IRON-MANGANESE FISCHER-TROPSCH CATALYSTS

By

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ABSTRACT

Various techniques were explored for the preparation of iron/manganese Fischer-Tropsch catalysts. Large surface area manganese oxides or iron/manganese oxides can be prepared but activation of the catalyst causes transformations which greatly reduce the catalysts surface area. A series of 10 Fe/90 Mn catalysts were prepared via different precursors and tested in a microreactor. A large variation in activity was observed for the various catalysts with a catalyst prepared via carbonate precipitation having the best activity and selectivity to liquid product in the gasoline range.

Six catalysts with iron/manganese ratios of 100/0, 57/43, 44/56, 22/78, 10/90, and 0/100 were investigated in a slurry reactor after a standard activation procedure and at identical process conditions. Of these iron-manganese catalysts, the 20/80 and 10/90 have the most stability although deactivation with time on stream occurs with all the catalysts.

INTRODUCTION

Attempts to study Kōlbel's iron/manganese catalyst produced reproducibility problems in the preliminary slurry tests. It was felt that the problem occurred in the preparation of the catalyst. Therefore work was initiated to examine the effect that the method of preparation has on the activity and selectivity of iron/manganese catalysts. While some work exists in the literature on Kōlbel's preparative method, little information is known on the preparation of this catalyst using precursors other than the hydroxide. This study had a three-fold objective:

1. Determine factors involved in the preparation of the catalyst.
2. Determine the activity and selectivity of iron/manganese catalysts prepared by different methods to verify if Kōlbel's method yields the catalyst with best activity and selectively characteristics.
3. Concurrently with the above studies, to conduct slurry reactor tests on catalysts with varying Fe/Mn ratios to determine the major differences in the selectivity and deactivation characteristics of these iron/manganese catalysts and identify which composition was most promising for more detailed study.

The data presented in this talk gives an overview of work completed in FY83.

DISCUSSION AND RESULTS

1. Catalyst Preparation

Kölbel's preparation of the iron/manganese catalyst involves the coprecipitation of a mixture of ferric nitrate and manganous nitrate. Several chemical properties of the system complicate the preparative procedure. Ferric nitrate precipitates at a lower pH then manganous nitrate so a rapid change in pH is required to prevent sequential precipitation from occurring. Manganous nitrate has appreciable solubility which varies with pH, so strict control of the pH is required. Also, the precipitated $Mn(OH)_2$ is unstable and wants to oxidize to a higher valence state. Several alternate preparative techniques were tried to determine if the resultant preparations (of identical composition) yield catalysts of equal quality, or if the preparative technique affects its performance.

The hydroxide coprecipitation can be made quantitative if the manganese species is oxidized to a higher valence state during the precipitation. Table 1 shows the chemistry involved. Potassium permanganate can be used as an oxidizing agent and either MnOOH or MnO_2 can be precipitated depending on the ratio of manganous nitrate to potassium permanganate. The precipitation can also be made quantitative by using ammonium carbonate instead of ammonium hydroxide. The resultant manganous carbonate is insoluble and fairly stable, while ferric carbonate is unstable at 90°C and decomposes to FeOOH.

An alternate approach tried was to prepare mixed crystals of an iron and manganese salts containing a decomposable anion. These are decomposed by pyrolysis to yield the resultant catalyst. A nitrate/citrate mixture was used since the nitrate decomposes at a low temperature and contains no element known to poison F-T catalysts. The formate system seemed interesting since iron formate is known to decompose directly to iron without forming an oxide intermediate.

During the preparation or activation of the catalyst the precursor will decompose into an oxide mixture. This happens during the drying step for those catalysts prepared via hydroxides of manganese. Figure 2 gives the phase diagram for the iron/manganese system. Mn_2O_3 will be the stable phase in the presence of air. It shows that at equilibrium a single phase material containing both iron and manganese exists for those compositions containing low iron contents. At higher iron contents the preparations contain two phases, hematite and Mn_2O_3. Therefore, unless sequential precipitation occurs, the compositions containing 10% Fe (on a metal-only basis) should be single phase. All the 10 Fe/90 Mn catalysts prepared via precipitation with ammonium hydroxide showed only the XRD pattern of poorly crystalline Mn_2O_3. Apparently the precipitated $Mn(OH)_2$ is decomposed and oxidized to Mn_2O_3 during the washing and drying step. This even occurs during the vacuum drying procedure carried out at 140°C.

A. Manganese Oxide Supports

Manganese can be precipiated to yield three definite hydroxide or hydrated oxides, MnO_2, MnOOH, or $Mn(OH)_2$. Small (20 gm) quantities of these were prepared by a batch precipitation technique at 90°C. The precipitates were filtered, washed with several liters of hot water, and vacuum dried at 140°C. Portions of these materials were heated in air or hydrogen for four hours at various temperatures. Their surface areas were measured by the nitrogen BET technique. The results (see Figure 3) show that the resultant manganese oxides exhibit a wide range of surface areas. However, these materials have greatly different resistances to sintering when heated in air or hydrogen. Also the surface area of the "as prepared" oxide made from $Mn(OH)_2$ is sensitive to preparation procedures since two larger batches (200 g) had much lower areas.

Surface area results for a number of precursors and MnO prepared by reducing these precursors at 400°C in hydrogen for four hours are given in Table 1. While MnO_2 has the largest surface area for the "as prepared" materials, $MnCO_3$ yield the highest surface area MnO. But of more significance, none of these pure manganese compounds yield a high surface area MnO, the form which exists under F-T conditions. The addition of a second oxide can greatly increase the surface area of the "as prepared" support and the resultant oxide mixture under reducing conditions. However, its effect on the activity of iron supported on such mixed oxides have not been investigated.

B. Iron/Manganese Catalysts for Microreactor Studies

A series of iron/manganese catalysts were prepared using different precursors. The work was limited to a single composition containing 10% Fe on a metal only basis. A batch precipitation technique was used except for the catalysts prepared via $Mn(OH)_2$. The precursors used and the analyzed compositions of these catalysts are given in Table 2. The preparation based on MnO_2 can be carried out both in basic or slightly acid solution. The acidic preparation causes the precipitation of MnO_2, and possibly some iron, then ammonia was added to insure complete precipitation of the iron. Because of the nature of the crystal structure of MnO_2 an appreciable amount of potassium is incorporated which cannot be removed by washing. In the case of MnOOH a trace of potassium remains due to the difficulty of washing these highly hydrated precipitates.

Surface area data for the as prepared catalyst and samples heated in hydrogen at 400°C for four hours were obtained by the nitrogen BET technique. The addition of 10% iron to the composition greatly increases the surface area of the catalysts prepared via $Mn(OH)_2$ (see Table 3). Again the catalyst prepared via the carbonate appears to be the most stable.

C. Iron/Manganese Catalysts for Slurry Reactor Tests

A series of iron/manganese catalysts with varying iron to manganese ratios were prepared for testing in the slurry reactor. These catalysts were prepared via precipitation of $Mn(OH)_2$. The precipitation was carried out at 90°C in a continuous precipitator similar to that used by Kölbel. The slurry from the precipitator was deposited on a Buchner filter, filtered, and washed with two liters of hot water. The filter cake was then immediately transferred to a vacuum oven and dried at 140°C overnight. The pH in the precipitator was maintained at approximately 9.0.

The composition of these catalysts varied from the target composition at the higher iron/manganese ratios (see Table 4). The iron appears to precipitate quantitatively, but the manganese precipitation is incomplete. The surface area of the catalysts increases with increasing iron content.

2. Microreactor Tests of 10 Fe/90 Mn Catalysts

The catalytic properties of the 10 Fe/90 Mn catalysts were screened in a 3/8" stainless steel microreactor. The "as prepared" catalyst was mixed with glass microbeads (0.5 g catalyst + 0.5 g beads), heated to 250°C in flowing nitrogen, then activated at 250°C in flowing carbon monoxide. At the end of the 24 hour activation period, the reactor was switched to syngas, the temperature raised to 275°C, and the pressure to 200 psig. The exact test conditions are given in Table 5. Product was collected in a cold trap (at 0°C), which disengaged gaseous from liquid products at 200 psig. The gaseous products were let down to atomspheric pressure and collected in sampling bottles for analysis by gas chromatography. The liquid product was removed from the trap, separated into aqueous and hydrocarbon phases and weighed. The small amount of product collected limited the type of analysis possible on the liquid phases. The water content of the aqueous phase was determined by Karl Fischer Analysis. The boiling point distribution of the liquid hydrocarbon phase was determined by gas chromatographic simulated distillation technique.

Data was collected on the activity and selectivity characteristics of each of the 10 Fe/90 Mn catalysts for a 72-80 hour time period. A typical example of the data collected is given in Table 6. The pertinent data obtained on eight of the 10 Fe/90 Mn catalysts tested are give in Tables 7A and 7B. The results indicate that for those catalysts prepared by precipitation with ammonium hydroxide, the best activity is exhibited by the vacuum dried catalyst prepared via $Mn(OH)_2$. Indeed, it appears that conversion of manganese to a higher valence state either during the precipitation, or during the drying step has an adverse effect on activity. This is unfortunate since one would like to do this to make the precipitation quantitative. Of the other methods for preparing the catalyst only the carbonate method appears useful.

The reason for the difference in activity of these catalysts which have the same nominal composition is not known. One possible explanation is that due to nucleation effects the iron species in these catalysts offer different resistance to reduction. A preliminary attempt was made to check this out by looking at the reduction characteristics using TGA techniques. Interpretation of the TGA data is difficult because during reduction the "as prepared" catalyst can show a weight change both due to reduction and loss of structural hydroxyl groups.

Figure 4 shows that on heating a catalyst prepared via $Mn(OH)_2$ in helium, water is lost over the entire temperature range up to 600°C. This is very similar to the behavior observed for alumina. If the dehydrated sample is then cooled and reheated in air a weight gain would be expected if the manganese is originally present in a lower valent state. The oxidation treatment should produce a mixture of Mn_2O_3 and Fe_2O_3, either in a free or combined form. A subsequent hydrogen reduction will then give an estimate of the total reduction extent in the catalyst. Figure 5 shows that TGA results for a 10 Fe/90 Mn catalyst prepared via the carbonate. In this case we see an appreciable fraction of the manganese is in the divalent valent state after dehydration.

The results of this TGA investigation on six of the 10 Fe/90 Mn catalysts and pure $MnCO_3$ and precipitated Fe_2O_3 are given in Table 8. The data indicates that all the catalysts contain manganese as a mixture of Mn^{+2} and Mn^{+3} with the formate containing nearly pure MnO after the decomposition in helium. Also, only in the case of the catalyst prepared via the formate is reduction complete. From the data one concludes that the manganese is reduced to MnO, but supplementary measurements specific to iron are needed to determine the extent of reduction of iron.

Since the catalysts are activated in CO, the reduction data in this gas would be more pertinent. However, due to the Boudouard reaction carbon is deposited on the catalyst at higher temperatures so that the TGA curve exhibits a minimum around 440°C. However, isothermal reduction curves can be obtained at lower temperatures. The data in Table 9 show that the catalysts prepared via $Mn(OH)_2$ and dried in various ways show different rates of reduction in CO. These differences correlated with those seen in the activity of the activated catalysts.

3. Slurry Reactor Tests

Concurrently with the studies on the 10 Fe/90 Mn catalysts a series of tests were made in a slurry reactor. These tests were limited to iron/manganese catalysts prepared via $Mn(OH)_2$ as described in Section 1C. The composition and surface areas for these catalysts are given in Table 4. The slurry reactor (see Figure 6) is the same as that used last year for the fused iron work. It is a 1-liter autoclave filled with 500 ml of normal paraffin wax. Catalyst is added to the molten wax, the autoclave sealed, purged and pressurized to 200 psig. An outlet tube fitted with a stainless steel filter is used to periodically adjust the liquid level to 500 cc. It is also fitted with a condenser on the gas outlet to minimize the loss of heavy wax fraction.

The test conditions for the slurry test are given in Table 10. The catalyst in all the tests were initially activated in an identical manner; an in-situ reduction with CO followed by synthesis conditions. A reduction temperature of 275°C is required in the slurry reactor, while 250°C is sufficient in the microreactor tests. Reproducibility between tests with the same catalyst was always achieved provided identical activation procedures were followed.

Six catalysts with iron/manganese ratios of 100/0, 57/43, 44/56, 22/78, 10/90 and 0/100 were investigated. During several of the tests at low space velocities or at high temperatures and thus high conversion, the impeller speed was varied to insure that bulk mass transfer and thermal resistances were minimal and that intrinsic kinetics were obtained. The results obtained for the iron/manganese catalysts are shown in Table 11. These studies showed that a one-to-one correspondence does not necessarily exist between gas-phase microreactor studies and thru-phase slurry studies. Also pure precipitated manganese did not show activity for synthesis gas conversion under our test conditions. Activation of these iron/manganese catalysts was found to have an important influence on their behavior.

Activity for conversion of syngas was found to increase with iron content of the catalyst. However, olefin selectivity in the C_2–C_4 fraction decreased with iron content. There are no large variations in the hydrocarbon distribution except that the catalysts with lower iron content seem to show a suppression of methane production. This phenomenon cannot be explained at this time. The liquid product produced is highly olefinic particularly at the low iron contents. Using a model for a mixed slurry reactor, activity coefficients were obtained for all tests showing that activity increases with the iron content of the catalyst. Arrehenius plots indicate activation energies between 17.3-19.3 kcal/mol, which is not too different from that found for unpromoted precipitated iron (24.5 kcal/mol) and fused iron (25.3 kcal/mol).

All of the iron/manganese studied showed aging effects. The conversion of CO falls rapidly with time on stream for those catalysts containing high iron contents (see Figure 7). The catalysts with the low iron/manganese ratios have much better stability, but still show loss of activity. Along with falling conversions the light olefin yield decreases with time on stream and the olefin content of the liquid product changes to a product containing more internal olefins rather than alpha-olefins.

CONCLUSIONS

1. The surface area of manganese oxides depends on the valence state of the manganese in the oxide and its method of preparation. But MnO is the stable form under F-T conditions and large changes in surface area occur when the various manganese oxides transform into this phase. Our

results indicate that the surface area of MnO produced from various precursors decreases in the order:

$$MnCO_3 > MnOOH = Mn(OH)_2 > MnO_2$$

2. The addition to MnO of a second oxide, such as iron, chromium, or titanium, increases its surface area and decreases its tendency to sinter.

3. The precipitation of manganous nitrate by ammonium hydroxide is not quantitative, but can be made quantitative by the oxidation of manganese to a higher valence state. However, this appears to have an adverse effect on the activity of the catalyst.

4. For catalysts prepared by a hydroxide precipitation technique the best activity is obtained by Kolbel's procedure involving the precipitation of $Mn(OH)_2$ and FeOOH, followed by vacuum drying. Indeed, it appears that conversion of manganese to a higher valence state either during the precipitation, or during the drying step has an adverse effect on its activity.

5. Iron/manganese catalysts prepared via carbonate precursors are as active as those prepared via hydroxide precursors. Of the other methods tried none yielded satisfactory catalysts.

6. The method of activation of these iron-manganese catalysts has an important influence on their behavior in both gas-phase and slurry-phase reactors. A higher activation temperature was required in the slurry reactor than needed in the gas-phase reactor when using a CO activation procedure. Work is needed to understand the factors involved in activation.

7. At our present level of understanding an activity test using a standard activation procedure does not appear to be an effective method for screening Fe/Mn catalysts.

8. Of the iron/manganese catalysts investigated in the slurry reactor, the 10/90 and 20/80 compositions have the most stability, although deactivation occurs with time on stream for all the catalysts. Along with falling conversions, the light olefin yield decreases and the olefin content of the liquid product changes to a product containing more internal olefins rather than alpha-olefins.

TABLE 1. Surface Area Data for Manganese-Based Supports

Preparation	SA (m^2/G) 140°/Vacuum	SA (m^2/G) 400°/4 hr/H_2	XRD Phase
$Mn(OH)_2$	23	19	α-Mn_2O_3
$Mn(OH)_2$-cp	25	27	α-Mn_2O_3
MnOOH	92	24	α-Mn_2O_3
MnO_2	144	4	γ-MnO_2
$MnCO_3$	4	35	$MnCO_3$
Mn-Cr Oxide (76/24)	225	(97)	α-Mn_2O_3
Mn-Ti Oxide (50/50)	379	263	———

TABLE 2. Chemical Analysis of 10 Fe/90 Mn Catalysts

Method	% Fe	% Mn	% K	% Fe (Metal Only Basis)
MnO_2-basic	5.3	46.2	1.3	10.0
MnO_2-acidic	5.4	48.2	2.0	9.7
$Mn(OH)_2$-vacuum dried	6.7	56.9	—	10.5
$Mn(OH)_2$-nitrogen dried	6.4	61.7	--	9.4
$Mn(OH)_2$-air dried	7.6	60.7	—	11.1
MnOOH	6.2	55.6	0.2	10.0
Carbonate	4.4	40.3	--	9.8
Formate	3.6	29.6	—	9.4
Nitrate/Citrate	5.7	55.1	—	9.4
Nitrate/Citrate/Celite	3.2	28.0	—	10.2

TABLE 3. Surface Area Data for 10% Fe/90% Mn Preparations

Preparation	SA (m^2/g) 140°C/Vacuum	SA (m^2/g) 400°C/4 hr/H_2
$Mn(OH)_2$-nitrogen dried	82	26
$Mn(OH)_2$-vacuum dried	82	30
$Mn(OH)_2$-air dried	62	27
MnO_2 (Acid)	86	15
MnO_2 (Basic)	144	8
MnOOH	114	13
$MnCO_3$	114	40
Nitrate - Citrate	14	16
Fe-Mn Formate	6	13

TABLE 4. Iron Manganese Catalysts for Slurry Reactor

Target Ratio	pH Filtrate	% Fe	% Mn	% Fe (Metal Only Basis)	BET SA m^2/g
10/90	9.1	6.7	56.9	10.5	82
10/90	9.5	6.4	60.1	9.6	—
20/80	9.2	15.0	53.8	21.8	105
35/65	8.7	28.2	35.5	44.3	121
50/50	9.1	36.1	27.5	56.8	171
50/50	9.2	35.8	24.9	59.0	—

TABLE 5. Pretreatment and Reactor Conditions for the Microreaction Test

1. <u>Pretreatment Conditions</u>

   Heat: RT-250°C in N_2

   Hold: Temp = 250°C

   Pressure = 14.5 psi

   CO Flowrate = 3600 cc/(hr)(g cat.)

   Time = 20 hr

2. <u>Reaction Conditions</u>

   Temperature = 275°C

   Pressure = 200 psi

   Gas = 1:1 CO/H_2

   Flowrate = 3600 cc/(hr)(g cat.)

TABLE 6. Microreactor Test Results for 10 Fe/90 Mn Prepared via $Mn(OH)_2$ and Vacuum Dried

Conversion Data			
Time on Stream	23	53	77
H_2 Conversion (%)	29.8	29.3	29.1
CO Conversion (%)	34.8	33.1	32.3
(H_2 + CO) Conversion (%)	32.8	31.2	30.5
Material Balance	92.9	96.2	95.3
Activity [mol CO/(hr)(g Fe)]	0.375	0.357	0.307
Mole % Olefin in Gas Fraction			
C_2	72.1	73.9	75.1
C_3	89.9	90.1	90.2
C_4	88.7	88.4	88.7
Rate Aqueous Phase Production (g/hr)	0.066	0.073	0.078
Rate Hydrocarbon Phase Production (g/hr)	0.036	0.047	0.048
Distribution in Hydrocarbon Phase			
C_4 - 205°C	60	68	70
205°C - 345°C	14	19	20
> 345°C	26	13	10
Carbon Distribution in Products (Atom %)			
CO_2	26.9	29.1	26.7
CH_4	3.6	3.2	3.3
C_2	6.1	5.4	5.3
C_3	5.9	6.8	5.3
C_4	2.6	3.6	4.1
Liquid Product (diff)	54.9	51.9	55.3
Oxygen Distribution in Products (Atom %)			
CO_2	53.8	58.2	53.3
H_2O	0.3	0.7	1.6
Unaccounted	45.9	41.1	45.1

TABLE 7A. Microreactor Activity Data*

Preparation Method	$Mn(OH)_2$ (Vacuum)	$Mn(OH)_2$ (Nitrogen)	$Mn(OH)_2$ (Air)	MnOOH
Conversion Data				
(H_2 + CO) Conversion (%)	31.2	9.6	15.9	12.9
Activity [mole CO/(hr)(g. Fe)]	0.357	0.145	0.171	0.175
Aqueous Phase Product (g/hr)	0.073	0.052	0.053	0.028
HC Phase Product (g/hr)	0.047	0.017	0.016	0.016
Mole % Olefin				
C_2	73.9	81.0	65.9	65.5
C_3	90.1	91.4	87.9	86.0
C_4	88.4	88.5	86.3	81.8
Distribution in Liquid Hydrocarbon Phase				
C_4 - 250°C	68	76	79	4
205°C - 345°C	19	18	12	26
> 345°C	13	6	9	70

*Data taken at 48 hours on stream.

TABLE 7B. Microreactor Activity Test*

Preparative Method	Carbonate	Formate	Nitrate/ Citrate	Nitrate/ Citrate/ Celite
Conversion Data				
(H_2 + CO) Conversion (%)	48.0	5.5	14.3	10.8
Activity [mole CO/(hr(g Fe))]	0.523	0.065	0.200	0.294
Aqueous Phase Product (g/hr)	0.118	0.002	0.034	0.035
HC Phase Product (g/hr)	0.055	nil	0.016	nil
Mole % Olefin				
C_2	47.4	75.7	89.1	25.9
C_3	85.2	91.1	92.5	72.4
C_4	84.8	35.9	92.6	75.7
Distribution in Liquid Hydrocarbon Phase				
C_4 - 205°C	99	—	95	—
205°C - 345°C	1	—	5	—
> 345°C	0	—	0	—

*Data taken at 48 hours on stream.

TABLE 8. TGA Results on Iron/Manganese Catalysts

Sample	He	He:Air	He:Air:H_2	CO
$Mn(OH)_2$-vacuum dried	-5.2	1.6	-11.7	-9.5 (455°C)
$Mn(OH)_2$-nitrogen dried	-3.2	3.2	-12.6	-10.5 (445°C)
$Mn(OH)_2$-air dried	-4.1	3.3	-12.6	-11.5 (440°C)
MnOOH	-6.8	1.8	-11.1	
$MnCO_3$	-32.0	5.7	-12.0	
Nitrate/Citrate	-7.0	1.4	-12.5	
Formate	-52.5	10.7	-13.4	
$MnCO_3$	-39.4	11.0	-10.5	-12.4
ppt Fe_2O_3	-11.5	0	-29.8	

1. $Mn_2O_3 \rightarrow MnO$: -11.3%; $Fe_2O_3 \rightarrow Fe$: 30.1%; Mixture = -13.2

2. Linear program to 700°C

TABLE 9. Isothermal Reduction of 10 Fe/90 Mn Catalyst in CO at 275°C[1]

% wt Loss	Preheat[2]	1 hr	1.5 hr	3 hr
Vacuum dried	3.4	8.4	10.0	11.0
Nitrogen dried	1.7	7.5	8.6	9.1
Air dried	2.3	9.3	9.9	10.0

$Mn_2O_3 \rightarrow MnO$: 11.3%; Mixture: 13.2%

[1] Catalyst prepared via hydroxide

[2] 30 minute linear preheat in helium to 275°C

TABLE 10. Process Conditions for the Slurry Reactor Tests

Catalyst:	Iron/Manganese
Particle Size:	< 44 Micron
Liquid Medium:	n-paraffin wax
Catalyst Loading:	100 grams/liter of slurry
Gas Space Velocity:	90-360 hr^{-1}
Temperature:	250-300°C
Pressure:	200 psig
Impellor Speed:	1000 rpm
Feed Gas Ratio:	$1H_2/1CO$

TABLE 11. Results of Slurry Reactor Tests
For Iron/Manganese Catalysts[1]

Fe/Mn - Ratio	60/40	40/60	20/80	10/90
(H_2 + CO) - Conversion (%)	61.7	54.5	38.7	2.39
Hydrocarbon Distribution, wt%				
CH_4	9.0	9.2	6.8	7.2
C_2-C_4	32.3	35.4	34.2	35.1
C_5^+	58.7	55.4	59.0	57.7
% Olefin in C_2-C_4 Fraction	59.5	56.7	79.5	70.7
Internal/Alpha-Olefin Ratio Oil	.63	.56	.26	.86
Liquid Product Composition, Vol%				
Aromatics	8	8	11	7
Olefins	64	65	72	73
Saturates	27	27	17	20
Activity Constant, k x 10^6 [2]	4.2	3.3	1.8	0.9

1. Process conditions: Activation in CO; $1H_2/1CO$, 275°C, 200 psig, and 180 hr^{-1}. Data taken at end 47 hour.

2. Activity constant obtained by fitting data to model developed of Satterfield for slurry reactor.

CHEMISTRY

Manganese

$$Mn^{+2} + 2\ OH^{-} = Mn(OH)_2$$

$$4\ Mn^{+2} + MnO_4^{-} + 7\ OH^{-} = 5\ MnOOH + H_2O$$

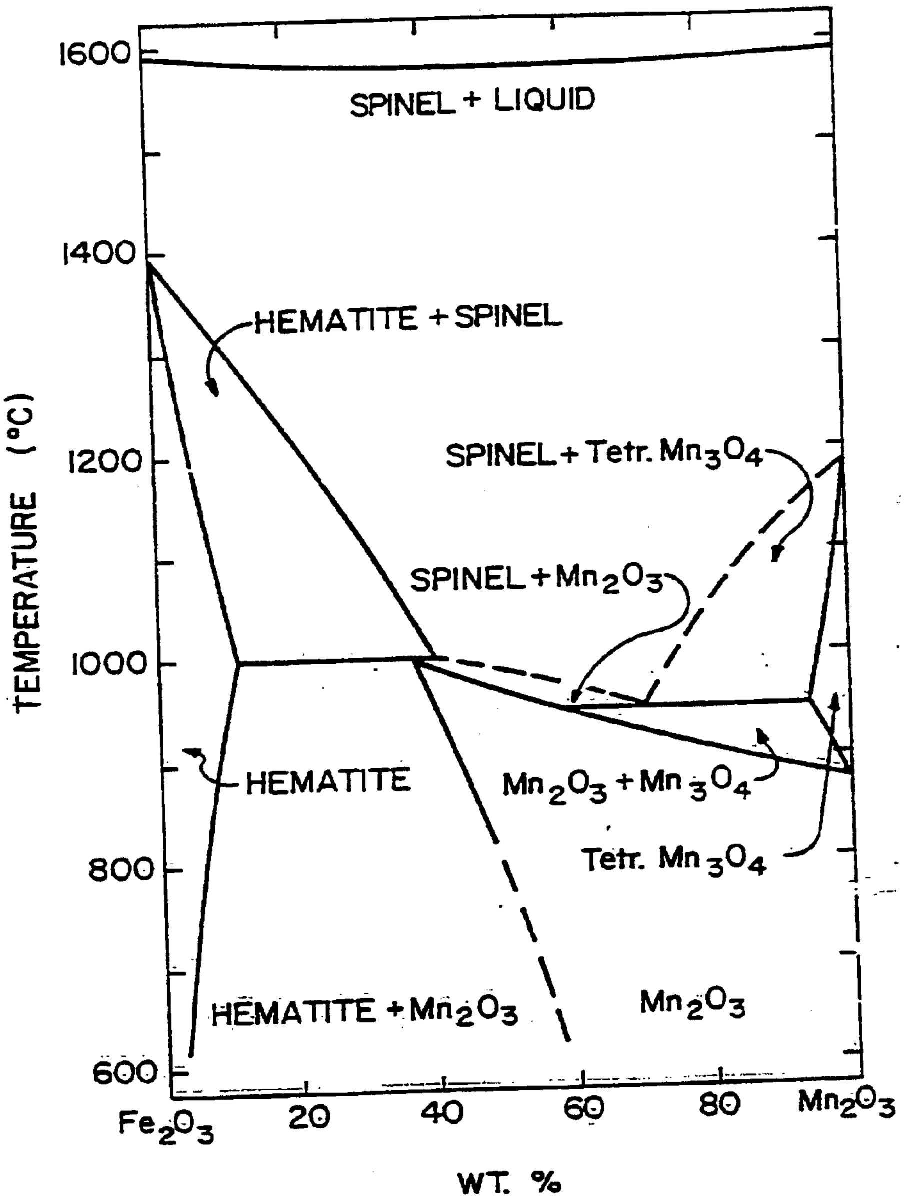
$$3\ Mn^{+2} + 2\ MnO_4^{-} + 4\ OH^{-} = 5\ MnO_2 + 2\ H_2O$$

$$Mn^{+2} + CO_3^{=} = MnCO_3$$

Iron

$$Fe^{+3} + 3\ OH^{-} = FeOOH + H_2O$$

$$Fe^{+3} + CO_3^{=} + H_2O = FeOOH + H^{+} + CO_2$$


1600
1400
1200
1000
800
600
TEMPERATURE (°C)
SPINEL + LIQUID
HEMATITE + SPINEL
SPINEL + Tetr. Mn_3O_4
SPINEL + Mn_2O_3
HEMATITE
Mn_2O_3 + Mn_3O_4
Tetr. Mn_3O_4
HEMATITE + Mn_2O_3
Mn_2O_3
Fe_2O_3
20
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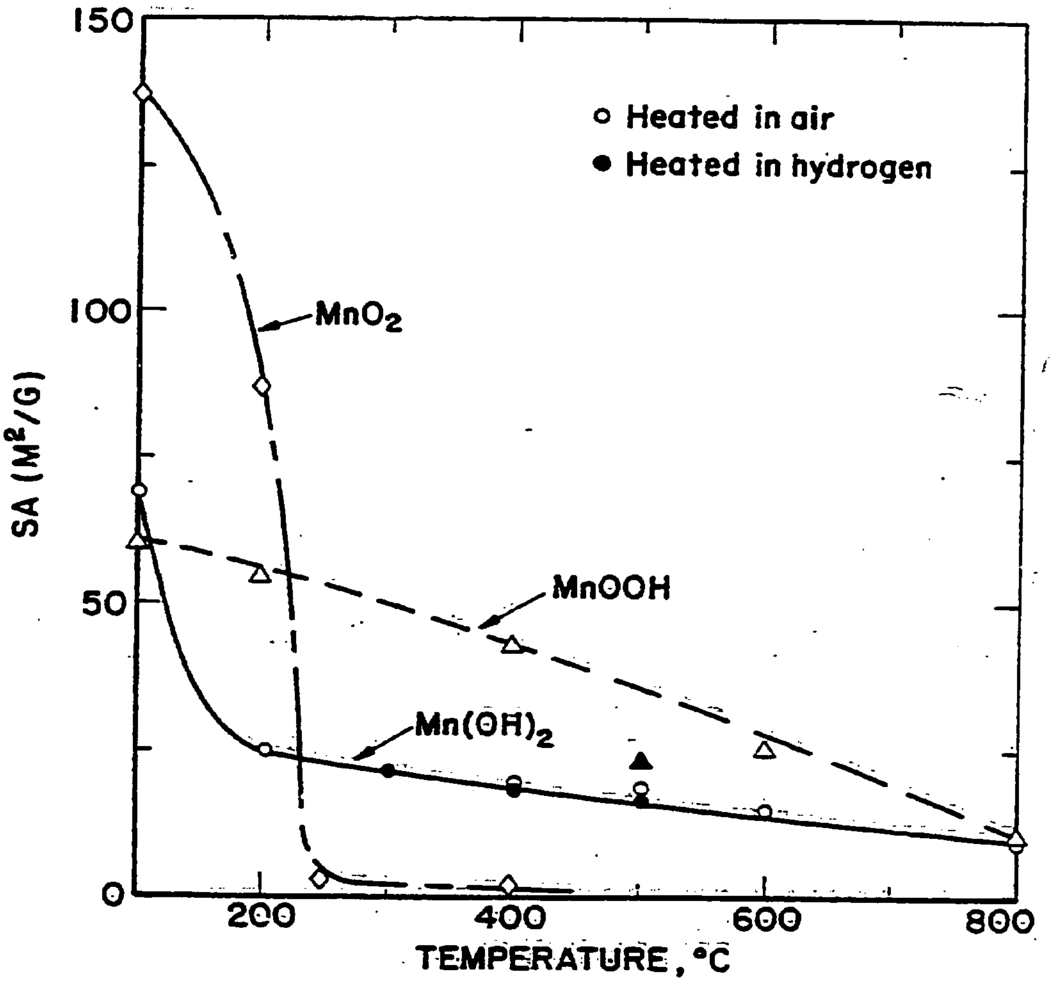
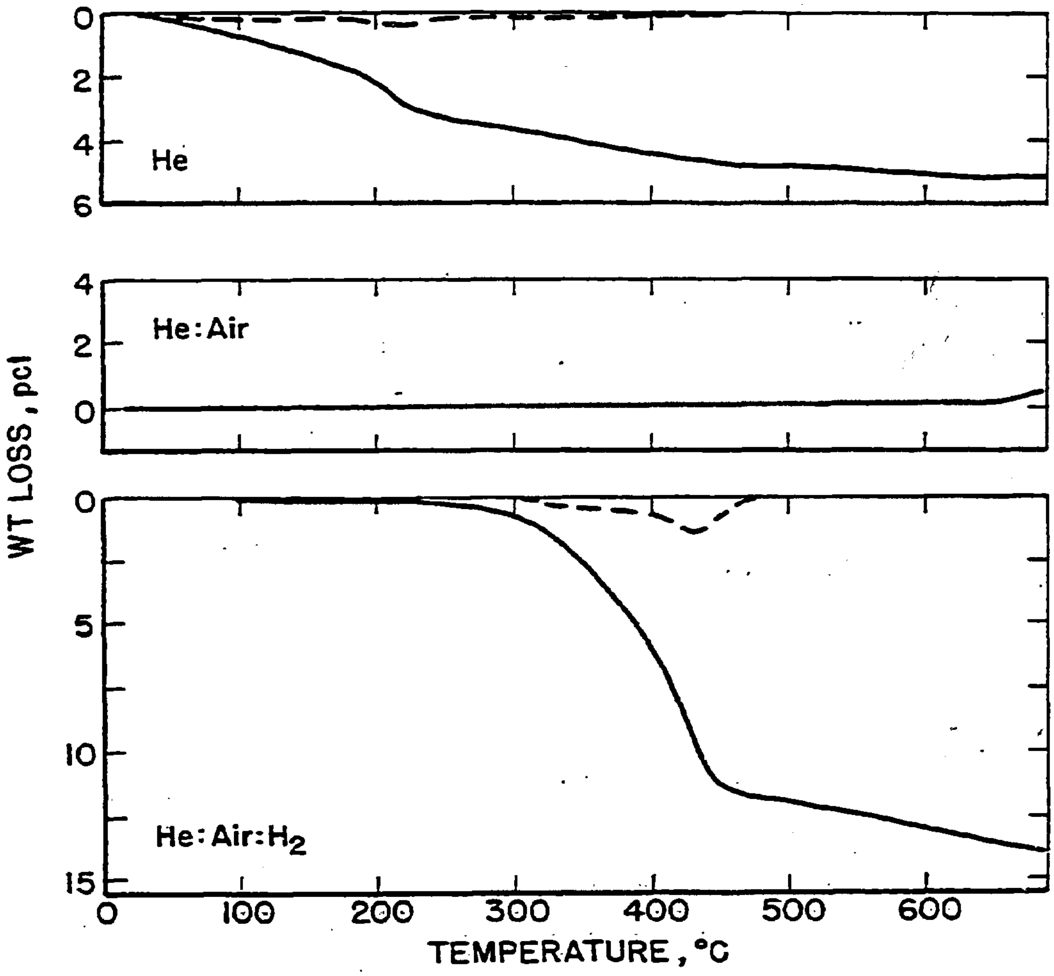
Mn_2O_3
WT. %

BSI-4224


150
100
50
0
SA (M²/G)
200
400
600
800
TEMPERATURE, °C
○ Heated in air
● Heated in hydrogen
MnO₂
MnOOH
Mn(OH)₂

BSI/4199

Ret 51540 10Fe/90Mn [$Mn(OH)_2$]



BSI/4197

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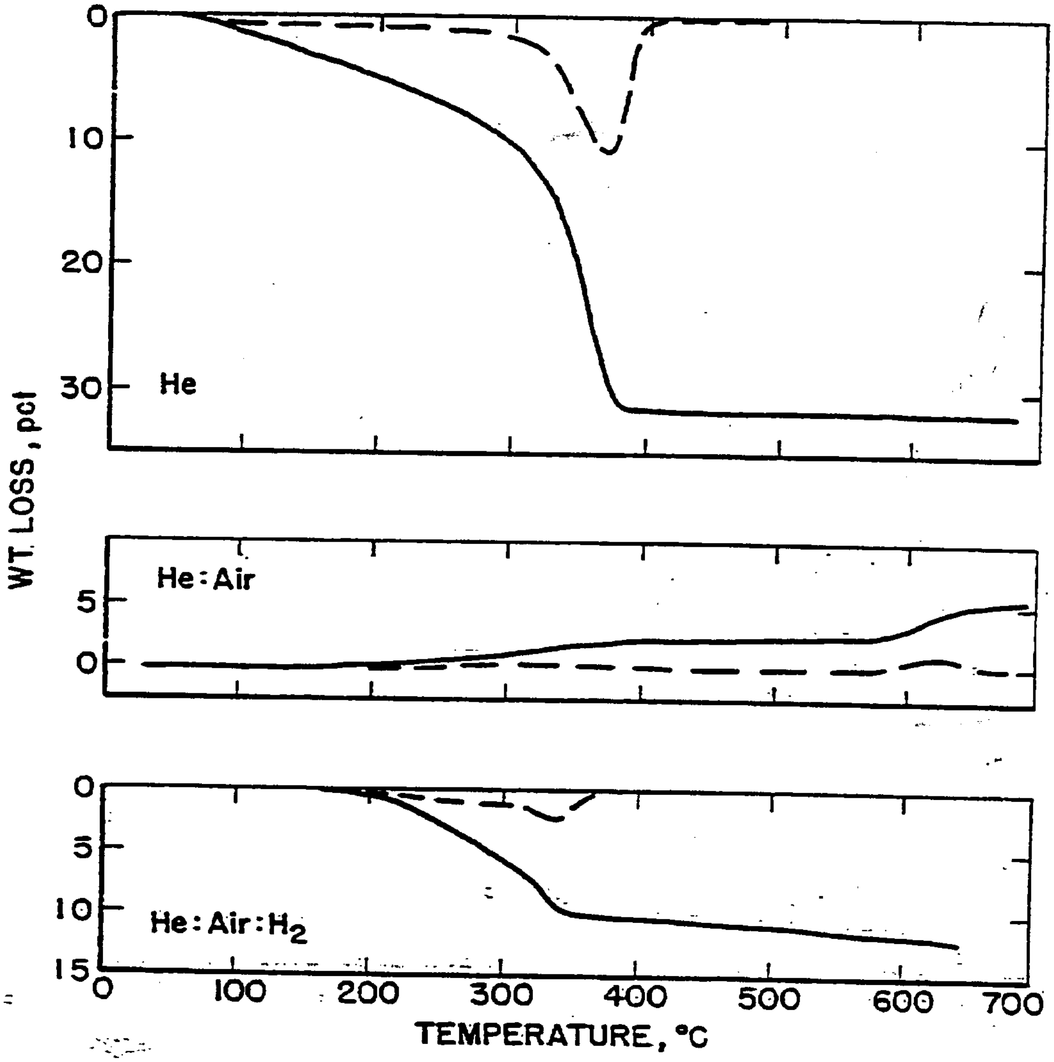

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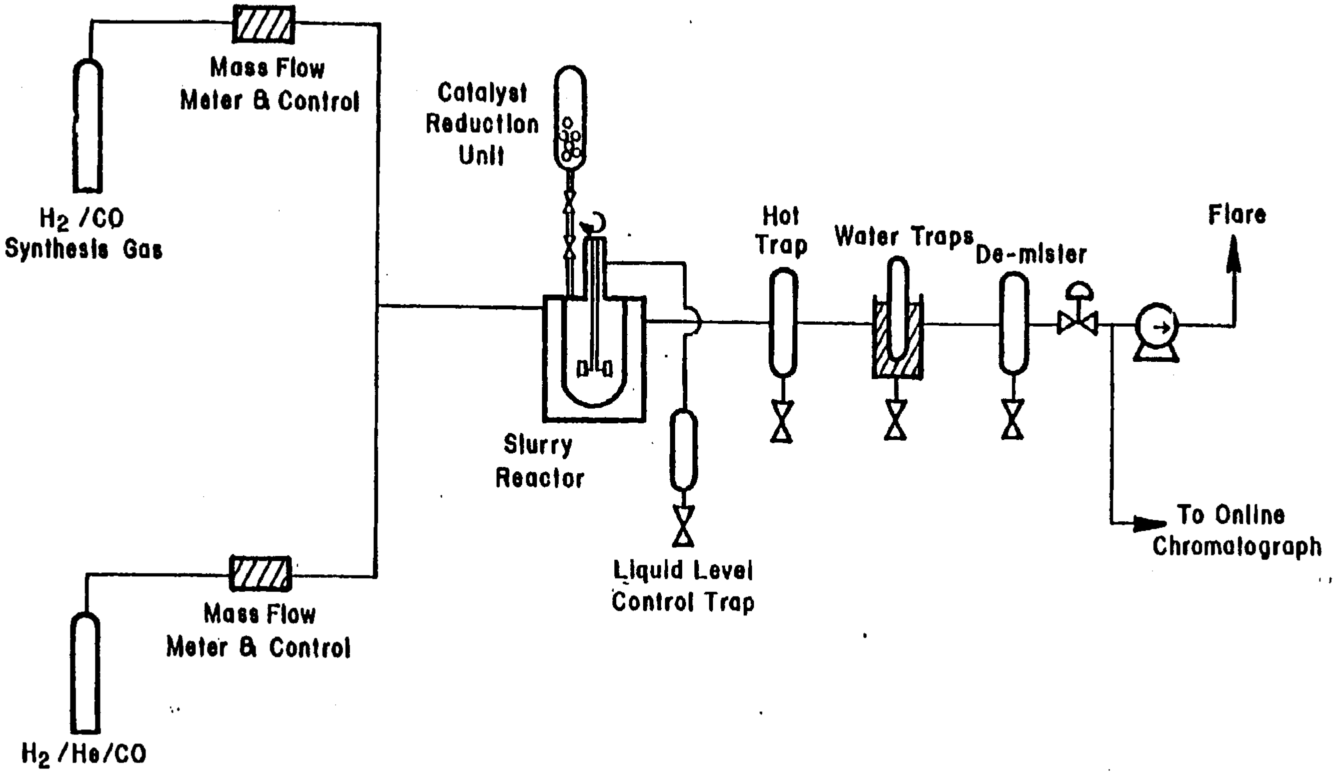
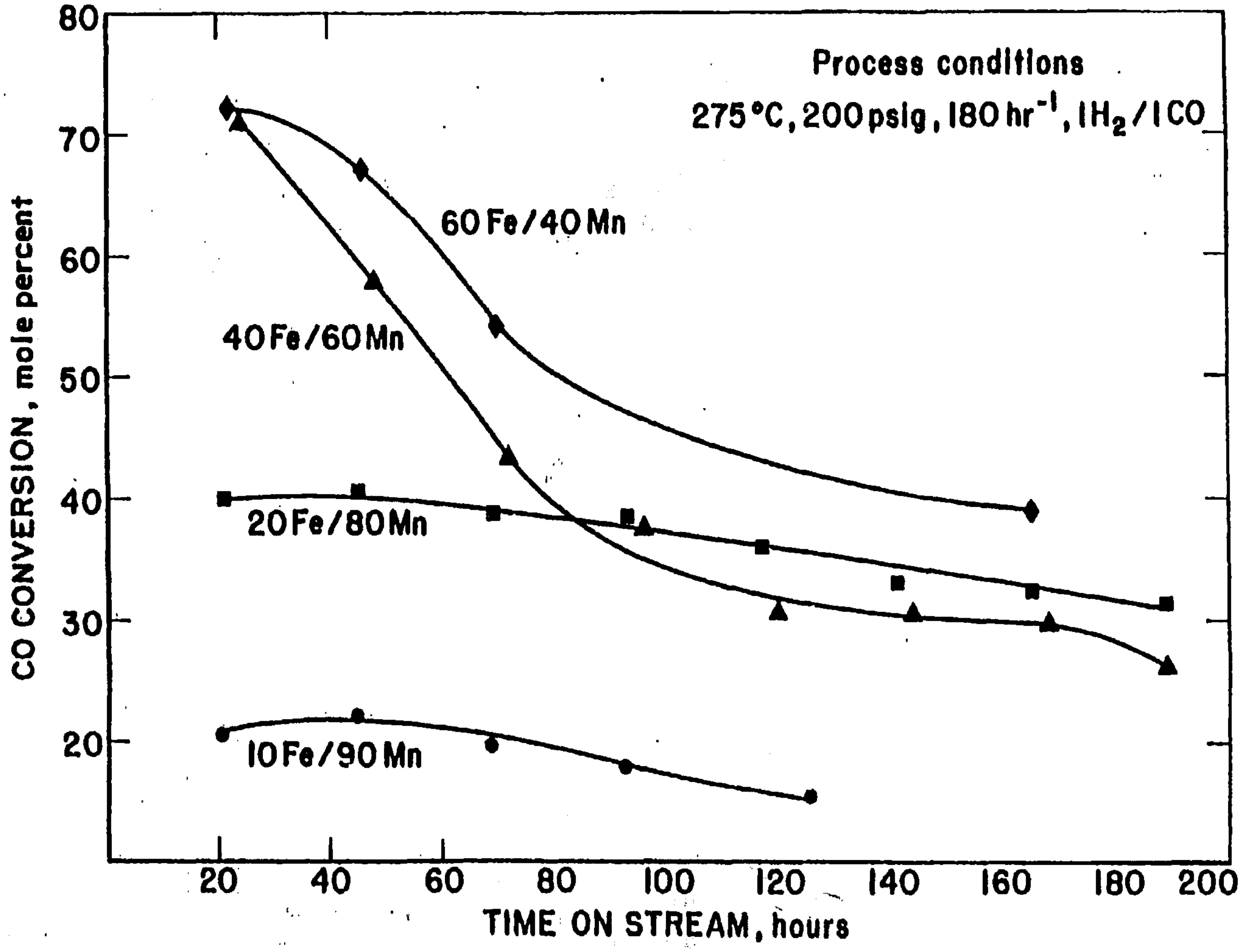


SCHEMATIC SLURRY REACTOR

BSI-257


Process conditions
275°C, 200 psig, 180 hr^{-1}, 1H$_2$/1CO
60 Fe/40 Mn
40 Fe/60 Mn
20 Fe/80 Mn
10 Fe/90 Mn
CO CONVERSION, mole percent
80
70
60
50
40
30
20
TIME ON STREAM, hours
20
40
60
80
100
120
140
160
180
200
USK4190