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MASTER

CATALYST AND PROCESS DEVELOPMENT FOR THE H_2 PREPARATION FROM FUTURE FUEL CELL FEEDSTOCKS

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ABSTRACT

The work done under this contract in the last quarter of 1978 was concerned with Phase I, which involved preliminary catalyst and process evaluation. The processes under study are hydrogen assisted steam reforming (HASR), catalytic partial oxidation (CPO), and autothermal steam reforming (ATR). Existing Engelhard test units were modified to carry out preliminary runs using the first two processes. Technical analysis to support work in this area consisted of heat and material balances constrained by equilibrium considerations. In a third task, the steam reforming of methanol to produce hydrogen was studied over two commercial low-temperature shift catalysts. Aging runs indicated good initial performance on both catalysts, but methanol conversion started to decline after a few hundred hours on stream.

TECHNICAL SUMMARY

TASK 1. PROCESS FEASIBILITY STUDIES

1.1 HYDROGEN ASSISTED STEAM REFORMING (HASR) G10-10

Three experimental runs were made using this process in an existing Engelhard reactor. The first run, made with a paraffinic naphtha over a nickel catalyst at 1500°F, was made to observe experimental problems, especially coking in the preheater section. At 1500°F, coke formed in the preheater. In a second run with the same naphtha at 1200°F and a weight hourly space velocity of 0.36, steady operations were observed for 10 1/2 hours with no sign of coking in the mixer or preheater section. In a third run, No. 2 oil was processed at 1500°F in the HASR type mode with a WHSV of 0.23 hrs^{-1}. Uniform coking was observed again in the packed bed preheater. After these observations, a redesign of the mixing and preheater section was made. In the mixing section, No. 2 oil is injected into the steam/H_2 mixture which enters in the annulus around the oil injection tube. A spiral preheater has been designed to permit rapid heating to reaction temperature with a short residence time. This was constructed during December, 1978.

1.2 CATALYTIC PARTIAL OXIDATION (CPO) G10-11

An existing Engelhard test rig was modified to perform this study. To calibrate this equipment, a short run was made with propane. It was observed that the Pt/Pd composition permitted partial oxidation of propane without coking at an O_2/C molar ratio of 0.62. However, the addition of steam served to dilute the stream and no evidence for steam reforming was observed. After this observation, a new catalyst composition was prepared for a run planned using No. 2 oil. This composition contains Pt/Pd/Rh on Corning cordierite with 300 cells/in^2. The rhodium was added to enhance the rate of steam reforming.

TASK 2. TECHNICAL ANALYSIS G10-20

A computer program (ATR-1) has been written to simulate the autothermal reactor system. The ATR-1 program can calculate reaction heats and the thermodynamic equilibrium composition for the products obtained from the partial oxidation and steam reforming reactions. The equilibrium composition calculated from this program for steam reforming of hydrocarbons has been checked with literature data, and very good agreement has been observed. The equilibrium composition calculated from this program for the partial oxidation reaction will be checked later with other published data.

LITERATURE SEARCH

A survey of Chemical Abstracts, for issues dated within the last ten years, covered steam reforming methods of natural gas, naphtha, methanol, other heavy feedstocks and some gasification methods of coal. A few references to catalyst compositions were found but most references cited only processes.

TASK 3. METHANOL REFORMING G10-30

Three commercial catalysts have been evaluated in the pilot plant for the steam reforming of methanol at low temperature (about 400°F). The three catalysts are Girdler's G66B, United Catalysts' T2130A, and ICI's 52-1. For each of the above low-temperature shift catalysts, the initial conversion of methanol was about 100% at 400°F, 6 psig, 440 hrs^{-1} H_2 space velocity with a feedstock containing 1.5 moles of water per mole of methanol. However, all of these catalysts show a decline in activity for methanol decomposition after a few hundred hours on stream. Since the phosphoric acid type fuel cell requires a feed free of methanol, none of the above catalysts are satisfactory at the conditions used. It was demonstrated that the product gas (dry basis) was close to the equilibrium value calculated thermodynamically. Thus, it appears that water gas shift function of these catalysts is still effective even after the sites for methanol decomposition are no longer as effective as with the virgin catalyst.

REVIEW OF TASKS

TASK 1 1.1 HYDROGEN ASSISTED STEAM REFORMING (HASR) - G10-10

The experimental apparatus was initially checked out in Run No. 7025 for the hydrogen assisted steam reforming (HASR) of naphtha (9% aromatics, 66% paraffins and 25% naphthenes) at 1500°F, H_2O/C ratio of 4.5 and a WHSV of 0.35 g naphtha/gcat/hr. It was observed that the reaction could reach steady state with hydrogen admitted in feed (H_2/C ratio of 0.68), and that severe coke formation was found in the preheater zone. After improving the design of the reactant mixer, the above reaction could be run (Run No.7035) for 10 1/2 hrs. under steady state conditions at 1200°F, 1 atm, WHSV of 0.36 g/g/hr, H_2O/C ratio of 4.5 and H_2/C ratio of 1.53. Therefore, HASR of naphtha could successfully be run in our unit without experimental difficulties.

The HASR of No. 2 oil was done (Run No. 7051) over a commercial NUA-21 catalyst at 1500°F, 1 atm, WHSV of 0.23, H_2O/C ratio of 5.0 and H_2/C ratio of 0.342. Since the steam reforming reaction is endothermic, the degree of conversion could be monitored by watching the temperature profile in the catalyst bed. For this run, the endothermic reaction died out after about 2 hours on stream, and coke was deposited uniformally over the length of the preheater section.

The coke found in the preheater was probably formed by hydrocracking of the unstable compounds present in No. 2 oil in the temperature range between 1200 to about 1500°F. Therefore, a spiral preheater which is designed to cut down the residence time in the preheater zone to about 0.2 sec. has been designed and constructed.

To run the reforming reaction higher than 1500°F, some other modifications of the experimental unit were necessary. All the modifications have been completed.

A shakedown run with H_2 and H_2O as feed (no oil admitted to the reactor) has been performed for about 1 hour at 1740°F at 1 atmosphere. Steady reaction temperature could be achieved under the above experimental conditions. The next run will be with No. 2 oil over a nickel catalyst, Engelhard's SF-3.

1.2 CATALYST PARTIAL OXIDATION - (CPO) G10-11

Some preliminary commissioning test runs have been made in the two stage reactor system with propane fuel; the initial test conditions selected were as follows:

Inlet Temperature: 360°C

Air/Fuel Ratio (w./w.): 6.71, 5.83

O_2/C (molar ratio): 0.72, 0.62

Pressure : 1 Atmosphere

Feed H_2O/C (molar ratio): 0,0.92

The catalyst used was a Pt/Pd composition loaded on a Torvex ceramic support. Exhaust gases were analyzed by a gas chromatograph and the resultant hydrogen concentrations are given below:

Air/Fuel Mass Ratio:	6.71	6.71	5.83
H_2O/C (molar ratio):	0	0.92	0
H_2(mole % dry basis):	22.15	19.90	22.79

It is apparent from the results that the addition of steam to this system did not increase the H_2 concentration. Several factors could explain these results. The Pt/Pd catalyst may not be effective for steam reforming to produce more hydrogen. Also, the space velocity used could be much too high for the steam reforming reaction.

The air/fuel ratios were high enough that no carbon formation occurred. The O_2/C molar ratio of 0.62 is still appreciably above the desired level (<0.35) for fuel cell operation.

The equipment was satisfactorily demonstrated in this run. A decision was made to add rhodium to the catalyst and to use a cordierite monolith in the next run. This will be made with No. 2 oil.

TASK 2. TECHNICAL ANALYSIS - G10-20

The disproposition reaction of CO to carbon (i.e. $2CO \rightarrow C + CO_2$) has been added to the existing ATR-1 computer program. The equilibrium composition at a given temperature and pressure is obtained by solving numerically a set of solutions to satisfy four equilibrium constants. The ATR-1 program will numerically search for a set of concentrations for each product component, so that the equilibrium constants for methanation, water gas shift, methane cracking and CO disproportionation reactions are satisfied simultaneously. Under the conditions free from the carbon deposition region, good agreement between ATR-1 and two literature references has been obtained as discussed in Table I.

The current ATR-1 program can calculate reaction heats at a given temperature. To satisfy the autothermal reactor system, some portion of the program will be revised so that the program can search for a condition where heats of reaction between partial oxidation and steam reforming are balanced.

LITERATURE REVIEW

Search No. 003013 (November 10, 1978) reviews the open literature and patents for the steam reforming of hydrocarbons (methane, naphtha, diesel fuel and methanol) for the last ten years. Most citations were processes from the patent literature while thermodynamic equilibrium calculations dominated the journal references. Of those patents citing catalyst compositions, the majority for high-temperature steam reforming were alumina supported nickel while for methanol, copper with zinc and chromium on alumina are prevelent.

Some unusual compositions were:

A) High-Temperature Steam Reforming:
   Nickel with barium or titanium or magnesium on γ-Al_2O_3
   Nickel with lanthanum and strontium on γ-Al_2O_3
   Nickel with uranium on α-Al_2O_3
   Nickel alumina magnesium spinel

B) Catalytic Partial Oxidation (No Steam Addition):
   Rhodium on γ-Al_2O_3

C) Methanol Steam Reforming:
   Copper with Cr, Mn, Zn or Al

TASK 3. METHANOL REFORMING G10-30

To generate hydrogen from methanol for future fuel cell systems, the activities of several commercial Cu/Zn oxide catalysts for low temperature steam reforming of methanol have been evaluated in the pilot plant. To determine experimentally the catalytic activity of a given catalyst at a given temperature and pressure, a portion of this catalyst was loaded into a fixed bed reactor and this sample was reduced in-situ in H_2 or in diluted H_2 at temperatures up to 230°C. After the sample reduction, a pre-vaporized feed containing 1.5 moles water per mole of methanol was subsequently admitted into the reactor and reaction were allowed to occur isothermally in the reactor at a given temperature and pressure. After exiting the reactor, the water present in the product gas was partially condensed (at 11°C), and the volume of the product was determined by a gas chromatograph. Using these experimental procedures, the methanol conversion over a given catalyst at a given temperature and pressure could be determined by calculating the carbon balance across the reactor, or by calculating the total amount of hydrogen produced in the product gas. In this report, the activity of each catalyst studied at their respective experimental conditions are summarized in Table 2.

The first sample studied was Girdler's G-66B catalyst. A 100 c.c. portion (14-20 mesh) was loaded into the reactor and reduced in pure H_2 at 230°C (Run No. 6989). The initial CH_3OH conversion of this sample was found to be only 77% at 440°F, 30 psig, 1.5 H_2O/CH_3OH feed (molar ratio) and 440 hr^{-1} space velocity. (The space velocity was defined as the ratio of volume of H_2 produced at S.T.P. at 100% CH_3OH conversion per volume of catalyst). Since the reduction reaction (i.e. $Cu^{2+} \rightarrow Cu^\circ$ or Cu^+) is exothermic, the reactor temperature was quickly raised to about 340°C as soon as hydrogen was admitted into the reactor. Thus, this sample was probably sintered thermally during the reduction step, and the low initial activity could be attributed to this improper reduction procedure. In order to increase the initial activity and to find a proper reduction procedure, a thermal microbalance was used to determine the initial and final reduction temperatures for Cu/Zn oxide catalysts.

When a sample is reduced, the CuO present in the virgin catalyst will be converted to Cu° (or Cu^+) and a weight loss due to this reduction reaction will occur. Therefore, by properly increasing the sample temperature at a given rate (i.e. 2.5°C/min), while flowing hydrogen through the reactor the initial and final reduction temperatures can be determined from the weight loss of the sample versus the sample temperature. As shown in Figure 1, the main weight loss of the sample occurred at temperatures between 140°C and 220°C. Therefore, the initial and final reduction temperatures were 140 and 220°C respectively. Furthermore, in order to avoid a rapid temperature rise due to the exothermic reduction reaction and, thus, to avoid any possible thermal sintering of the sample, it is also advantageous to reduce the sample with diluted H_2, so that the degree of reduction and thus the amount of heat released can easily be controlled. As described in Table 3, a reduction procedure was standardized which permits a Cu/Zn oxide sample to be reduced at the lowest possible temperature in diluted hydrogen, and this procedure was used to reduce all of the commercial Cu/Zn oxide catalysts evaluated in this work.

Using the standard reduction procedure, a new sample of G-66B was reduced and its' initial activity was found to be 100%. However, the activity started to decline after about 90 hours on stream. For example, at 147 hours, the methanol conversion was 92%.

The results of Run No. 6989 and Run No. 6996 indicated that reduction procedure was very important to the initial activity of a Cu/Zn oxide catalyst.

Since T-2130A from United Catalyst Inc. replaces G-66B on the commercial market, the activity of T-2130A was tested with the above experimental procedure. At 440°F, 30 psig and space velocity of 1780 hr^{-1}, the initial activity was 97% methanol conversion, but it declined to 85% conversion after 45 hours on stream (Figure 3, Run No. 7009). For the experimental run at 400°F, 6 psig and space velocity of 440hr^{-1}, the methanol conversion could be maintained at 100% for the first 150 hours, but it gradually declined to 89% at 300 hour (Figure 4, Run No. 7016). Since the experimental conditions used in Run No. 7016 is the reactor design criteria for a 1.5 kw fuel cell reformer system, it may be concluded that methanol leakage from the reformer will start to occur after a short operating period, if T-2130A is loaded into the reformer.

XRD analysis on a sample of virgin T-2130A catalyst showed the presence of some nitrate impurities. In order to find out the effect of these nitrate impurities on its catalytic activity for steam reforming of methanol, a recalcination procedure which would decompose all the nitrate impurities was sought. Again, a thermal microbalance was used to monitor the weight loss of a sample during calcination while the sample temperature was increased at 5°C/min. As shown in Figure 2, the minimum decomposition temperature of this catalyst was 230°C. Furthermore, XRD analysis showed the absence of nitrate impurities after a sample was calcined for 2 hours at 260°C. Therefore, a sample of this catalyst was further calcined in air at 260°C for 12 hours to remove all nitrate impurities before reduction. The activity of this re-calcined catalyst (Run No. 7045) was found to be at 100% CH_3OH conversion for the first 200 hours, but the activity also declined afterward. Thus, by removing the nitrate impurities from T-2130A, the activity could be increased slightly, but this improvement still could not meet one of prototype fuel cell design requirements, that is, about 10,000 hours of catalyst life at 100% CH_3OH conversion. Unreacted methanol can not be tolerated in the phosphoric acid type fuel cell.

The ICI-52-1 catalyst was also evaluated in this study. As shown in Table 2, Figure 3 and Figure 4, a reduced sample of this catalyst had a slightly longer life in both high space velocity and low space velocity tests. But the catalyst life is still too short to satisfy the fuel cell reformer requirement.

Since the commercial Cu/Zn oxide catalysts are very sensitive to chloride and sulfur impurities present in the reactants, a 20c.c sample of a 5% Ag/Al_2O_3 catalyst was installed in front of a ICI 52-1 sample in Run No. 7082 as a sulfur and chloride guard. As shown in Figure 3, the methanol conversion was approximately the same as that determined in Run No. 7076. Though the sulfur and chloride impurities present in this Ag/Al_2O_3 guard are currently being analyzed, it is likely that the decline in activity found in the previous runs were not significantly influenced by the sulfur or chloride impurities present in the feed.

The effect of mass velocity on the catalytic activity was also investigated in Run No. 7092. For this run, the space velocity was maintained at 1780 hr^{-1}, but the mass velocity of the reactants admitted into the reactor was increased four times as compared to that of Run No. 7076. The methanol conversion obtained in this run was close to that observed in Run No. 7076, indicating that, within the experimental range studied, the heat and mass transfer effects on the catalytic activity were not significant.

For low temperature steam reforming of methanol over Cu/Zn oxide catalysts, there are two chemical reactions occuring simultaneously in the reactor. i.e.

Methanol Decomposition: $CH_3OH \rightarrow CO + 2H_2$ -------------(1)
Water gas shift: $CO+H_2O \longrightarrow CO_2+H_2$ -----------------(2)

At a given temperature, pressure and a H_2O/CH_3OH feed ratio, a computer program (called METHANOL) has been written to calculate the thermodynamic equilibrium composition of the product gas due to the above two reactions. Some results of these calculations are shown in Table 4.

The dry gas compositions as determined experimentally (given in Table 5) were close to the equilibrium compositions given in Table 4. Therefore, it may be concluded that the product composition (dry gas) from methanol reforming over Cu/Zn oxide catalysts are close to the thermodynamic equilibrium composition, though it is not in actual equilibrium.

FUTURE PLANS (FIRST QUARTER 1979)

Phase 1 of the contract will be completed in the next quarter. Major items to be accomplished in each task are outlined below:

TASK 1. PROCESS FEASIBILITY STUDIES

- Install the new mixer and preheater into the test unit. Run the hydrogen assisted steam reforming of No. 2 oil at 1750°F over 4 commercial steam reforming catalysts.
- Complete the test run for the catalytic partial oxidation of No. 2 oil with and without steam over the sample composed of Pt/Pd/Rh.

TASK 2. TECHNICAL ANALYSIS

- Revise the computer program ATR-1 to search for conditions where the heats of reaction between partial oxidation and steam reforming are balanced.
- Compare results from the above revised program with calculations performed at Jet Propulsion Laboratories.
- Disucss the thermodynamic calculations for this task with a consultant, Dr. Henry Van Ness, of Rennsylaer Polytechnic Instutute.

TASK 3. METHANOL REFORMING

- Run a process variable study with ICI 52-1 to find conditions where methanol decomposition is accomplished for longer periods of time.
- Test a catalyst prepared by Engelhard for the methanol decomposition reaction and couple it with a low-temperature shift catalyst.

TABLE 1

EQUILIBRIUM COMPOSITIONS FOR STEAM REFORMING OF HYDROCARBONS

Hydro-carbon	Temp. (°F)	Feed Ratio H_2O/C	O_2/C	Pressure (atm)	Data Source	Mole % in Product Gas H_2O	CH_4	CO_2	CO	H_2
CH_4	1200	2.0	0.0	1.0	ATR-1	19.25	4.32	6.80	10.61	59.02
					Schlatter[1]	19.17	4.27	6.80	10.64	59.12
CH_4	1400	4.0	0.0	1.0	ATR-1	36.27	0.05	6.68	7.57	49.44
					Schlatter[1]	36.24	0.04	6.69	7.56	49.47
CH_4	1340	1.5	0.0	1.0	ATR-1	9.94	1.97	3.58	17.55	66.96
					Perry Chilton[2]	9.95	1.99	3.59	17.53	66.94
C_3H_8	1800	4.0	0.0	12.0	ATR-1	41.60	0.04	5.85	9.92	42.60
					Schlatter[1]	41.57	0.04	5.87	9.89	42.62
C_9H_{20}	1800	2.0	0.0	12.0	ATR-1	20.42	0.34	4.42	19.73	55.09
					Schlatter[1]	20.40	0.34	4.44	19.71	55.11

(1) M. J. Schlatter, Special Report No. 2 AD456740, NTIS (1965)

(2) Chemical Engineers' Handbook, 5th edition, McGraw-Hill, N.Y. (1973)

TABLE 2

SUMMARY OF RESULTS ON STEAM REFORMING OF METHANOL (1.5 H_2O/CH_3OH FEED)

Run No.	Catalyst	Temp. (°F)	P psig	% CH_3OH Conversion	S. V.* hr^{-1} H_2	Comment **
6989	G-66B (100c.c)	440	30	~77	440	Reduction in H_2 at 230°C
6996	G-66B (100c.c)	440	30	~100	440	Standard reduction procedure. Activity decline after 90 hrs.
7009	T-2130A (20c.c)	440	30	97	1780	Activity started to decline after 15 hrs. on stream.
7016	T-2130A (100c.c)	400	6	100	440	Activity remained at 100% conversion for 150 hrs. It started to decline afterward.
7045	T-2130A (100c.c)	400	6	100	440	Recalcined sample. Activity started to decline after 200 hrs. on stream.
7058	ICI 52-1 (100c.c)	400	6	100	440	After 320 hrs. at 100% conversion activity started to decline.

$$* \text{ Space Velocity} = \frac{\text{c.c of } H_2 \text{(at s.t.p.) produced at 100\% Methanol conversion}}{\text{c.c of catalyst}}$$

** Standard reduction procedures were used for sample pretreatments except Run No. 6989.

TABLE 2 CONTINUED

SUMMARY OF RESULTS ON STEAM REFORMING OF METHANOL (1.5 H_2O/CH_3OH FEED)

Run No.	Catalyst	Temp. (°F)	P psig	% CH_3OH Conversion	S. V.* $hr^{-1}H_2$	Comment **
7076	ICI 52-1 (20c.c)	440	30	100	1780	Activity started to decline after about 21 hrs. on stream.
7082	ICI 52-1 (20c.c)	440	30	100	1780	Load 5% Ag/Al_2O_3 (20c.c) in front of ICI 52-1 as sulfur and chloride guard.
7092	ICI 52-1 (80c.c)	440	30	99	1780	Effect of mass velocity on % methanol conversion.

$$* \text{ Space Velocity} = \frac{\text{c.c of } H_2 \text{(at s.t.p.) produced at 100\% Methanol conversion}}{\text{c.c of catalyst}}$$

** Standard reduction procedures were used for sample pretreatments except Run No. 6989.

TABLE 3

STANDARD REDUCTION PROCEDURE FOR LOW-TEMPERATURE WATER GAS SHIFT CATALYSTS

1. Pressure test with N_2 at 200 psig at R. T.
2. Flow N_2 at ~60 l/hr, increase temp. to 120°C in N_2.
3. Admit H_2/He mixture to the reactor (~1:1 volume rate). Total flow rate is about ~60 l/hr. Stay for ~1hr at 120°C.
4. Increase the reactor temp. at 15°C/hr to 180°C. Stay for 1 hour at 180°C.
5. Increase the reactor temp. to 200°C. Hold for 1 hour.
6. Reduce the total flow rate to 40 l/hr by cutting down N_2 flow. After ~1 hr, further decrease N_2 flow and increase H_2/He flow to maintain ~40 l/hr flow rate.
7. Flow H_2/He (8.5% H_2) through the reactor for 4 hours at 200°C, 1.5 CFH H_2/He over-night.
8. Increase the reactor temp. to 230°C at 10°C/hr and let reactor temp. line out at 230°C.
9. Final reduction in H_2 for 1 hour at 230°C.
10. Admit 1.5 H_2O/Ch_3OH (molar ratio) feed. Stop H_2.
11. Experimental Conditions:

    35 cc/hr of feed (53% CH_3OH by weight)
    30 psig, 230°C

TABLE 4

EQUILIBRIUM COMPOSITION OF THE PRODUCT FROM STEAM REFORMING OF METHANOL AND WATER GAS SHIFT REACTIONS

Temp. (°F)	Pressure psig	H_2O/CH_3OH*	% CH_3OH Conversion	% Dry Gas Composition H_2	CO	CO_2
440	30	1.50	100	74.73	1.01	24.24
		2.14	70	74.87	0.48	24.64
		3.75	40	74.95	0.21	24.85
400	6	1.50	100	74.82	0.67	24.49
		2.14	70	74.92	0.31	24.77
		3.75	40	74.97	0.13	24.90

* The values given in this column is the ratios of total moles of water in feed to the total moles of methanol converted.

TABLE 5

DRY GAS COMPOSITION

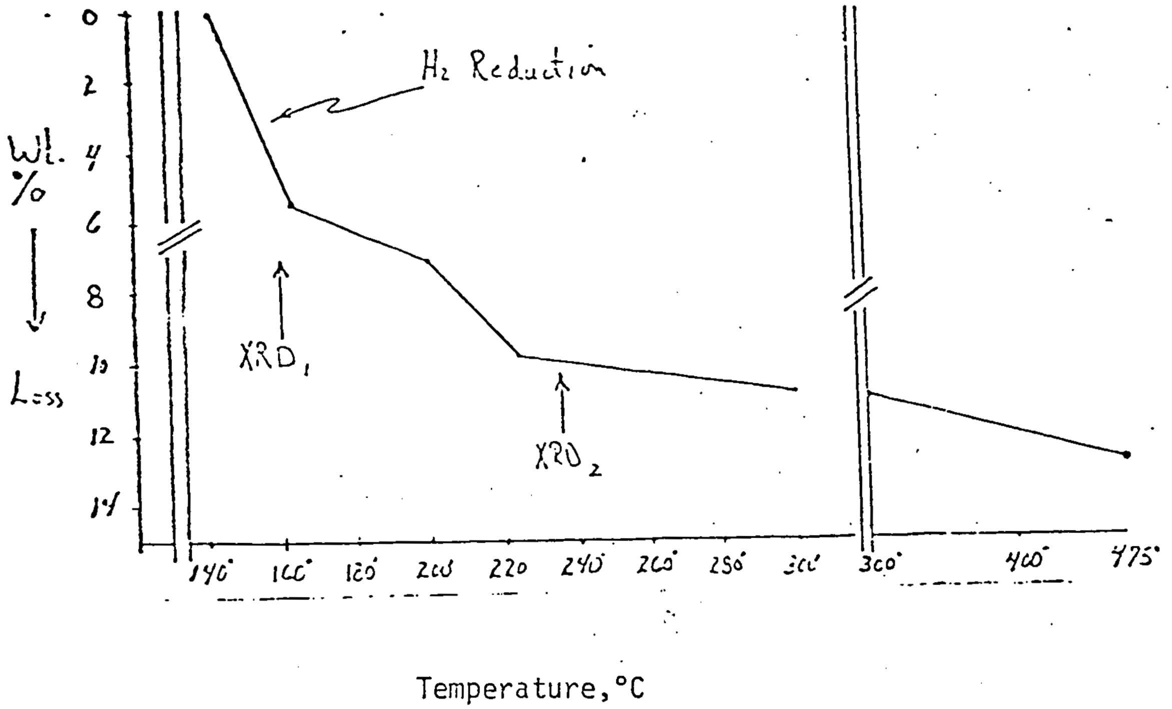
Catalyst	Run No.	Hours on Stream	% CH_3OH Conversion	Pressure psig	Temperature °F	% Gas Composition		
						H_2	CO	CO_2
G66-B	6989	24	70	30	440	73.95	0.26	25.79
		73	40	30	440	73.79	0.53	25.68
	6996	8	100	30	440	73.76	0.38	25.86
		147	92	30	440	73.75	0.35	25.86
ICI 52-1	7058	72	100	6	400	74.12	0.65	25.23
		142	100	6	400	74.42	0.30	25.28
		271	100	6	400	74.46	0.26	25.27
		339	97	6	400	74.71	0.26	25.03
		414	96	6	400	74.84	0.23	24.93

FIGURE 1

TEMPERATURE PROGRAMMED REDUCTION OF VIRGIN T2130A CATALYST

Microbalance Conditions:

Dried in He flow to 83°C/30 mins
Reduced in H_2 from amb. to 475°C @ 2.5°C/min



XRD Results

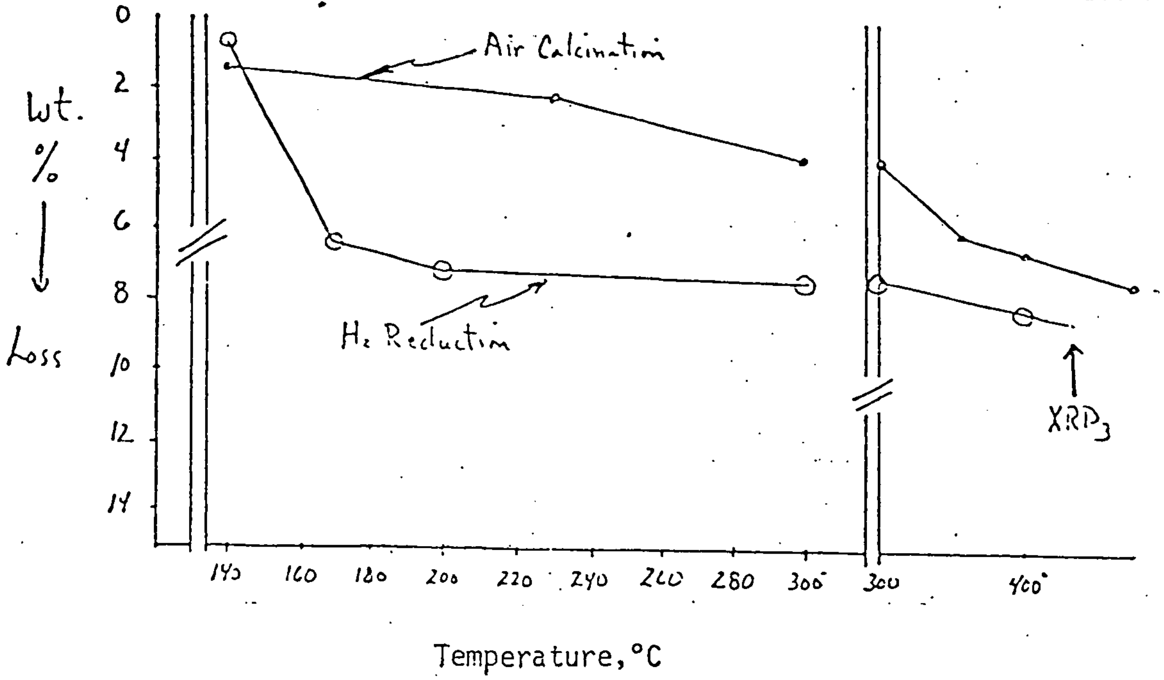
Virgin (as received) → ZnO, CuO w/some Zinc Nitrate Hydroxide

XRD_1 (160°C) → ZnO, CuO w/some Zinc Nitrate Hydroxide

XRD_2 (235°C) → ZnO, CuO w/other possible phases (Cu, CuZn alloy)

FIGURE 2

TEMPERTURE PROGRAMMED REDUCTION OF A RECALCINED T2130A SAMPLE

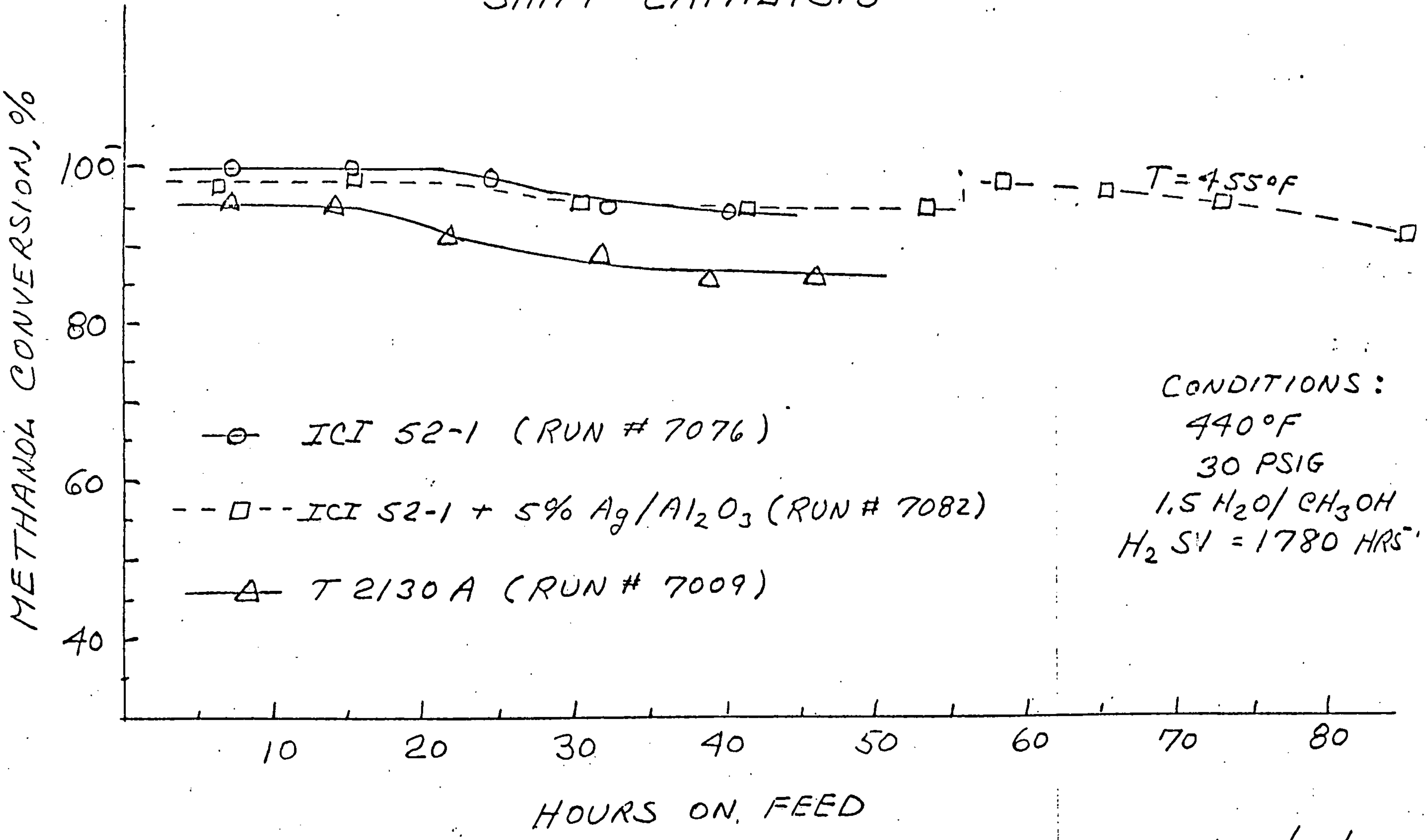


Heated in Air flow to 490°C @ 5°C/min
Self cooled in He flow for 80 min.
heated in H_2 to 490°C 2.5°C/min.

XRD Results

XRD3 (490°C Air, 435°C $H_2 \longrightarrow$ Cu + ZnO)

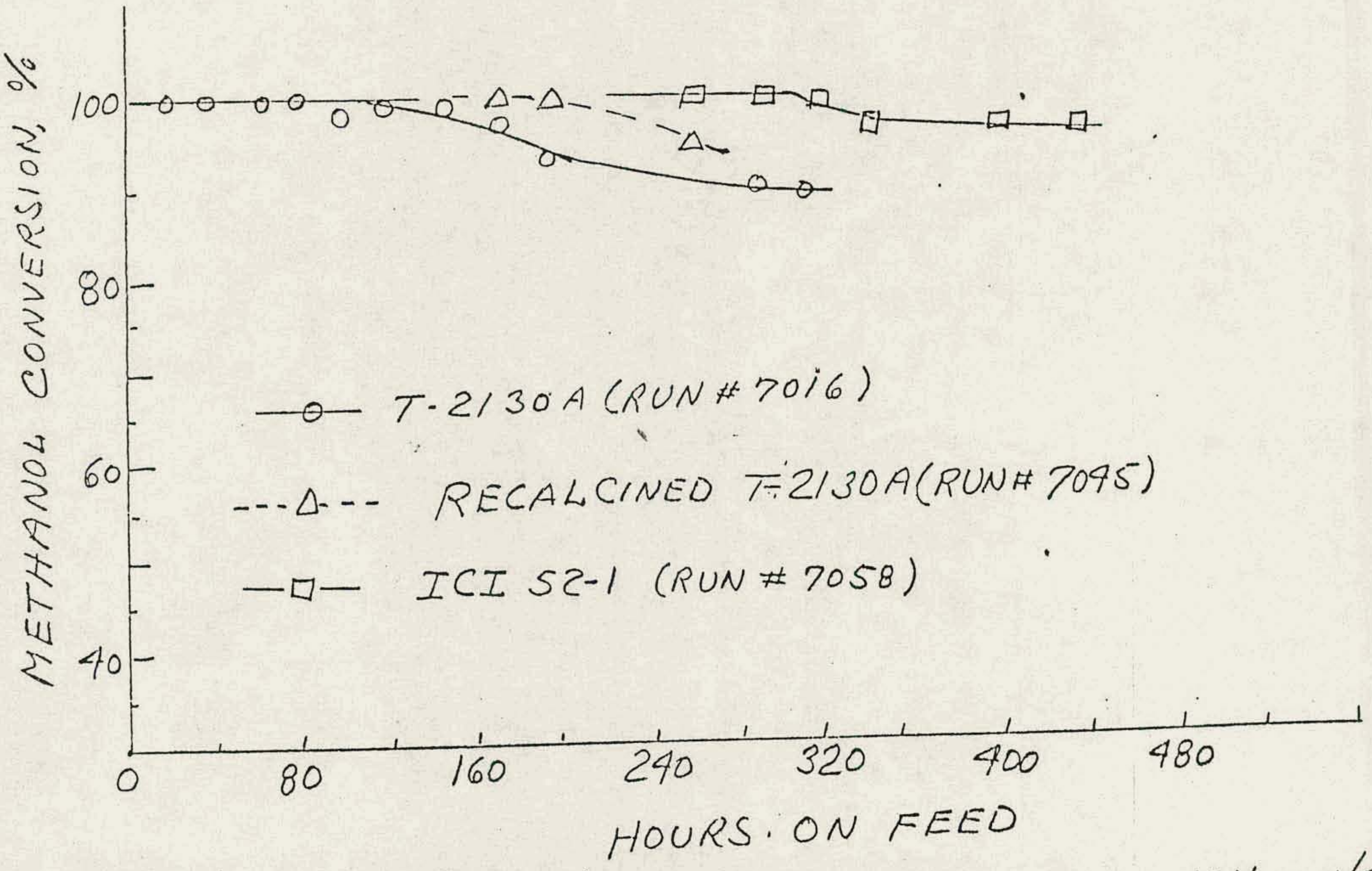
FIGURE 3 METHANOL DECOMPOSITION OVER LOW-TEMPERATURE WATER GAS SHIFT CATALYSTS



HSH 1/22/79

FIGURE 4 AGING RUNS FOR THE STEAM REFORMING OF METHANOL

(400°F, 6 psig, H_2 SV = 400 HRS^{-1}, 1.5 H_2O/CH_3OH)



HSH 1/22/79