A lower amount of water addition was investigated next. Run No. 10454-77 started with expected productivities but the catalyst performance declined sharply after the water addition was started. The mass balance indicated a significant amount of unaccounted CO_2 in the product, suggesting more water going to the reactor than measured. The run was aborted. When the system was taken apart, we discovered that a significant amount of slurry had left the reactor. A mixture of catalyst slurry and water was found in a trap on the gas-liquid separator return line. We believe there were surges in the water injection system as well as the reactor during the run. The water injection system needed significant modifications to improve the operation of the system. In view of other priorities, no further water injection experiments were conducted in this program.

REACTION MODEL

A simple reaction model was developed to predict trends during the lab studies[24]. The model was based on the rate expressions for methanol synthesis[25], methanol dehydration[8], and water-gas shift[26] as given in Table 5. For a CSTR, the rates of reactions were computed from the outlet component fugacities. The order of methanol dehydration reaction (N) was assumed to be 1 for simplicity. A computer program was written which would calculate product rates for given rate constants and operating conditions, or alternately back-calculate rate constants at a given condition and product rate.

CATALYST ACTIVITY MAINTENANCE STUDY

Life Run with Texaco Gas

A life run (Run No. 11483-81) was conducted for DME/methanol synthesis with S3-86/Catapal (4.33:1) catalysts using Texaco gas. The operating conditions were 250°C, 750 psig, and 6000 GHSV. The anticipated DME/methanol ratio at these conditions was about 2. Results of the life run are presented in Figures 24 and 25. Initial DME productivity was somewhat higher than expected, but it also showed a sharper initial drop. Over about 620 hours on-stream, DME productivity showed a steady decline. Initially, methanol productivity increased slightly. However, it remained steady most of the run and declined towards the end.

Rate constants were estimated using the DME/methanol model described above and are presented as a function of on-stream time in Figure 26. An exponential decay expression was used to correlate the rate constants with on-stream time. The results are summarized in Table 6. Both the methanol and dehydration catalysts showed a decline in activity. However, the methanol catalyst (S3-86) had a much larger decline (4.4%/day) compared to the dehydration catalyst (Catapal, 1.3%/day). Also, while the Catapal appeared to be stabilizing in the second half of the run, the BASF S3-86 seemed to be declining faster. The deactivation rate of the S3-86 catalyst is very high for commercial application. However, the decline rate was not large enough to have an impact on the results from the process variable study, which was typically conducted between 50 and 150 hours on-stream.

After the run, the spent catalyst was analyzed for Fe and Ni to check for metal carbonyl poisoning. Results from atomic adsorption tests indicated about 120 ppm Fe and 35 ppm Ni on the catalyst. This suggests only a small pick-up of Fe and Ni from their initial levels of about 70 ppm and 20 ppm, respectively. Hence, Fe or Ni can be ruled out as possible causes for deactivation.

Table 5

REACTION MODELS

METHANOL SYNTHESIS:

$$r_1 = k_1 \, f_{CO}^{\frac{1}{3}} \, f_{H_2}^{\frac{2}{3}} \left(1 - \frac{f_{MEOH}}{K_{eq_1} f_{CO} f_{H_2}^2}\right)$$

METHANOL DEHYDRATION:

$$r_2 = k_2 \, f_{MEOH}^{N} \left(1 - \frac{f_{DME} \, f_{H_2}}{K_{eq_2} f_{MEOH}^2}\right)$$

WATER-GAS SHIFT:

$$r_3 = k_3 \, f_{CO} \, f_{H_2O} \left(1 - \frac{f_{CO_2} \, f_{H_2}}{K_{eq_3} f_{CO} \, f_{H_2O}}\right)$$

FIGURE 24

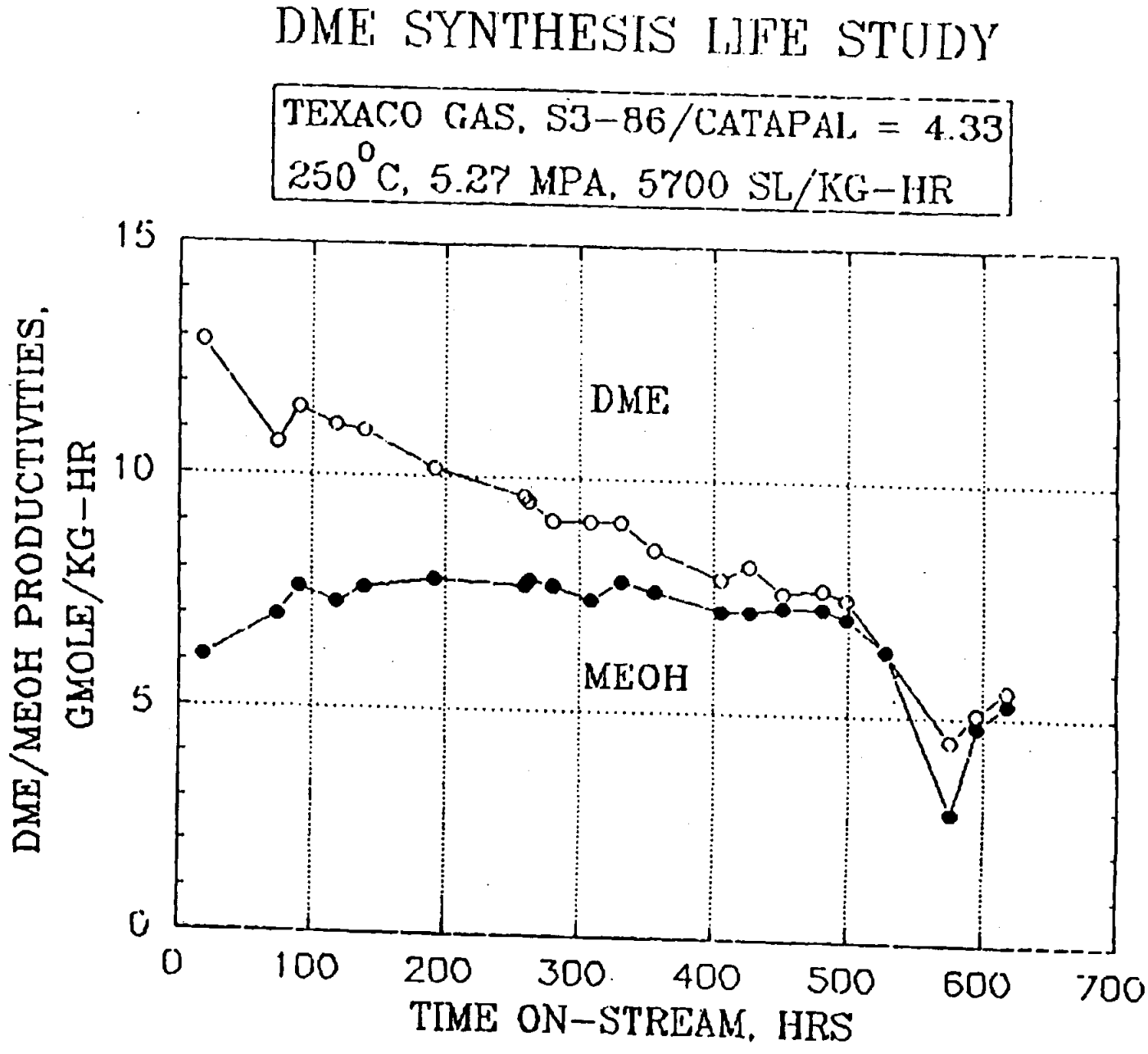

DME SYNTHESIS LIFE STUDY
TEXACO GAS, S3-86/CATAPAL = 4.33
250°C, 5.27 MPA, 5700 SL/KG-HR
DME/MEOH PRODUCTIVITIES, GMOLE/KG-HR
15
10
5
0
DME
MEOH
0
100
200
300
400
500
600
700
TIME ON-STREAM, HRS

FIGURE 25

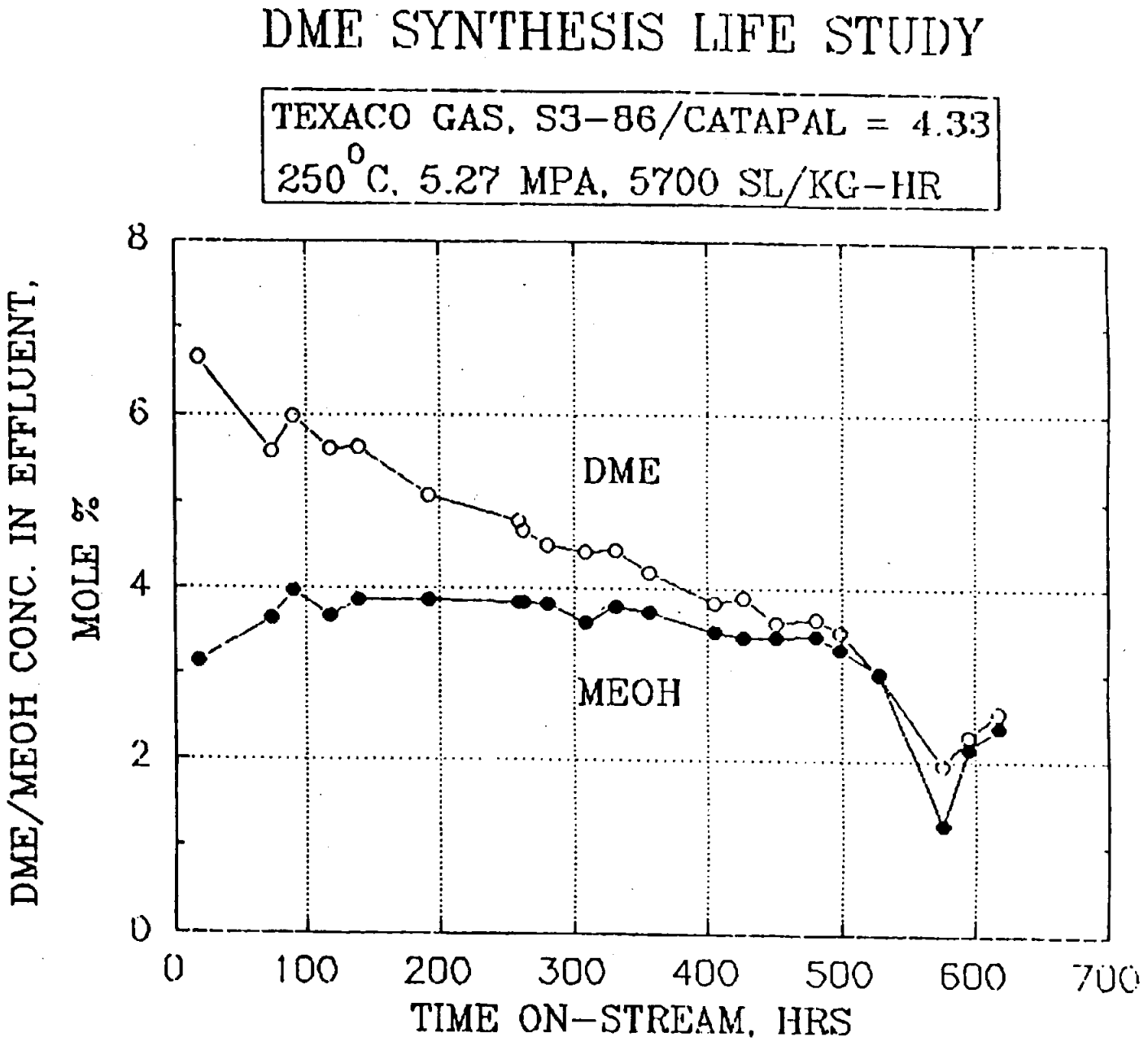

DME SYNTHESIS LIFE STUDY
TEXACO GAS, S3-86/CATAPAL = 4.33
250°C, 5.27 MPA, 5700 SL/KG-HR
DME/MEOH CONC. IN EFFLUENT, MOLE %
DME
MEOH
0
2
4
6
8
0
100
200
300
400
500
600
700
TIME ON-STREAM, HRS

FIGURE 26

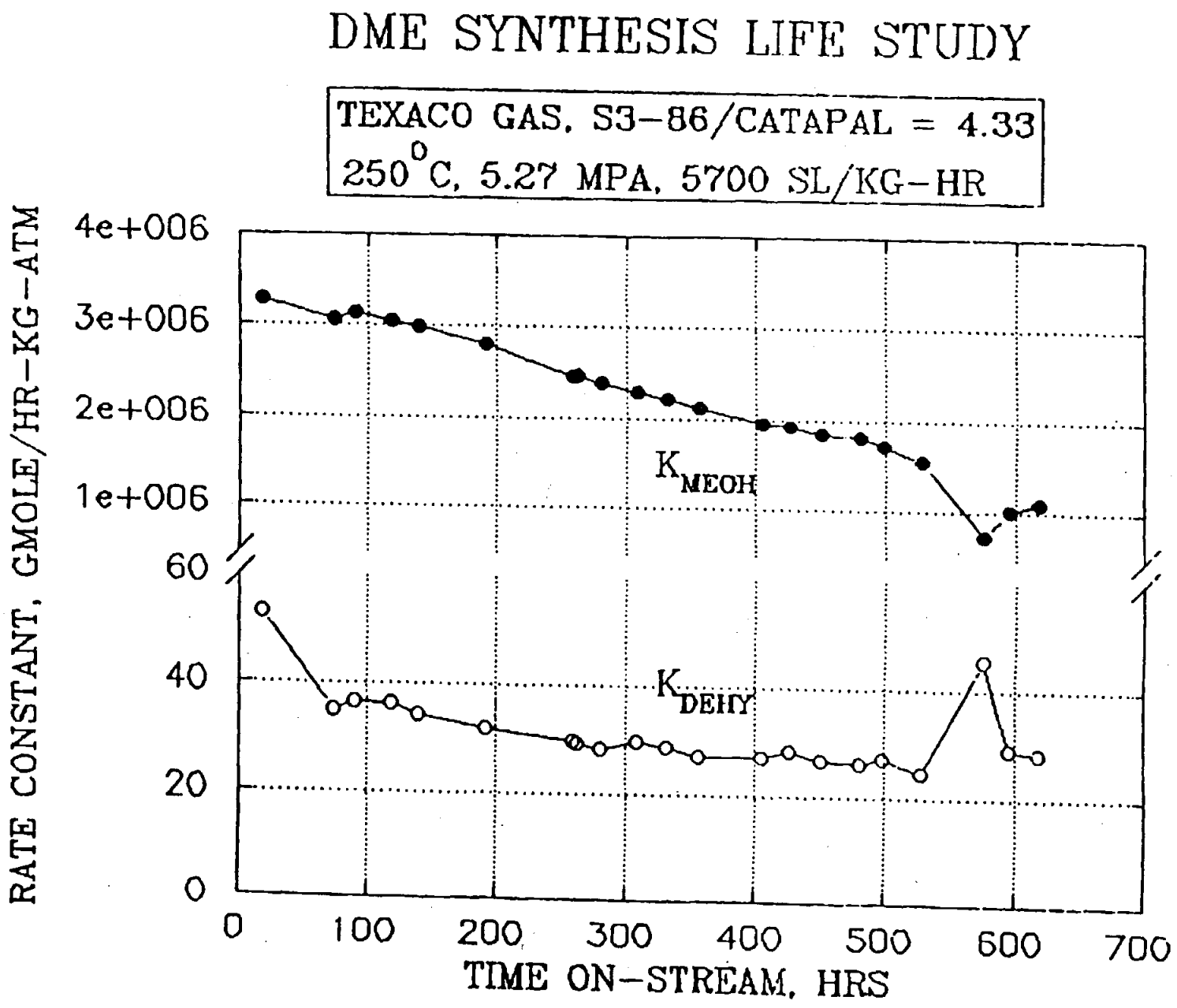

DME SYNTHESIS LIFE STUDY
TEXACO GAS, S3-86/CATAPAL = 4.33
250°C, 5.27 MPA, 5700 SL/KG-HR
RATE CONSTANT, GMOLE/HR-KG-ATM
4e+006
3e+006
2e+006
1e+006
60
40
20
0
K_{MEOH}
K_{DEHY}
0
100
200
300
400
500
600
700
TIME ON-STREAM, HRS

Table 6

DEACTIVATION RATES DURING DME SYNTHESIS LIFE RUN (RUN NO. 11483-81)

EXPONENTIAL DECAY EXPRESSION FOR RATE CONSTANTS:

$$k = k_0 \cdot \exp (- \alpha \cdot t / 100)$$

where k = rate constant, gmole/hr-kg-atm

k_0 = initial rate constant, gmole/hr-kg-atm

α = deactivation rate, %/day

and, t = on-stream time, days

ON-STREAM TIME, HOURS	METHANOL CATALYST BASF S3-86 α, %/DAY	DEHYDRATION CATALYST CATAPAL α, %/DAY
50 - 620	4.4	1.3
50 - 330	3.3	2.4
330 - 620	6.3	< 1

Based on information available from literature, a possible cause of the deactivation is deposition of coke on the S3-86. The spent catalyst was analyzed for graphitic carbon using Raman Spectroscopy. Out of the four spectra of the spent catalyst, two spectra had bands where a peak of graphite was expected. Slurry with fresh catalyst only showed bands for mineral oil. This confirms the presence of some coke on the spent catalyst. Quantification, however, is not possible from this technique. Analysis of a spent catalyst from a previous methanol life run (Run No. 10892-45) also indicated graphitic carbon (four out of five spectra). Therefore, coking as a main cause of deactivation cannot be confirmed.

XRD analysis of the spent catalyst was conducted to measure Cu crystallite size. Results indicate Cu crystallite size grew from 90Å to about 220Å, which is somewhat higher than about 150Å expected for spent LPMEOH catalyst. It should be noted, however, that the temperature control of the reactor during the entire run was excellent (248–252°C). Hydrothermal sintering could, however, occur as higher water concentration exists in the LPDME reactor compared to the LPMEOH reactor.

Life Run with Shell Gas

A second life run (Run No. 11782-03) was conducted with S3-86/Catapal (4.33:1) catalysts using Shell gas instead of Texaco gas as feed. Operating conditions similar to the Texaco gas life run were used: 250°C, 750 psig, and 6000 GHSV. As indicated above, there was some growth in Cu crystallite size during the life run with Texaco gas. Texaco gas contains high amounts of CO_2, which reduces the extent of the water-gas shift. Thus, a significant amount of water (as much as 2%) is present in the reactor using Texaco gas as a feed. Shell gas, on the other hand, contains less CO_2, less H_2, and more CO, which helps the shift reaction go much further. Hence, water concentration in the reactor with Shell gas is lower. If the deactivation is indeed due to hydrothermal sintering, the catalyst should be much more stable with Shell gas.

DME/methanol productivities as well as effluent concentrations during the life run are presented in Figures 27 and 28. Initial productivities were close to expected. However, over 500 hours on-stream, DME productivity showed a steady decline. Methanol productivity was steady earlier, but declined later in the run.

Rate constants were estimated using the DME/methanol reaction model and are presented as a function of on-stream time in Figure 29. An exponential decay expression was used to correlate the rate constants with on-stream time. The results are compared with the Texaco gas life run in Table 7. The deactivation rates were very similar for both runs. The methanol catalyst (S3-86) had a much larger decline rate compared to the dehydration catalyst.

The spent catalyst was analyzed for Cu crystallite size as well as Fe, Ni, Cl^-, S, and graphitic C. The results are compared with those from earlier life runs with Texaco gas in Table 8. The Cu crystallite size growth was similar during both runs. This indicates that hydrothermal sintering may not be the main cause of deactivation since water concentration in the reactor during the Shell gas run was much lower than during the Texaco gas run. The chemical analysis of the spent catalysts does not show any significant poisoning of the catalyst. Raman Spectroscopy analysis did not detect the presence of any graphitic carbon. Therefore, coking as the main cause of deactivation cannot be confirmed.

FIGURE 27

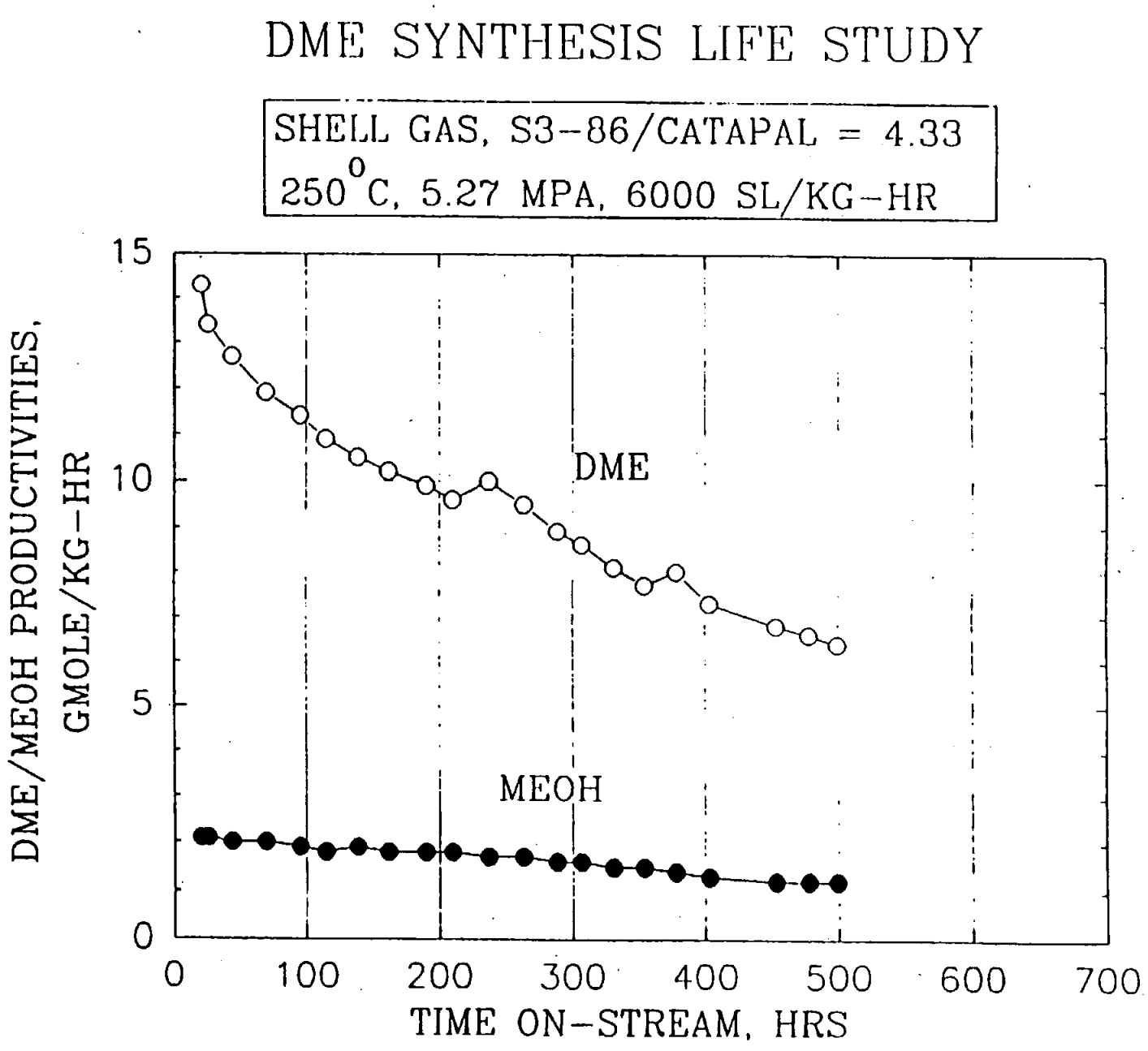

DME SYNTHESIS LIFE STUDY
SHELL GAS, S3-86/CATAPAL = 4.33
250°C, 5.27 MPA, 6000 SL/KG-HR
DME/MEOH PRODUCTIVITIES, GMOLE/KG-HR
15
10
5
0
DME
MEOH
0
100
200
300
400
500
600
700
TIME ON-STREAM, HRS

FIGURE 28

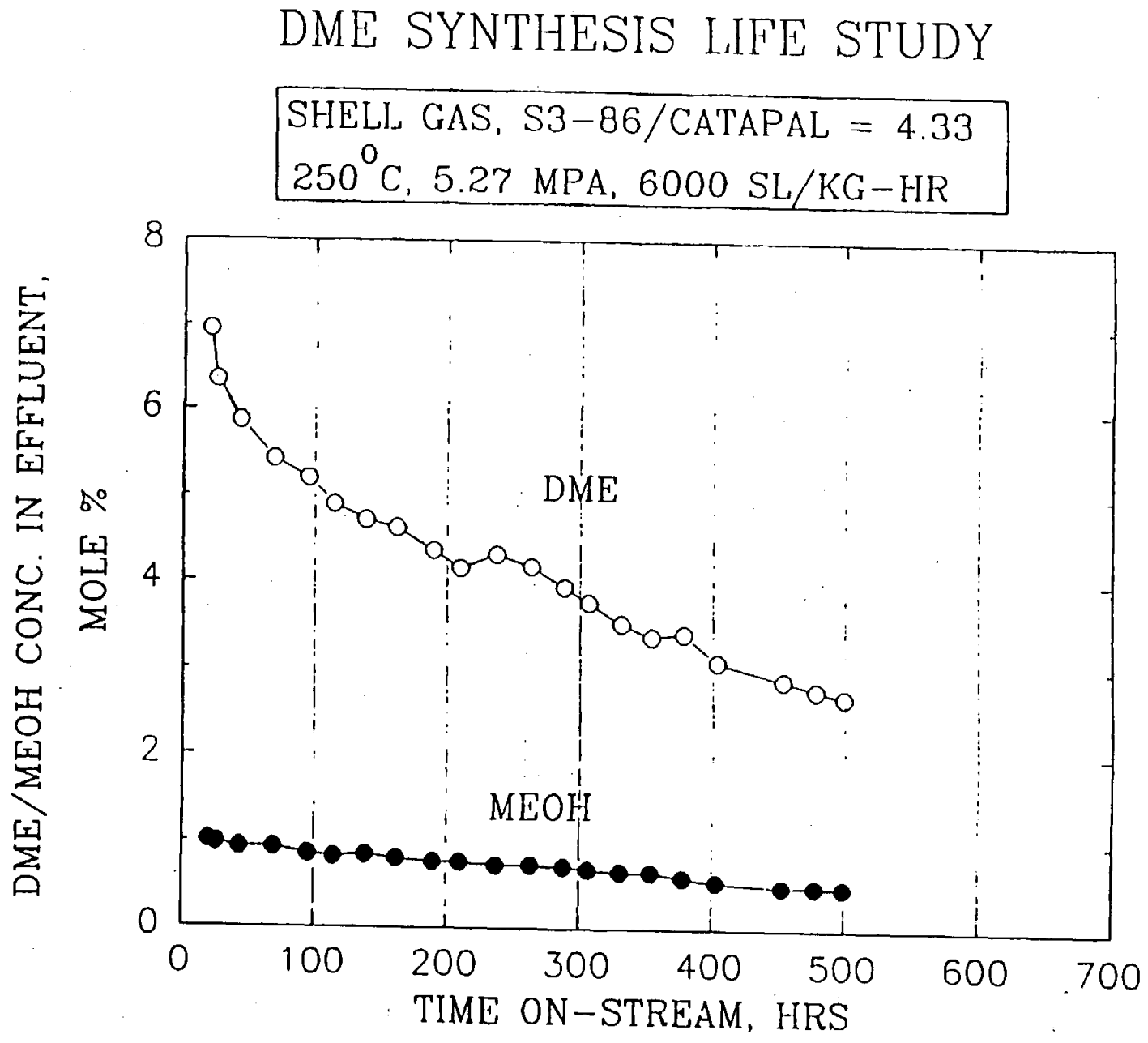

DME SYNTHESIS LIFE STUDY
SHELL GAS, S3-86/CATAPAL = 4.33
250°C, 5.27 MPA, 6000 SL/KG-HR
DME/MEOH CONC. IN EFFLUENT, MOLE %
DME
MEOH
0
2
4
6
8
0
100
200
300
400
500
600
700
TIME ON-STREAM, HRS

FIGURE 29

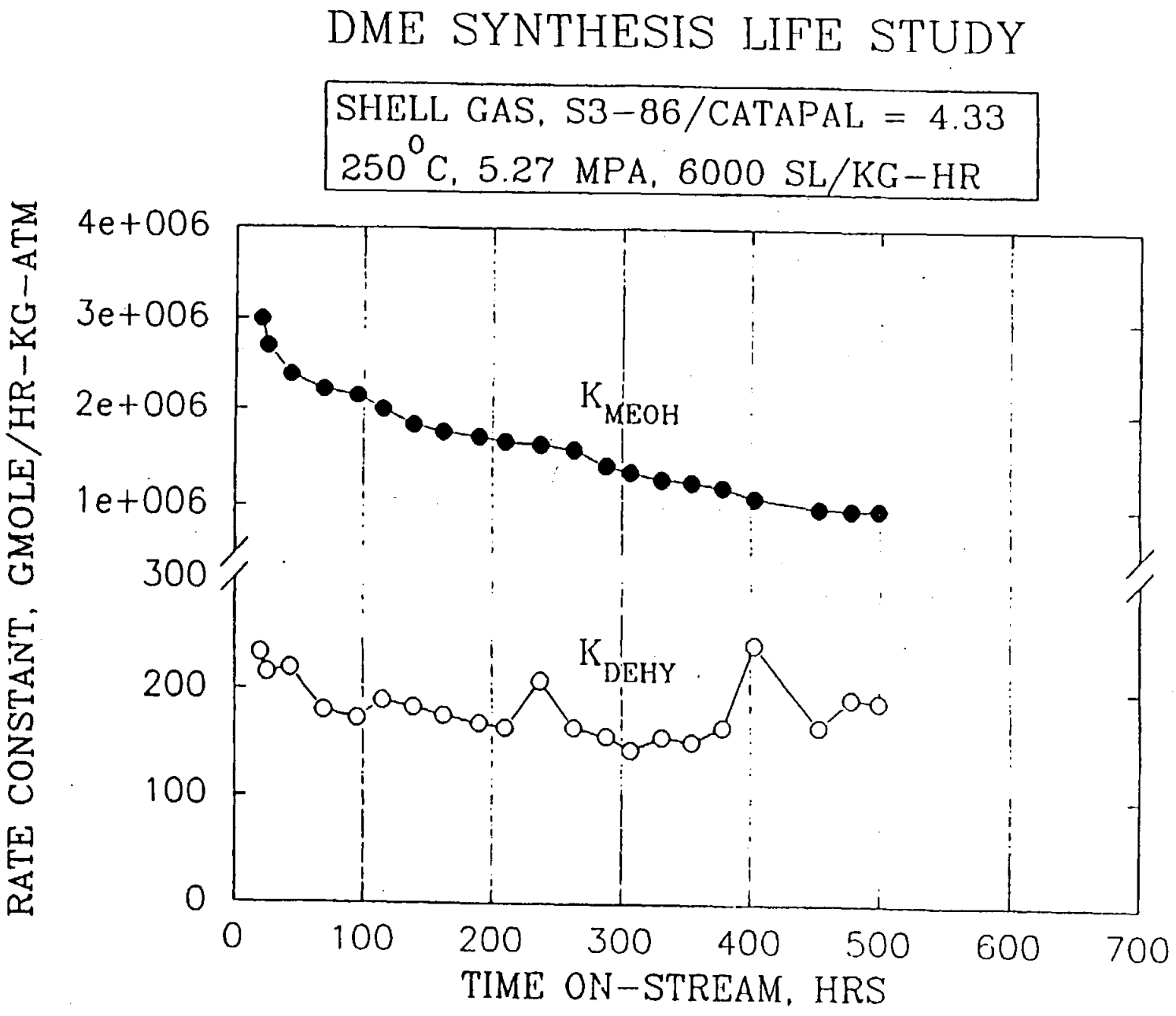

DME SYNTHESIS LIFE STUDY
SHELL GAS, S3-86/CATAPAL = 4.33
250°C, 5.27 MPA, 6000 SL/KG-HR
RATE CONSTANT, GMOLE/HR-KG-ATM
4e+006
3e+006
2e+006
1e+006
300
200
100
0
K_{MEOH}
K_{DEHY}
0
100
200
300
400
500
600
700
TIME ON-STREAM, HRS

Table 7

DEACTIVATION RATES DURING DME SYNTHESIS LIFE RUNS

EXPONENTIAL DECAY EXPRESSION FOR RATE CONSTANTS:

$$k = k_0 \cdot \exp (- \alpha \cdot t / 100)$$

where k = rate constant, gmole/hr-kg-atm

k_0 = initial rate constant, gmole/hr-kg-atm

α = deactivation rate, %/day

and, t = on-stream time, days

FEED GAS	RUN NO.	ON-STREAM TIME, HOURS	MEOH CATALYST BASF S3-86 α, %/DAY	DEHY. CATALYST CATAPAL α, %/DAY
TEXACO	11483-81	50-620	4.4	1.3
SHELL	11782-03	50-500	4.8	< 1

TABLE 8 Analysis of Catalyst Samples				
Analysis	**Method**	**Fresh Catalyst**	**Spent Catalyst Texaco Gas Run (Run No. 11483-81)**	**Spent Catalyst Shell Gas Run (Run No. 11782-03)**
Cu Cryst. Size	XRD	90Å	220Å	225Å
Fe	Atom. Ads.	70 ppm	120 ppm	40 ppm
Ni	Atom. Ads.	220 ppm	35 ppm	75 ppm
Cl^-	Atom. Ads.	<150 ppm	<150 ppm	<150 ppm
S	Atom. Ads.	<50 ppm	<50 ppm	<50 ppm
Graphitic C	Raman Spect.	No	Yes	No

A life run for methanol synthesis with DME injection is recommended to see if DME produces by-products that are detrimental to catalyst stability. Also, life runs at conditions which would inhibit coking are suggested. For example, operating at a lower temperature (240°C) or higher space velocity (9000 GHSV) could improve stability. Catalyst systems with lower alumina proportions may have better catalyst life as lower DME and H_2O concentrations will exist in the reactor. Additional DME life studies are suggested for future programs.

SEDIMENTATION TESTS FOR DEHYDRATION CATALYST

Sedimentation tests were conducted for Catapal gamma alumina, BASF S3-86, and their mixtures. The purpose of these tests was to compare slurry properties of the dehydration catalyst to that of the methanol catalyst. The sedimentation tests show a collective effect of particle properties such as size, density, shape and orientation, and interference from neighboring particles. Fluid viscosity and density also affect the sedimentation rate. Fast settling rate and tighter packing are preferred slurry properties. Smaller packing volume is also desirable from a volumetric productivity point of view, since it allows loading of more catalyst (weight basis) into a fixed reactor volume.

The tests were conducted with 19 grams of catalyst and 77.85 grams of Drakeol-10 oil in a 100 ml graduated glass cylinder. The separation line between the concentrated and the dilute phase was noted visually. Results of these tests are summarized in Table 9 and Figure 30. As expected from the density and particle size difference, the alumina has a slower settling rate and looser packing than the methanol catalyst. However, the difference is not large. The 80/20 mixture, which is considered optimum for DME synthesis, is only slightly different than the methanol catalyst. Also, the two catalysts did not separate into two visible layers. Hence, the slurry property of the mixture is quite acceptable.

TABLE 9
Sedimentation Test for Methanol and Dehydration Catalysts in Drakeol-10 Oil
(19 gms of catalyst in 77.85 gms of oil)

BASF S3-86	100%	80%	50%	0%
Catapal	0%	20%	50%	100%
Time, Min		Volume of Slurry, ml		
0	98	98	99	99
15	56	68	70	79
30	37	45	48	55
45	32	37	41	49
60	30	34	36	44
75	29	32	34	40
90	28	31	32	37
105	28	30	31	35
120	27	29	30	33
960	27	28	29	32

CATALYST PREPARATION FOR LAPORTE DME RUN

LaRoche Chemicals was contracted to heat treat about 2,000 lbs of Catapal alumina for use as a dehydration catalyst at LaPorte. A 200 lb trial batch was prepared by LaRoche. The surface area (SA) for this lot was about 200 m^2/g as compared to Air Products' laboratory prepared Catapal with a SA of about 225 m^2/g. Temperatures in the LaRoche pilot plant were greater than 550°C, in contrast to the lab heat treatment at 500°C. However, the temperatures required in the two units to produce similar products were not expected to be the same.

The LaRoche heat-treated Catapal was activity tested in the 300 cc autoclave (Run No. 11483-94). The tests were conducted with Texaco gas at 250°C, 750 psig, and 6000–9000 GHSV. BASF S3-86 was used as the methanol catalyst with S3-86/Catapal ratio of 4.33. DME and methanol productivities from these two tests are compared with those from lab prepared Catapal catalysts in Figure 31. Two lab prepared catalysts are presented in the figure: Catapal heat treated at a typical temperature of 500°C (SA=225 m^2/g) and Catapal heat treated at 550°C (SA=200 m^2/g). The performance of the pilot scale preparation (Batch A) of Catapal appears to be about the same as both the lab prepared Catapal catalysts.

Loss on Ignition (LOI) tests were conducted on the pilot scale (Batch A) and the lab prepared aluminas. Results from these tests are summarized in Table 10. The pilot plant prepared alumina had significantly higher weight loss from ambient to 300°C (physical water). However, both the catalysts showed about 1% weight loss from 300 to 500°C (chemical water). The higher physical water in the pilot batch was probably due to readsorption of water during cooling and packing. This was not a concern since this water would be removed in the reactor which is typically at 250°C. The chemical water content, however, must be kept at a minimum (around 1%) as it remains in the alumina at reaction temperatures.

FIGURE 30

SEDIMENTATION TEST FOR METHANOL AND DEHYDRATION CATALYSTS IN DRAKEOL-10

(19 GMS OF CATALYST IN 77.85 GMS OF OIL)

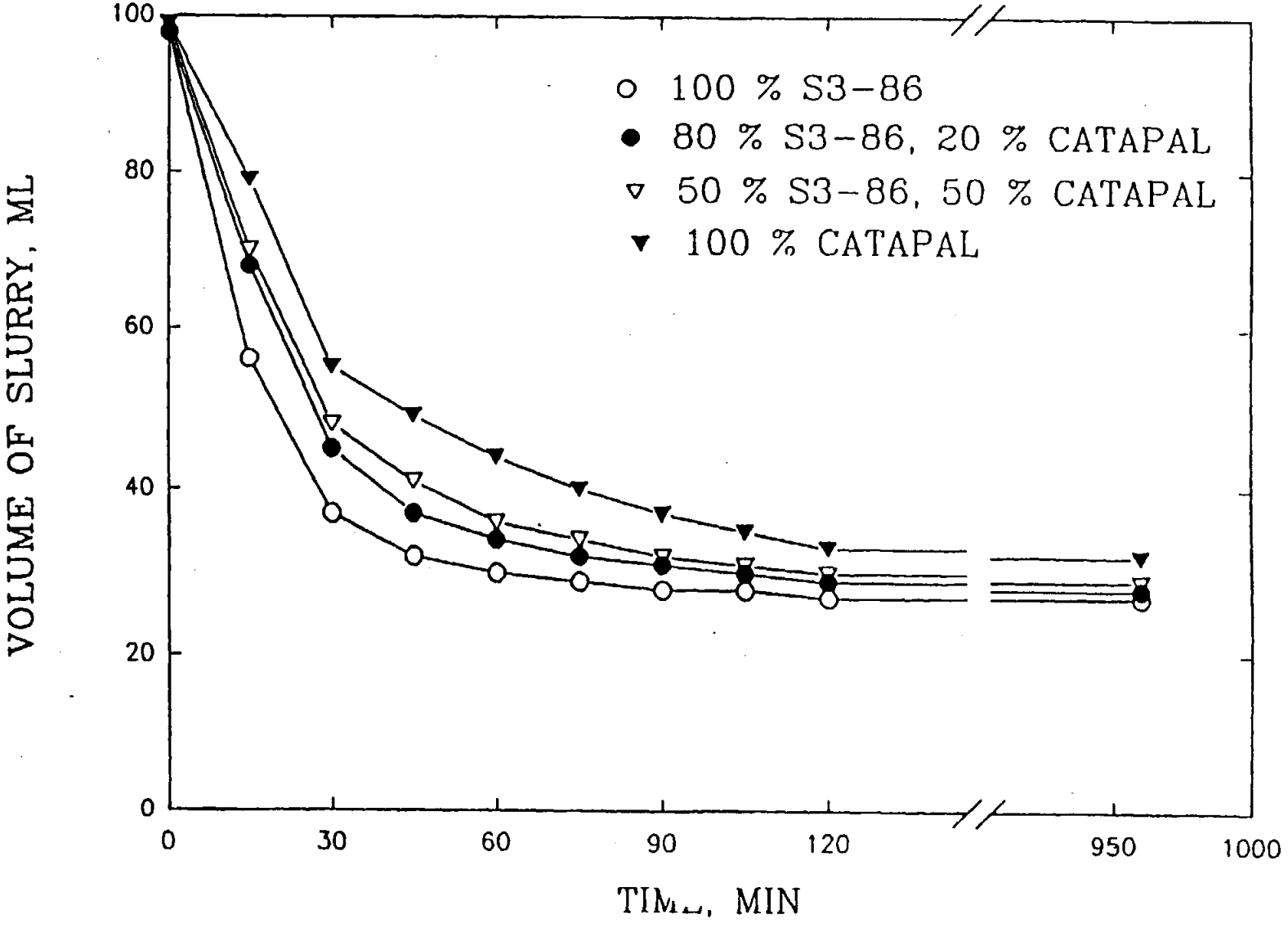


FIGURE 31

SCALE-UP OF ALUMINA PREPARATION FOR DME SYNTHESIS

(METHANOL CATALYST : S3-86 (81%), TEXACO GAS, 250°C, 750 PSIG)

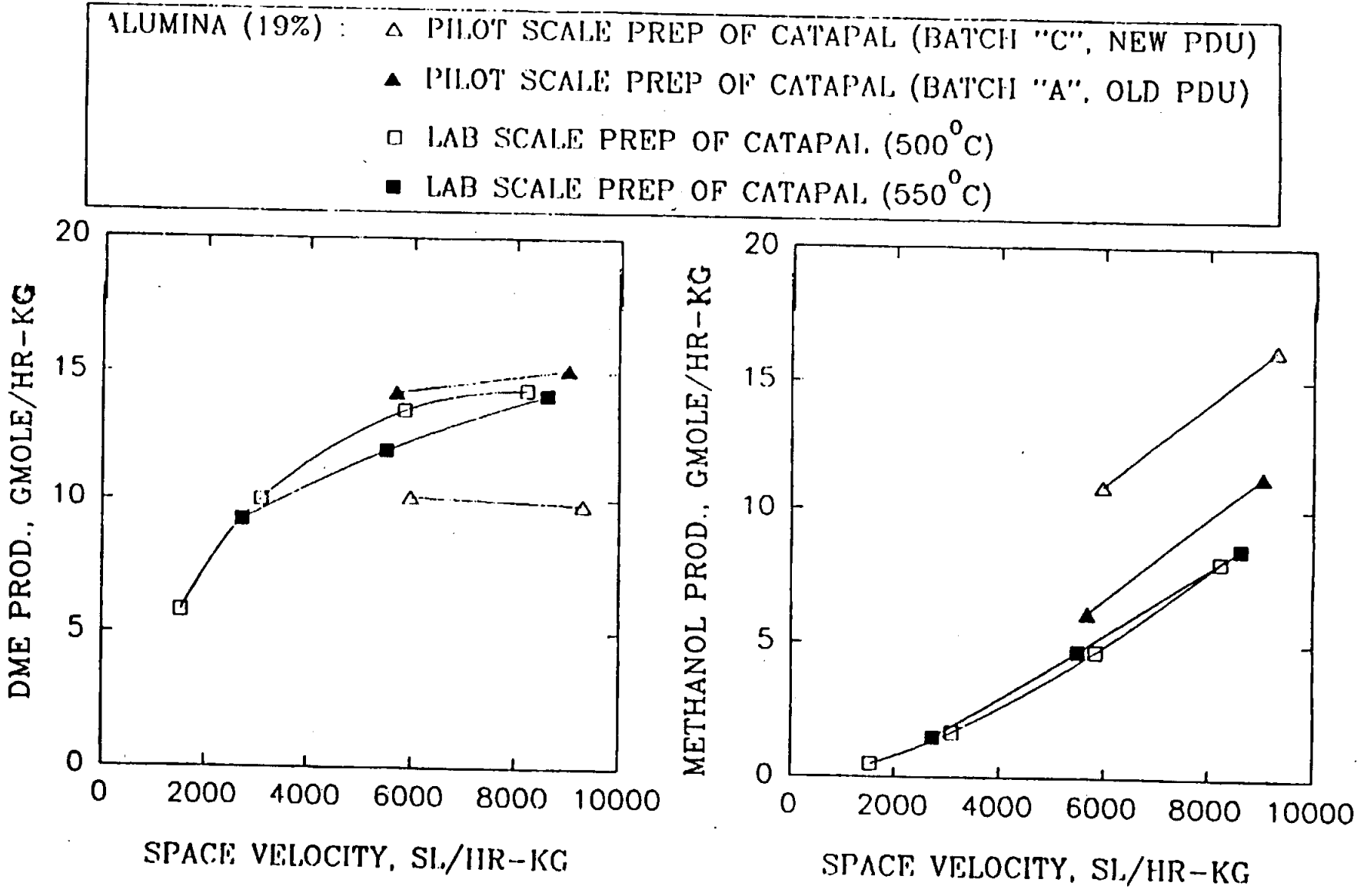


TABLE 10
Loss on Ignition (LOI) Test Results for Catapal Samples

Catalyst	Lab Heat Treated Catapal	Old Pilot Plant Heat Treated Catapal Batch A	New Pilot Plant Heat Treated Catapal Batch C (Double Heat Treat)
Weight Loss from Ambient to 300°C	0.4%	3.8%	1.2%
Weight Loss from 300 to 500°C	1.2%	1.1%	1.7%

While work continued with LaRoche to get higher SA alumina with low water content, LaRoche switched to a new pilot unit and had difficulties in producing the same quality material as the old pilot unit. The old pilot unit was no longer available. After several trials, LaRoche was able to bring the LOI down to a reasonable level. The LOI from 300 to 500°C for the alumina (Batch C), which was heat treated twice in the new pilot unit, was about 1.7% compared to 1.2% for the heat treated Catapal (see Table 10). The surface area for this batch was about 250 m^2/g, which was our target level. The activity test (Run No. 11728-18) of this batch indicated significantly less DME and more methanol productivities than the lab prepared as well as the old pilot unit (PDU) prepared aluminas (see Figure 31). This indicated lower than expected activity for Batch C. Considering slightly higher than expected LOI and SA along with lower activity, it appeared that the heat treatment was incomplete.

LaRoche modified the new PDU to allow lower alumina feed rate, resulting in higher heat treatment temperature. However, an activity test on a sample from this batch (Batch D) did not show any improvements over Batch C. Also, the LOI and SA were slightly higher than expected indicating that the heat treatment was still incomplete.

At that point, LaRoche indicated that they could not make any further improvements in the heat treatment. Their new PDU was a direct fired heat treater while the old PDU was an indirect fired rotary kiln. They referred us to Vista Chemicals, which frequently gets Catapal heat treated at Discovery Chemicals on a toll basis. Discovery Chemicals has an indirect fired rotary kiln. Contacts with Vista Chemicals revealed that they have a commercial heat treated gamma alumina powder catalyst, Catapal-G. However, the SA of Catapal-G is lower than our lab prepared alumina (150 vs. 225 m^2/g).

Since we were close to the start up of the DME demonstration at LaPorte, no further work was conducted on the scale-up. It was decided to use alumina from Batch A at LaPorte, which had acceptable properties and enough alumina available for the LaPorte operations (200 lbs).

EFFECT OF REDUCTION PROCEDURE ON DME SYNTHESIS

During the DME R&D work, the methanol catalyst was always activated using dilute hydrogen (2% H_2 in N_2) for simplicity. The methanol catalyst was loaded along with the dehydration catalyst and then the activation was carried our in the reactor.

The run plan at LaPorte involved first a methanol run, followed by two DME runs. Reduction using dilute syngas (2.1% CO, 1.4% H_2, and 0.5% CO_2 in N_2) has been proven for the LPMEOH process and is preferred operationally in the AFDU at LaPorte. So, the "routine" methanol catalyst (100%) activation using dilute syngas was planned for the first run. However, in case of problems with alumina addition, the fall back plan called for reducing the mixture of the two catalysts for the second run. Therefore, it was important to check if the dilute syngas reduction was equivalent to dilute hydrogen reduction for DME synthesis.

A test (Run No. 11782-25) was conducted with dilute syngas reduction in the 300 cc autoclave. A mixture of BASF S3-86 catalyst and LaRoche prepared Catapal (Batch A) was used for this test with a ratio of about 4.33. The activity of the catalyst mixture was checked using Texaco gas at 250°C, 750 psig, and 6000 GHSV. DME and methanol productivities from this run are compared with earlier results from hydrogen reduction (Run No. 11483-21) in Figure 32. DME productivity was about 20% lower when the dilute syngas was used for activation. This was a surprising result. Therefore, the system was thoroughly checked for the potential presence of metal carbonyls, specifically $Fe(CO)_5$ and $Ni(CO)_4$. The carbonyl levels were found to be insignificant. The dilute syngas run was repeated (Run No. 11782-28). The results reproduced well with the earlier experiment. A hydrogen reduction run (Run No. 11782-31) then followed these two runs. The hydrogen reduction results also reproduced. Therefore, the difference between the two activation procedures is believed to be real.

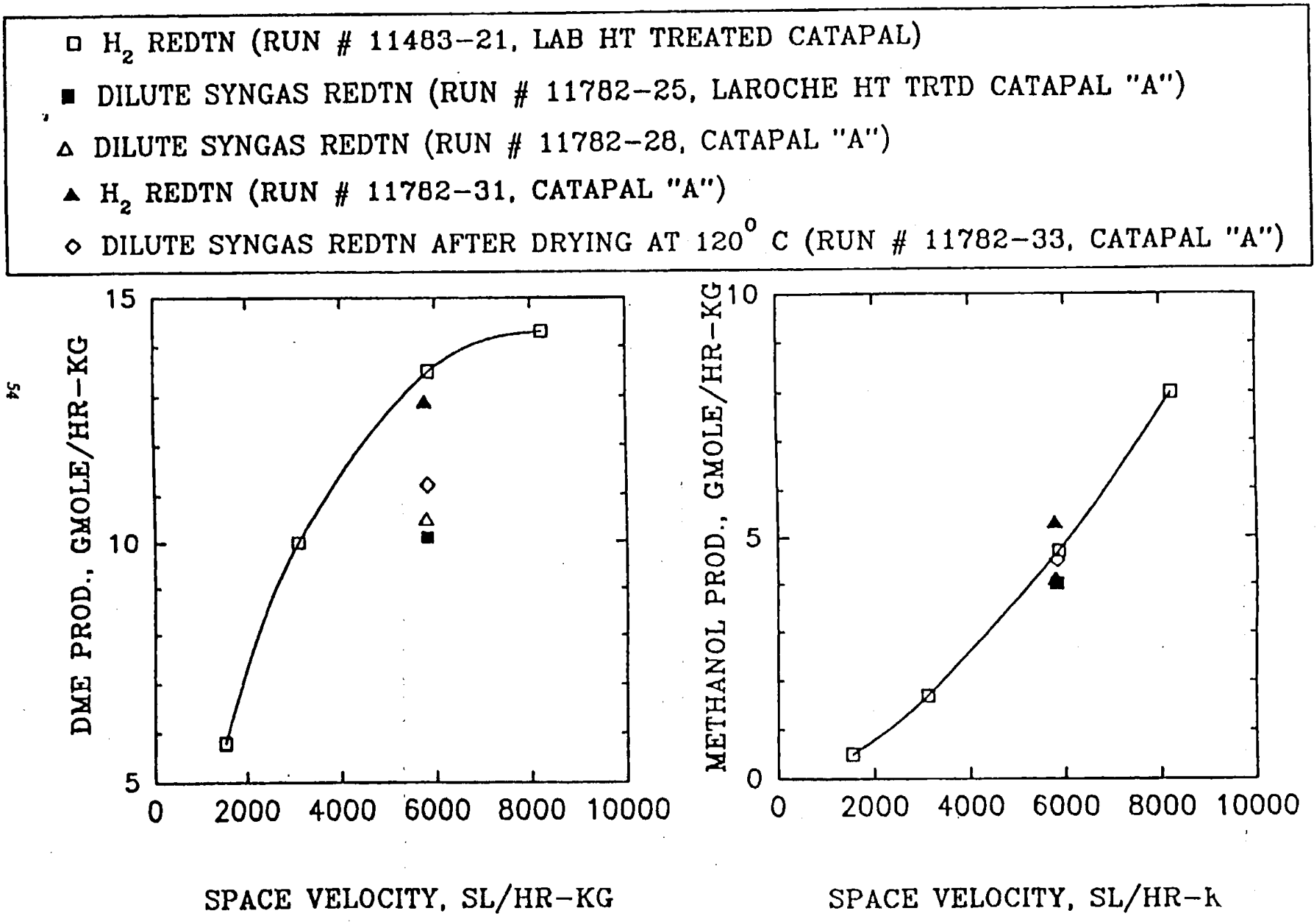
One possible reason could be that the water released from alumina interferes with the dilute syngas reduction. The dilute syngas reduction starts at a lower temperature than dilute hydrogen reduction. Therefore, we decided to dry the alumina before syngas reduction. The drying was conducted in the reactor at 120°C to simulate the limitations at LaPorte. The results from this run (Run No. 11782-33) indicate some improvement in activity. However, a significant difference remained between the two reductions. Perhaps the lack of complete drying at 120°C is important. A run with completely dry alumina would be worthwhile to confirm the water effect. With the LaPorte operation coming up, it was recommended that hydrogen reduction be used for catalyst mixture if we operated under the fall back plan.

Cn/ZnO CRYSTALLITE SIZE GROWTH DURING DME SYNTHESIS

Cu/ZnO crystallite sizes were measured for various spent methanol catalysts from the DME studies. The results are summarized in Table 11 along with other important parameters such as on-stream time, feed gas, and reduction gas. For comparison, results from LPMEOH runs (10454-37, 84) using 100% BASF S3-86 are included. The LPDME results include screening runs (11483-21, 16, and 10454-56), process variable runs (11483-72, 10454-43), life runs (11483-81, 11782-03), and reduction runs (11782-25, 28, 31, 33). For the screening as well as process variable DME studies, the Cu and ZnO crystallite sizes of the spent catalyst were close to LPMEOH (130–170Å and 60–90Å vs. 150Å and 90Å for LPMEOH). DME life studies indicated somewhat higher Cu crystallite

FIGURE 32 EFFECT OF REDUCTION PROCEDURE ON DME SYNTHESIS

(81% BASF S3-86, 19% CATAPAL, 250°C, 750 PSIG)



sizes (220Å). This suggests that over the long term, the product water could be sintering the catalyst. Cu crystallite sizes were also higher (220Å) when dilute syngas was used for reduction. This supports the hypothesis that water from alumina could be sintering the methanol catalyst.

TABLE 11
Cu/ZnO Crystallite Size Growth During DME Synthesis

	Run No.	Catalyst	% Methanol Catalyst	Feed Gas	Reduction Gas	On-Stream Time hrs	Cu Cryst. Size ·Å	ZnO Cryst. Size Å
LPMEOH	10454-37	S3-86	100	Texaco	Dil. H_2	85	158	93
LPMEOH	10454-84	S3-86	100	Texaco	Dil. H_2	200	147	88
LPDME Screening	11483-21	S3-86/Catapal Lab-500	81.25	Texaco	Dil. H_2	60	130	65
LPDME Screening	11483-16	S3-86/Catapal Lab-500	93.75	Texaco	Dil. H_2	80	162	82
LPDME Screening	10454-56	S3-86/Catapal Lab-550	81.25	Texaco	Dil. H_2	50	168	88
LPDME PVS	11483-72	S3-86/Catapal Lab-500	81.25	Texaco	Dil. H_2	190	171	89
LPDME PVS	10454-43	S3-86/Catapal Lab-500	81.25	Shell	Dil. H_2	205	150	57
LPDME Life	11483-81	S3-86/Catapal Lab-500	81.25	Texaco	Dil. H_2	620	220	83
LPDME Life	11782-03	S3-86/Catapal Lab-500	81.25	Shell	Dil. H_2	500	225	81
LPDME Reduction	11782-25	S3-86/Catapal Batch A	81.25	Texaco	Dil. Syngas	20	210	120
LPDME Reduction	11782-28	S3-86/Catapal Batch A	81.25	Texaco	Dil. Syngas	20	230	140
LPDME Reduction	11782-31	S3-86/Catapal Batch A	81.25	Texaco	Dil. H_2	20	170	110
LPDME Reduction	11782-33	S3-86/Catapal Batch A	81.25	Texaco	Dil. Syngas After Insitu Drying	20	180	120

FUEL TESTS ON DME/METHANOL MIXTURES

Three DME/methanol mixtures were measured for their fuel properties. These mixtures were prepared with nominal DME concentrations of 1, 2, and 4 mole%. Southwest Research Institute (SwRI) was contracted to perform the measurements of flash point, Reid Vapor Pressure (RVP), and octane number. Results from these tests are compared with methanol produced at LaPorte and M85 (85 vol% methanol in gasoline) in Table 12. With small amounts of DME added, significant improvements in both flash point and RVP were observed over methanol. With a flash point of 7°C and an RVP of 6.4 psi, methanol alone has a cold-start problem in winter conditions. Adding DME to methanol brings those properties closer to those of M85, an acceptable automobile fuel. The

results indicate an average octane number of about 101 for the mixtures compared to 99 for LaPorte methanol and 97 for M85. These results are encouraging and more tests with DME/methanol mixtures would be worthwhile.

TABLE 12
SwRI Test Results on DME/Methanol Mixtures

Blend	DME, mol% nominal	DME, wt% Gravimetric	Flash Pt. °C	RVP, psi @ 37.8°C	Octane # RON	Octane # MON
1	1	1.52	-15	5.85	118.5	86.4
2	2	3.02	-25	8.40	120+	86.2
3	4	5.94	-40	12.60	113.0	84.5
LaPorte Methanol	NA	NA	7	6.4	111.1	87.0
M85	NA	NA	-65	10.3	108.8	85.6

SUMMARY AND CONCLUSIONS

The new one-step DME process significantly improves the syngas conversion efficiency of the LPMEOH process. This improvement can be achieved by replacing a portion of methanol catalyst with a dehydration catalyst in the reactor, resulting in the product methanol being converted to DME, thus avoiding the thermodynamic equilibrium constraint of the methanol reaction. Overall, this significantly increases syngas conversion per pass.

The selectivity and productivity of DME and methanol are affected by the catalyst system employed as well as operating conditions. In this study, three alternative methanol catalysts and five dehydration catalysts were investigated. A preferred catalyst system, consisting of a physical mixture of a methanol catalyst (81%) and a gamma alumina (19%) was identified. An improvement of about 50% in methanol equivalent productivity was achieved compared to the LPMEOH process. Improvement in methanol activity has the greatest potential to further enhance process performance.

A process variable study was completed with the preferred catalyst system. Results indicate that higher pressure and CO_2 removal benefit the process significantly. The "ideal" H_2/CO ratio in the feed for DME synthesis is 1 compared to 2 for methanol synthesis. Also, unlike methanol synthesis, DME synthesis does not need any CO_2 in the feed. Limited life studies were performed with the preferred catalyst system. Methanol catalyst appeared to deactivate somewhat higher than expected while the dehydration catalyst seemed to be stable. More work is needed to improve stability. However, the catalyst system is sufficiently stable to demonstrate the process at a larger scale in a slurry bubble column.

Sedimentation tests indicated only slightly lower settling rates for alumina compared to the methanol catalyst. Also, the two catalysts did not separate into two visible layers. Hence, the slurry property of the mixture was considered quite acceptable. The dehydration catalyst preparation was successfully scaled-up to produce larger quantities of material required for a demonstration at LaPorte.