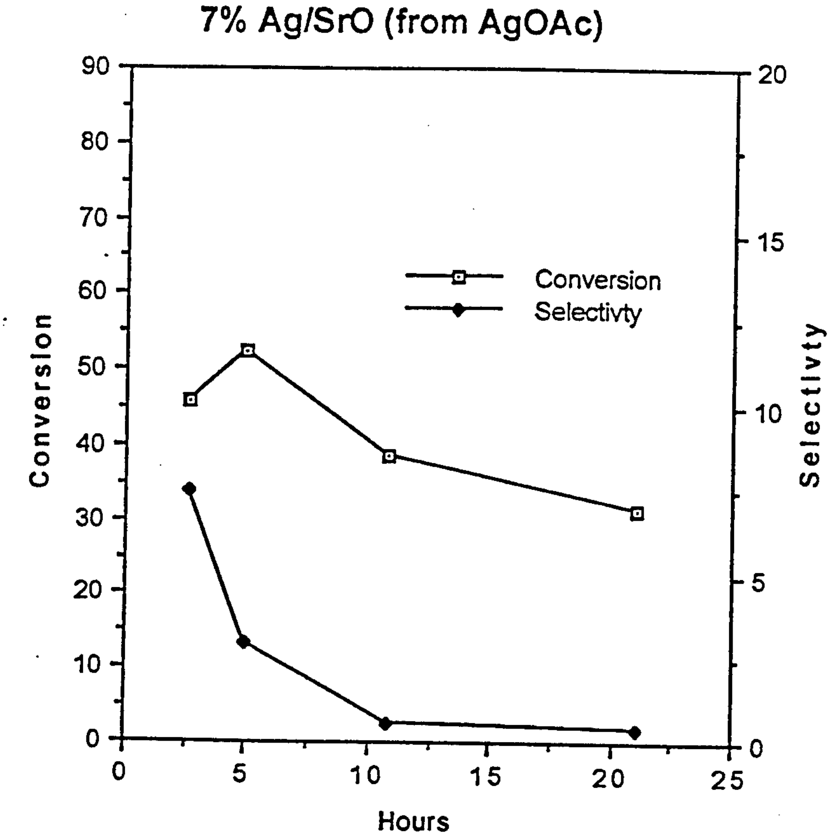
Figure 3.2.1 - 7% Ag/SrO Performance for Isobutanol at 380°C, 1 atm and 13.3 Total sccm



The capillary column was re-calibrated at several different concentrations of methanol in N_2. The results indicate that the molar response factors at all concentrations are the same. This suggests that the missing carbon is being deposited on the catalyst.

A 17 wt % Ag/SrO prepared from $AgNO_3$ was tested as before with a 24.8 mol % of MeOH in N_2 feed stream. MeOH conversion and isobutanol selectivity are shown in Figure 3.2.3. The carbon balance ranged from 75-88 mol %. The selectivity to isobutanol was about 6 mol % for the first 6 hours.

Figure 3.2.2 - 7% Ag/SrO Performance for Isobutanol at 380°C, 1 atm and 13.3 Total sccm



The same catalyst that gave the results in Figure 3.2.1 was tested again. The methanol conversion and isobutanol selectivity is shown in Figure 3.2.4. Carbon balance was between 75 - 81 mol %. Total isobutylaldehyde and isobutanol selectivity fell from an initial value of ~16 mol % to ~4 mol % in 6 hours. The conversion/selectivity profiles were similar except for a shift in reaction time. The reactor system was producing near reproducible results.

Figure 3.2.3 - 17 % Ag/SrO Performance for Isobutanol at 380°C, 1 atm and 13.3 Total sccm

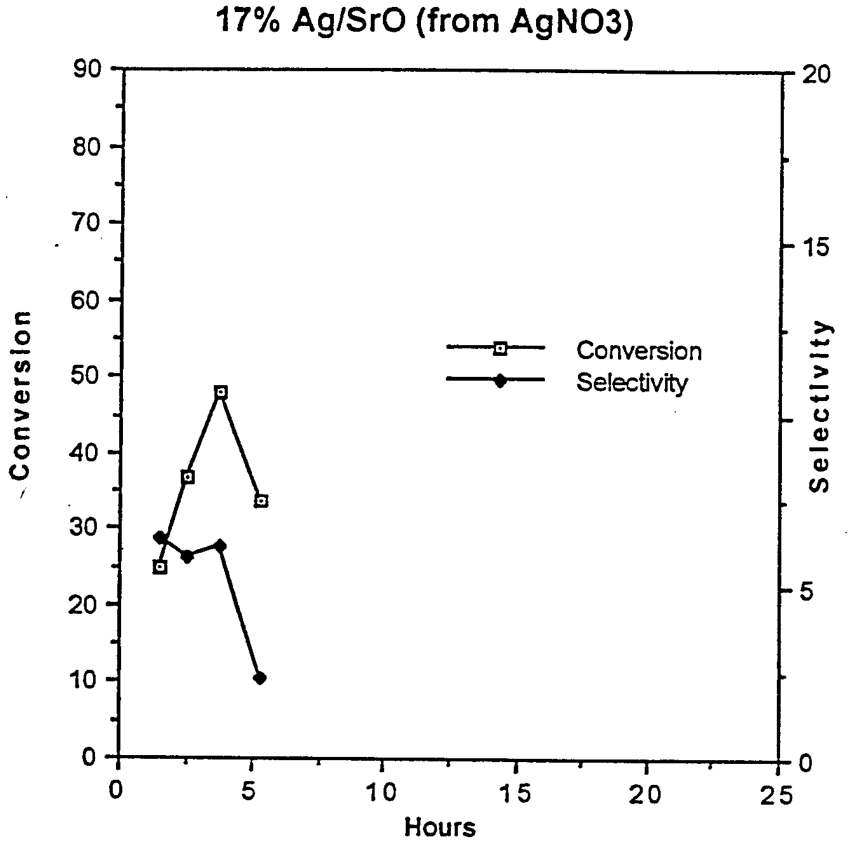
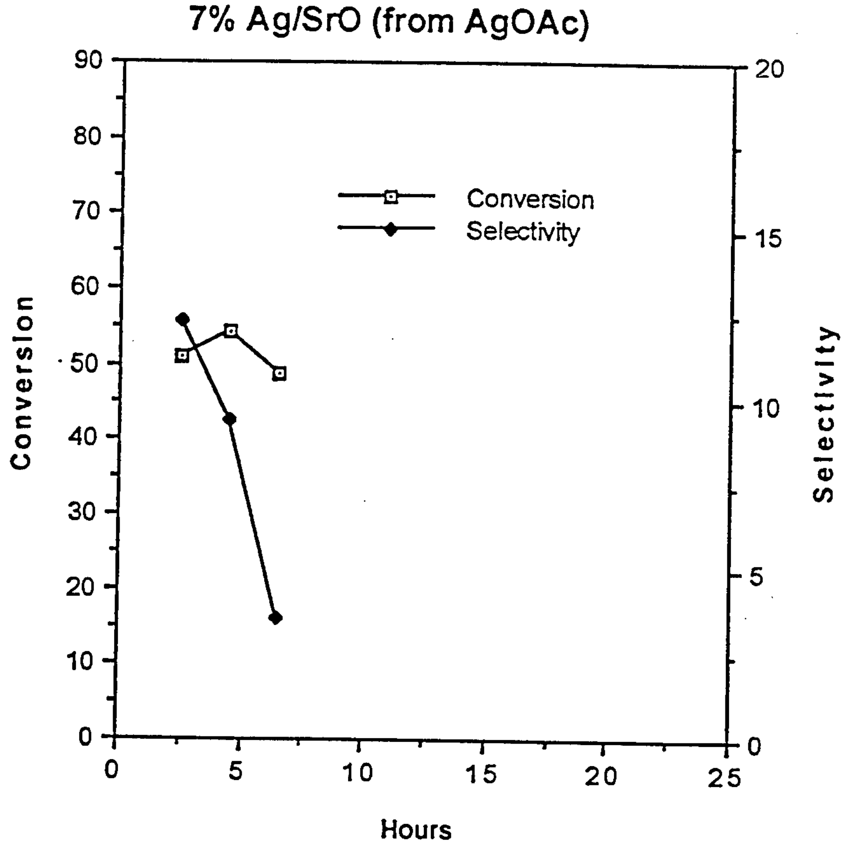


Figure 3.2.4 - 7% Ag/SrO Performance for Isobutanol at 380°C, 1 atm and 13.3 Total sccm



It was also noted that carbon balances improved as the catalyst deactivated suggesting that carbon may have been deposited on the catalyst surface.

A set of four Ag/SrO catalysts was prepared according to Table 3.2.1, and each catalyst was evaluated with a 24.8 mol % in N_2 feed. In each case, there was a decay in activity regardless of the method of calcination. The catalysts lost the ~10 mol % selectivity for isobutanol after 5-6 hrs. on stream.

Table 3.2.1 - Ag/SrO Compositions

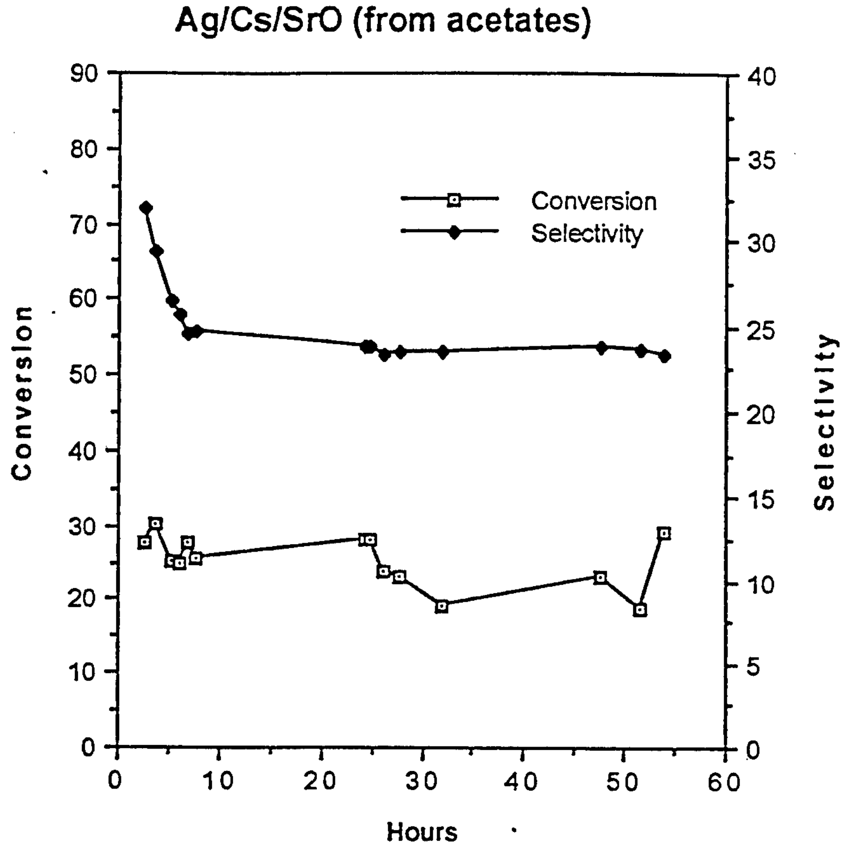
Ag Precursor	Wt % Ag by Prep.	Calcination	Avg. C. Bal.
AgOAc	7	quartz tube	74%
AgOAc	7	Au crucible	76%
$AgNO_3$	7	quartz tube	81%
$AgNO_3$	7	Au crucible	76%

These catalysts should be compared with a Ag/Cs on SrO catalyst that is being evaluated for methanol conversion. In Figure 3.2.5, the plot clearly shows that the performance did not change after 60 hours of operation. The loading of Ag and Cs was 5.8 and 7.3 wt %, respectively. The plotted selectivity refers to combined isobutyraldehyde and isobutanol. At 48 hours the product composition is shown in Table 3.2.2. The carbon balance was 86%, and C_2 and C_3 hydrocarbons were also detected along with propionaldehyde. These components should increase the carbon balance to 100% and probably slightly change the useful C_3 and C_4 selectivity. The appropriate response factors are being determined. The most important finding is that the addition of Cs produces a more stable catalyst and decreases the amount of CO produced. The CO_2 that before appeared to react with the SrO to form a carbonate now is detected in the gas phase.

Table 3.2.2 - Mol % Product Selectivity at 48 Hours

Product	Mol %
CH_4	6.1
DME	1.1
isobutylaldehyde	17.5
isobutanol	6.1
C_6^+	4.0
CO	39.3
CO_2	25.9

Figure 3.2.5 - Methanol Conversion and C_3 - C_4 Oxygenate Selectivity vs. Time on Stream at 380°C, 1 atm, and 13.3 Total sccm



Since the initial report of ~60 hrs. on-stream the same catalyst has now been extended to ~200 hrs. During this time interval, the temperature was increased from 380 to 410°C at 170 hrs. Two plots are provided: Figure 3.2.6, which is a time extension of Figure 3.2.5, reflects selectivity to isobutyraldehyde and isobutanol and Figure 3.2.7 reflects selectivity to isobutyraldehyde, isobutanol, ethanol, propionaldehyde and 1-butanol. Typical product slates at 380°C and 410°C are shown in Table 3.2.3. In general, the carbon mass balance is between 77-90 mol %, the catalyst is operating at 1 atm of pressure, the mol % of methanol in the feed is 24.8 (balance N_2), the contact time is ~2 seconds, and the wt. % Ag and Cs is 5.8 and 7.3, respectively.

Table 3.2.3 - Product Compositions From Methanol over Ag, Cs on SrO

Compound	Mol % Selectivity	
	380°C	410°C
Methane	7.3	10.0
Ethylene	0.5	0.5
Ethane	2.8	2.8
Propylene	0.5	0.6
Propane	1.6	1.1
DME	1.2	0.9
Methyl formate	-----	0.3
Ethanol	-----	0.4
Propionaldehyde	4.2	3.2
Isobutyraldehyde	9.7	7.3
n-butanol	2.5	2.3
isobutanol	4.8	3.8
C_6	1.7	1.3
CO	42.4	49.2
CO_2	20.8	16.2
MeOH Conv (%)	34.8	44.2

The effect of Cs is dramatic with respect to lifetime. Other controls are in progress: Cs only on SrO; Ag, K on SrO; variation of Ag/Cs on SrO and other Group VIII on SrO to determine if lifetime can be enhanced with Cs.

The first control, Cs on SrO, when tested under standard conditions of one atmosphere, 380°C, mol % methanol of 24.8, and contact time of ~2 seconds, quickly deactivates. Figure 3.2.8 illustrates the decay profile. Carbon balance is between 64-81%. Therefore the composition for an active catalyst is Ag, Cs on SrO.

The Cs was replaced with K in the Ag, Cs on SrO composition and tested under the above conditions. Figure 3.2.9 shows the typical deactivation profile. The carbon balance is between 65-84%. Of the Group 1 metals, Cs is superior to K.

Figure 3.2.6 - Methanol Conversion and Isobutyraldehyde and Isobutanol Selectivity vs. Time On Stream

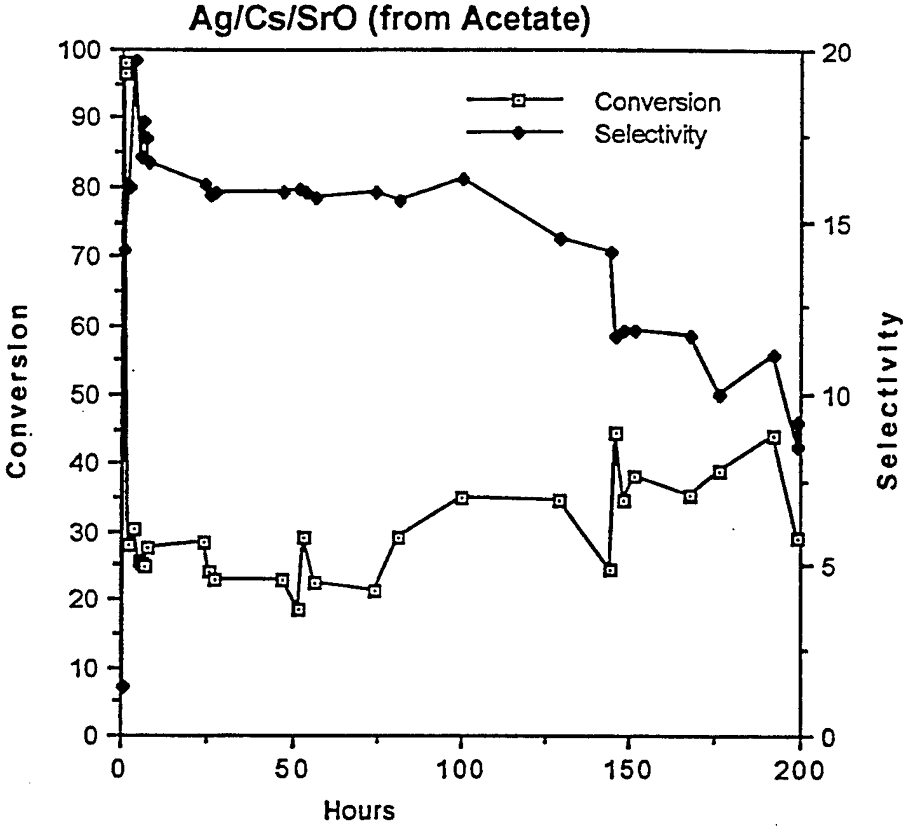


Figure 3.2.7 - Methanol Conversion and Ethanol + Propionaldehyde + Isobutyraldehyde + n-Butanol + Isobutanol Selectivity vs. Time On Stream

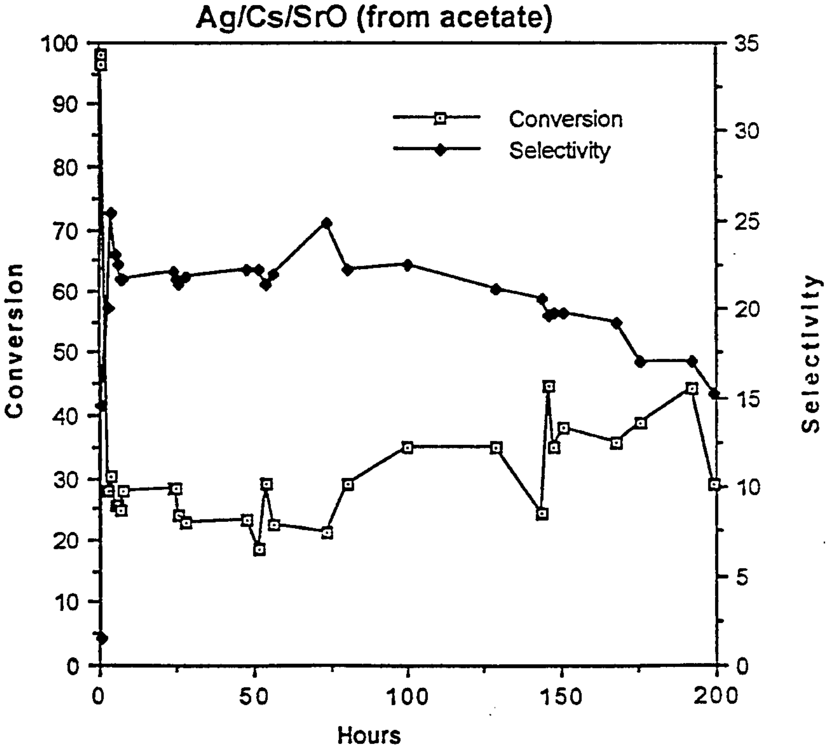


Figure 3.2.8 - Methanol Conversion and Ethanol + Propionaldehyde + Isobutyraldehyde + n-Butanol + Isobutanol Selectivity vs. Time On Stream

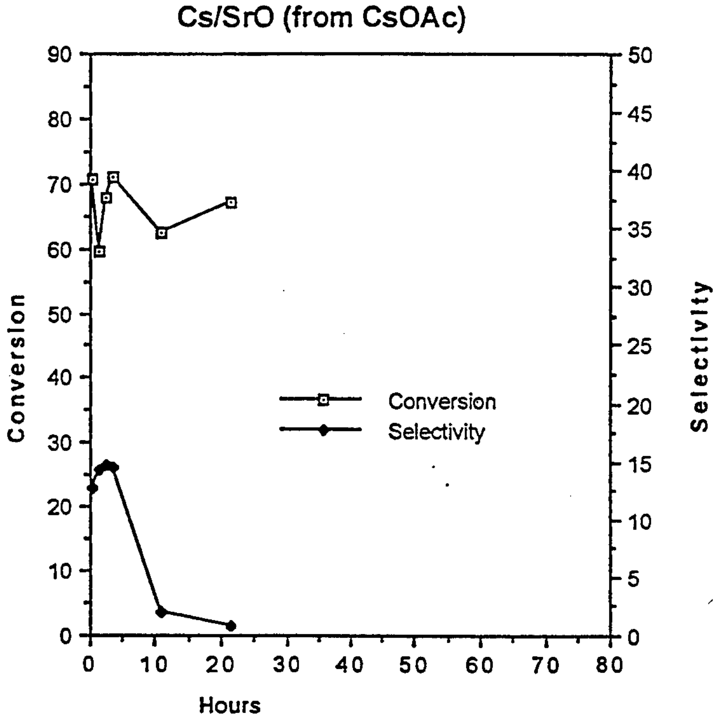
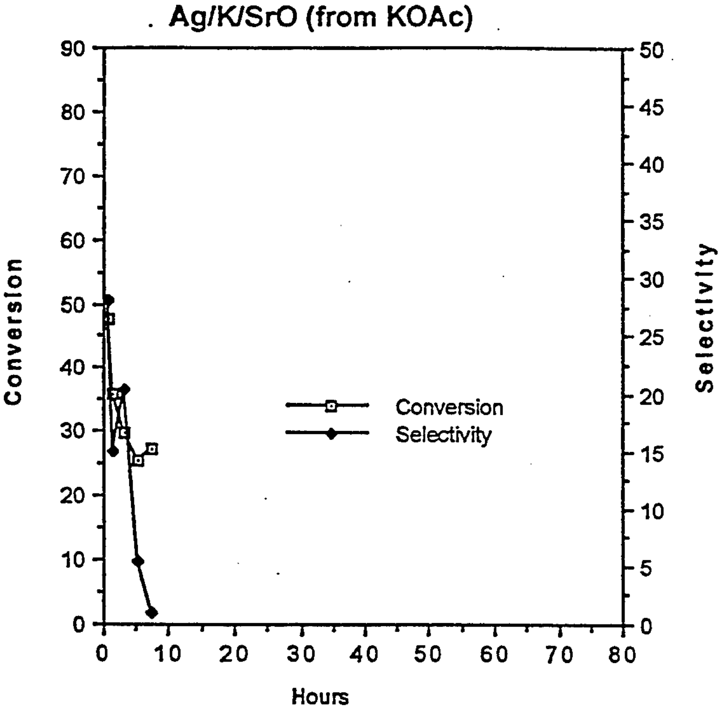


Figure 3.2.9 - Methanol Conversion and Ethanol + Propionaldehyde + Isobutyraldehyde + n-Butanol + Isobutanol Selectivity vs. Time On Stream



Previous catalyst compositions of Ir on SrO were active for the conversion of methanol to isobutanol; however, the catalysts deactivated quickly. Cesium was added to this composition, but a gain in lifetime was not observed. Carbon balance was between 57-80%.

The composition of Ag, Cs on SrO has the best lifetime of the catalysts tested to date. In addition it appears that this three component system is unique.

Dimethyl Ether to Ethylidene Diacetate

An attempt was made to run three identical batch autoclave runs on the hydrocarbonylation of dimethyl ether to ethylidene diacetate and to represent these runs as product selectivity vs time. The existing autoclave did not have sampling capabilities. Table 3.2.4 summarizes the three individual experiments.

The product selectivity vs. reaction time, Figure 3.2.10, appears to be consistent with the sequential reactions of DME to methyl acetate to acetic anhydride and then to ethylidene diacetate. The ethyl iodide probably comes from the sequence of methyl iodide to ethyl iodine and begins to appear at the longer reaction time. However, the ethyl acetate at 30 minutes is probably from the reaction between methyl acetate, lithium iodide and ethyl iodide. This suggests that ethyl iodide is made and reacted at 30 and 45 minutes.

During the depressurization of the autoclave after the run is cooled to room temperature, it is most likely some unreacted DME and some of the most volatile products, like acetaldehyde, is lost. The % recovered MeI is consistent with a venting loss of volatile organics. If the yield based on DME charged is normalized to an initial charge of 0.1978 mol DME, then the yields become 79.9, 81.3 and 72.4, respectively.

One research area has been identified that would simplify the homogeneous hydrocarbonylation of dimethyl ether to ethylidene diacetate, especially with respect to catalyst separation from the organic products. This involves heterogenizing the homogeneous hydrocarbonylation catalyst.

Table 3.2.4 - Identical Batch Autoclave Runs to Represent Reaction Product Profile vs Time

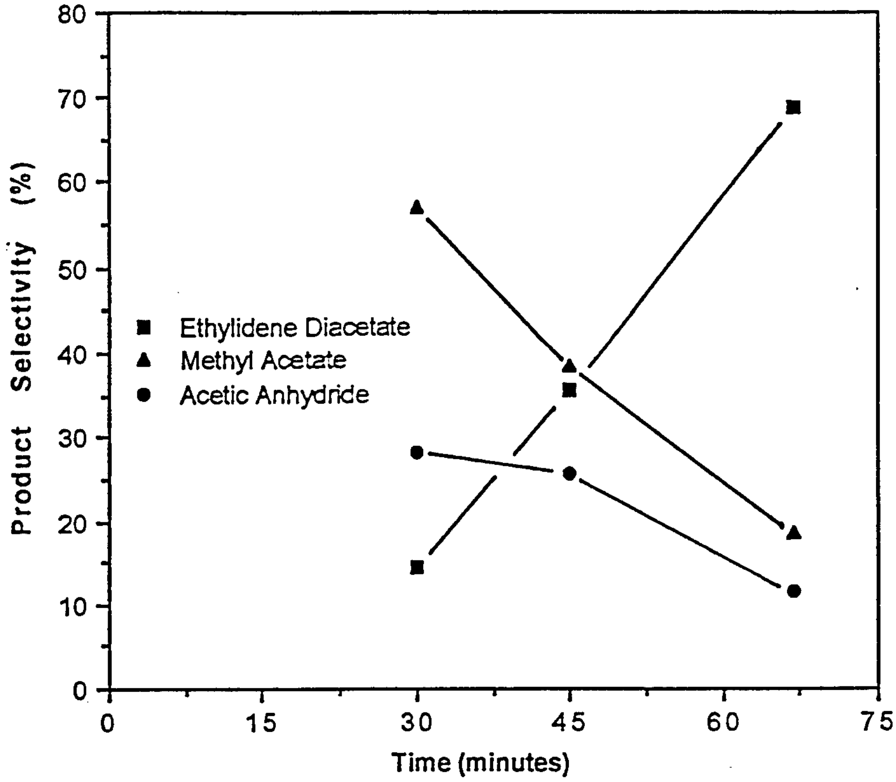
	MMOL	MMOL DME EQUIV.	Sel	MMOL	MMOL DME EQUIV.	SEL	MMOL	MMOL DME EQUIV.	SEL
DME init.	213	----	----	197.8	-----	----	208.7	-----	----
AcH*	----	----	----	0.1	0.1	0.1	0.1	0.1	0.1
MeOAc	90.3	90.3	57.1	61.7	61.7	38.4	26.7	26.7	18.6
EtI*	----	----	----	----	----	----	0.2	----	----
EtOAc*	0.05	0.05	0.03	0.4	0.4	0.2	1.2	1.2	0.8
HOAc*	2236.2	----	----	2254	----	----	2252.8	----	----
Ac2O*	44.8	44.8	28.3	41.4	41.4	25.7	16.6	16.6	11.6
EDA*	11.5	23.0 158.2	14.5	28.6	57.2 160.8	35.6	49.3	98.6 143.2	68.9
Rxn Time (min) **			30			45			67
Yield based on DME Charged:		74.3			81.3			68.6	
Recovered MeI:		62.2			62.2			60.0	

*From GC analysis

** Mol DME equiv. per mol Rh per min: 7.0, 4.7 and 2.8, respectively

*** $RhCl_3.3H_2O$, 0.75 mmol; MeI, 63.4 mmol; LiI, 11.2 mmol; LiOAc, 12.1 mmol

Figure 3.2.10 - Product Selectivity vs Time Profile for the Hydrocarbonylation of Dimethyl Ether to Ethylidene Diacetate



A literature search was initiated to find references on heterogenizing a carbonylation catalyst.

3.2.3 2QFY95 Objectives

Future plans for Task 3.2 will focus on the following areas:

- Continue to develop the concept of methanol to isobutanol over compositions of Ag, Cs/SrO with the goal of increasing oxygenate selectivity.
- Initiate catalyst development work on the cracking of ethylidene diacetate to vinyl acetate and acetic acid.
- Prepare carbonylation catalyst candidates for immobilization on supports.