III SYNTHESIS OF AROMATIC HYDROCARBONS

Introduction

Single-stage direct conversion of synthesis gas into aromatic hydrocarbons is a demonstrated catalytic process. Combination of acidic synthetic zeolites, such as Mobil's ZSM-5, and FTS catalysts have been shown by Chang et al.[1,2], Seitzer,[3] and Rao et al.[4] to produce benzene, toluene, and mixed xylenes from syngas with high selectivity. Combinations of catalysts selective for methanol synthesis and ZSM-5[5-7] or other zeolites[8] have also been shown by Shamsi et al.,[5] Bruce et al.,[6] and Varma et al.,[7] to produce BTX with high selectivity. The zeolite may synergistically convert the unstable intermediate synthesis products, olefins or alcohols, into the more thermodynamically stable aromatics. However, the advantage of single-stage reaction is generally offset by the disadvantage of nonoptimal operating conditions of sequential reactions. As a consequence, Mobil has developed the methanol-to-gasoline (MTG) process with ZSM-5 to convert syngas into gasoline following conventional methanol synthesis, a commercially established technology.

Single-stage aromatics synthesis has two principal disadvantages: (1) the compromised operating conditions have suboptimal yields and (2) the catalytic active components are deactivated by carbon deposition (coking). FTS or methanol synthesis is thermodynamically favored at low temperature and high pressure, whereas conversion of olefins or alcohols to aromatics is favored at high temperature and low pressure. Low temperature operation (500 K) slows conversion into aromatics, whereas high temperature operation (700 K) tends to produce too much light alkane, especially methane, and also tends to promote rapid deactivation because of carbon deposition on the catalyst. Thus, the synergistic potential of dual-function catalysts to produce high selectivity and high conversion has not been realized, and two-stage processing is currently a more attractive technology.

Direct aromatic hydrocarbon synthesis over a dual-function catalyst with unusually low concentration of hydrogen in the reactant gas has the potential advantages of high aromatic yields, stoichiometrically and thermodynamically limited methane yield, relatively dry product gas, and nearly complete hydrogen consumption. The principal difficulty in processing low hydrogen syngas is the need to suppress the greater tendency for carbon deposition on the catalyst and subsequent catalyst deactivation. In our previous study (Section II), we found the sulfur-treated iron catalysts did not deactivate during FTS synthesis with $H_2/CO = 1$ syngas. Therefore, we investigated several combinations of zeolites with the the coking-resistant sulfur-treated fused iron catalysts for FTS performance and aromatic hydrocarbon production in a fixed-bed reactor with low hydrogen syngas.

Background

Achieving the goal of efficient single-stage conversion of olefins to aromatics depends on identifying one or more catalysts that use low-hydrogen syngas, especially those that resist formation of deactivating carbon. The single-stage conversion of syngas to aromatic hydrocarbons is a feasible and demonstrated concept. The unique aspect of our approach is the evaluation of catalyst performance under conditions expected to favor relatively severe carbon deposition, i.e., low H_2/CO ratio (0.5) and moderately high temperature. The selection of candidate catalysts is discussed below following a brief review of earlier research on the direct conversion of syngas to aromatics. Finally, carbon deposition is discussed in detail.

Direct Synthesis of Aromatic Hydrocarbons

Several reports of direct conversion of syngas to aromatic hydrocarbons have been published the last decade. Both promoted FTS and methanol synthesis catalyst components with a strongly acidic zeolite component have been examined with varying degrees of success.

In an early study, Chang et al.[1,2] reported results for iron, zirconia, and ZnO/Cr_2O_3 catalysts combined with ZSM-5 molecular sieve zeolite under the conditions $H_2/CO = 1$, 644 K, and 3.5 MPa. Addition of the zeolite produced aromatic hydrocarbons and greatly decreased the olefin selectivity, but yields were only 5 wt% with the balance methane and light alkanes. The ZnO/Cr_2O_3/ZSM-5 catalyst fared better at 700 K and 8.3 MPa, with 70 wt% aromatics, while the ZrO_2/ZSM-5 catalyst at 700 K and 8.3 MPa produced nearly 85 wt% aromatics. Selectivity for aromatics in the C_{5+} fraction was very high (97%) for the last two catalysts.

In general, FTS catalysts tend to form light hydrocarbons at temperatures favorable to conversion of intermediate olefins to aromatics over the zeolite. Low selectivity for aromatics (about 10 wt%) was reported for copper chromite-promoted iron with a Y-type zeolite.[3] Similar results were found for Fe/ZSM-5 and Fe-Co/ZSM-5 bifunctional catalysts.[4] Conversion to aromatics by several 9 wt% Co/ZSM-5 catalysts varied from 8 to 25 wt% selectivity, depending on method of preparation, with physical mixture of components giving the greatest aromatic yield.[5] Thoria-promoted Co/ZSM-5 at 595 K and 2 MPa with $H_2/CO = 1$ gave selectivities[9] approaching 10 wt% with a high yield of methane and moderate deactivation (50% loss in activity after approximately 150 h). Several studies with zirconia[6,7] or MnO_2-promoted[8] Ni-Co alloys with ZSM-5 have shown sustained (>200 h) aromatics production of up to 30 wt% with $H_2/CO = 1$, 523 K, and 0.1 MPa.

However, two-stage conversion currently is the method of choice for FTS routes to aromatics. Superior results were obtained for Ru/ZSM-5[10] and ZrO_2-promoted Ni-Co/ZSM-5[11] combinations in separate reactors because optimal operation of the zeolite requires temperatures at which typical FTS catalysts produce methane and tend to deactivate. A similar situation applies to the well-known and recently commercialized Mobil process using conventional methane synthesis with Cu-ZnO and methanol-to-gasoline (MTG) conversion with ZSM-5.

Direct aromatics production with alcohol/zeolite catalyst combinations has been examined for unpromoted $ZnO-Cr_2O_3/ZSM-5$ (discussed above),[1] Pd-promoted[12] $ZnO-Cr_2O_3/ZSM-5$, and several Pd/zeolite[13] catalysts. The best selectivities of these catalysts were 85 wt% (700 K and 8.3 MPa), 41 wt% (654 K and 2 MPa), and 51 wt% (627 K, 2.1 MPa, H-exchanged mordenite zeolite), respectively. Since the Mobil process with its very high gasoline range (C_{5+}) and aromatic hydrocarbon selectivity sets the standard for two-stage synthesis gas processing, current catalyst performance fails to provide adequate incentive for direct single-stage production of aromatics by this route, i.e., the combination of ZHSM-5 and a methanol synthesis catalyst.

Effect of Promoters in FTS Catalysis

Over the past 60 years, researchers have sought ways to modify conventional FTS catalysts to achieve a narrow product distribution in the gasoline range. A key difficulty is the high yield of light alkanes. More recent work[14,15] has shown that chemical modification of iron FTS catalysts permits formation of light olefins in the C_2 to C_4 range and suppression of methane.

Several investigators have reported that the use of Mn and alkali promoters increases light olefin selectivity of iron FTS catalysts. A manganese, potassium, and zinc-promoted iron catalyst (100 Fe : 100 Mn : 10 ZnO : 4 K_2O) operating at 595 K, 1 MPa, and H_2/CO ratio of 1 can achieve a product distribution of 70.9 wt% C_2 to C_4 olefins. This catalyst appears to be able to operate at a low degree of polymerization without giving the high yield of methane (9.6 wt%) predicted from Shultz-Flory statistics. Abbot et al.[16] have shown that the addition of sodium (Na/Fe = 0.1) and manganese (Mn/Fe = 0.4) to alumina-supported iron catalysts produces a stable catalyst with high selectivity for light olefins and concurrent suppression of methane selectivity. Ratios of olefins/paraffin equal to 5 are observed in the range C_3 through C_5, with methane selectivity reduced to less than 10% at 550 K, 800 kPa, and CO/H_2 ratio of 2. Deckwar et al.[17] observed, at 1.2 MPa, 570 K, and CO/H_2

ratios of 1.68 and 1.87, the product distribution of an Mn/Fe catalyst with C_2 through C_4 hydrocarbon yield of 77.2 wt% and 74.5 wt%, and C_2 through C_4 olefin yield of 57.1 wt% and 50.3 wt% for slurry-phase and fixed-bed reactors, respectively.

Selective poisoning also enhances the selectivity of iron for light olefins, suppresses methane production, and most importantly may greatly inhibit carbon deposition. We have demonstrated (see Section II) that sulfur-treated fused iron preferentially decreased methane formation and increased the olefins to n-paraffin ratio for light hydrocarbons during FTS reaction at 0.1 to 2 MPa, 573 to 593 K, and H_2/CO ratio = 1-2. The ratio of ethylene to ethane was about 15 for the sulfur-treated catalyst. C_3 through C_6 hydrocarbons produced from this catalyst were also highly olefinic, having an average ratio of olefins to n-paraffin of about 10. The product distribution consisted of 69.6 wt% C_2 through C_4 olefins and 75.2 wt% C_2 through C_4 olefins plus paraffins.

Unlike the reduced untreated fused iron catalyst, which deactivated with time on-stream, the medium-level sulfur-treated fused iron catalyst showed continued steady evolution of CO_2 and hydrocarbon products with syngas exposure time. After 24 h, the total hydrocarbon rate at 573 K for the medium-level sulfur-treated catalyst was about half the rate of untreated catalyst. The selectivity of the medium-level sulfur-treated fused iron catalyst with almost a threefold reduction in methane yield and nearly 90% olefin selectivity for the light hydrocarbons was most encouraging. The roughly twofold decrease in activity can be offset by higher operating temperature, that is, the sulfur-treated catalyst operating at 573 K had about the same activity for C_{2+} hydrocarbon production as the untreated catalyst at 523 K. The adequate activity, low methane selectivity, high selectivity for light olefins, and coking resistance of this catalyst make it a good candidate for FTS in a fluid- or fixed-bed reactor operating above 600 K to suppress wax production.

Carbon Deposition

Thermodynamics of syngas conversion can be invoked to predict the catalyst phase and the product distribution for equilibration. The phase diagram[18,19] for iron carbides (Fe_3C and Fe_2C) and iron oxide (Fe_3O_4), given an equilibrated gas mixture at 700 K, shows that under the conditions of the proposed work Fe_3O_4 and both carbides would be stable. The initial feed gas has considerably greater carburizing thermochemical potential than the equilibrated gas; consequently, bulk iron carbides always form during FTS. Iron carbides are also thought to rapidly catalyze formation of filamentous carbon, which can lead to fouling. Thus, operating temperatures are kept below 533 K in fixed beds[20] to avoid catalyst disintegration and plugging of the bed. Studies of the rate of carbon formation for syngas at 1 MPa and 573 K have shown a relationship between PCO/P_{H_2} and the rate of carbon deposition.

A similar situation exists for reduced metal Co and Ni catalysts, except that the Ni oxide (NiO) is always unstable and the carbide (Ni_3C) is typically thermodynamically unstable in the presence of equilibrated gas. Nickel catalysts are capable of operating under severe coking conditions during hydrocarbon steam re-forming. Pretreatment of nickel on magnesium aluminate supports with fractional monolayers of chemisorbed sulfur has shown[21] that operation well into the region of carbon deposition is feasible. At elevated temperature (>500 K), chemisorbed sulfur on single-crystal surfaces has been shown in our laboratory to become locally mobile[22] and to segregate at surface dislocations or randomly occupy high coordination sites on crystal planes. Rostrup-Nielsen[21] has suggested that random distribution of sulfur on metal surfaces inhibits the nucleation and growth of carbon by an ensemble effect; i.e., a group of six or seven associated carbon chemisorption sites may be required for nucleation of carbon. Therefore, random occupation of those sites by adsorbed sulfur atoms at half-coverage could decrease the rate of carbon deposition by two orders of magnitude. In this scenario, FTS of steam re-forming requires ensembles with fewer sites to act as reaction centers (e.g., three adjacent sites) so that the poisoning has much less effect on the desired reactions.

Another explanation of the inhibiting effect of sulfur chemisorption on carbon deposition is selective blockage of high coordination sites. Deposition of catalyst carbon may be associated with surface dislocations, such as steps and ledges, that have high coordination with an adsorbing atom or molecular fragment. Such sites may be responsible for hydrogenation activity (such as methane formation) and may accumulate coke in the same way as noble metal naphtha re-forming catalysts. Note that Pt/Al_2O_3 naphtha re-forming catalysts operate under conditions that greatly favor carbon deposition, yet these catalysts are used for months without regeneration.

Experimental Results

Sulfur Treatment of FTS Catalysts

In our preceding studies with sulfur-treated fused iron catalysts, we found that partially sulfur-covered iron surfaces produced fewer saturated light alkanes than did untreated catalysts and exhibited no observable coking. The medium-level sulfur-treated iron catalysts prepared as described previously were mixed with zeolite and tested at 2 MPa for their ability to produce aromatics in syngas with H_2/CO ratio $= 0.5$. A new sulfur-treated catalyst, Ru/Al_2O_3, was also prepared for this study using the same sulfur treatment procedure.

Medium-level Sulfur Treatment of Ru/Al_2O_3 Catalyst

The alumina-supported ruthenium FTS catalyst was treated with H_2S until sulfur was chemisorbed to a coverage of about one-half saturation. Following a more severe passivation procedure (exposure to 99.5% CO at 523 K subsequent to 10.4% C_2H_4/He), the rate of sulfur adsorption at 425 K was slowed to about monolayers per hour in a recirculating stream of 10 ppm H_2S in 100-kPa H_2. After removal of the carbon overlayer in 1-atm H_2 at 773 K, the catalyst was removed from the sulfur treatment apparatus, reduced and tested for aromatics sysnthesis performance in the fixed-bed FTS reactor system.

The aromatics synthesis performance of the medium-level sulfur-treated fused iron catalyst, the medium-level sulfur-treated alumina-supported ruthenium, the clean alumina-supported ruthenium, and the fused iron standard catalyst, all in combination with Union Carbide Na-Y zeolites [sodium content: 0.2 wt% (LZY-52), 2.0 wt% (LZY-62), and 10 wt% (LZY-82)] were examined in a fixed-bed reactor at 2 MPa, H_2/CO ratio = 0.5, and 548 to 700 K (Table III-1). The catalyst bed was a physical admixture of the FTS and zeolite catalyst powders (10/14 mesh) of various weight ratios (zeolite/FTS catalyst ratio = 4 or 10) maintained at a constant temperature. Typically, CO conversion was about 20% at a gas hourly space velocity (GHSV) of 1×10^4 to 2×10^4 h^{-1}. GHSV is defined as the hourly flow rate (NTP) of CO + H_2 per unit volume of the FTS catalyst component.

After 2 h at 573 K, the methane yield of the sulfur-treated fused iron only and of the Na-Y zeolite combination was 11 and 15 wt%, respectively. The oxygenate (methanol and dimethylether) and aromatic (benzene, toluene, ethylbenzene, and xylenes) yields of the sulfur-treated fused iron, Na-Y zeolite combinations were much greater than the yield of fused iron alone. The amount of oxygenates initially produced (after 2 h) depended heavily on the sodium weight loading of the zeolite of the mixed catalyst (Table III-1). The chain growth parameter, α, decreased substantially from 0.71 to 0.34 with increased oxygenate and aromatic hydrocarbon selectivity. The methane yield remained low and decreased slightly for catalysts with the smallest zeolite component.

However, the combination fused iron and zeolite catalysts were prone to deactivation by carbon deposition in hydrogen-deficient syngas. After 24 hours of synthesis reaction, the product distribution typically resembled that of the sulfur-treated fused iron catalyst alone (Figure III-1). The decreased oxygenate and aromatics yields were nearly matched by the increased olefin yield, suggesting that the zeolite component of the mixed catalyst was deactivated, probably by carbon deposition. Deactivation was most pronounced for the zeolite with low sodium weight

Table III-1

SYNTHESIS OF AROMATICS AND OXYGENATES BY MIXTURES OF SULFUR-TREATED FUSED IRON AND ZEOLITE CATALYSTS

Catalyst	Medium-level Sulfur Treated Fused Iron	Medium-Level Sulfur-Treated Fused Iron + LZY-82 Zeolite (1:4 by wt)	Medium-Level Sulfur-Treated Fused Iron + LZY-52 Zeolite (1:4 by wt)	Medium-Level Sulfur-Treated Fused Iron + LZY-62 Zeolite (1:10 by wt)	Medium-Level Sulfur-Treated Fused Iron + LZY-52 Zeolite (1:10 by wt)			
Temperature (K)	573	573	573	573	573	650	650	700
Pressure (MPa)	2	2	2	2	2	2	2	2
H_2/CO Ratio	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Run Duration (h)	24	2	2	2	2	1.5	23.5	1
Production Rate[a] (nmol/g/s)								
C_1	53.86	262.28	326.62	162.09	165.78	153.32	222.39	193.67
C_2	43.07	63.66	183.18	33.27	62.66	58.13	67.63	59.87
C_3	34.71	106.90	166.96	39.69	31.40	52.06	72.97	56.90
C_4	17.30	53.11	119.34	20.40	15.49	26.98	47.47	25.26
Oxygenates	2.17	451.00	173.49	190.19	176.47	272.47	14.34	205.10
Aromatics	0.03	0.00	59.67	11.21	13.67	54.24	4.72	20.55
TOTAL	401.16	1743.20	2901.80	870.10	950.20	1662.60	1080.10	1199.60
Chain Growth Factor[b]	0.52	0.34	0.71	0.45	0.61	0.56	0.50	0.40
1-Butene to Butane Ratio[c]	0.85	0.00	0.78	0.00	0.07	0.12	0.70	0.06
Methane Selectivity[d]	14.76	11.54	11.53	15.60	15.10	8.58	22.00	14.20
Oxygenate Selectivity	1.24	57.00	15.10	51.71	39.90	38.60	3.61	38.20
Aromatic Selectivity	0.52	0.00	11.90	5.61	6.30	16.80	2.51	8.08

---

[a] GHSV = 600 h^{-1}; Product rate for each carbon number includes n-paraffins and α- and β-olefins; total product rate is on a carbon-atom basis.

[b] Average chain growth parameter (α) for C_{3+} hydrocarbons.

[c] Average olefin to paraffin ratio for C_2 to C_6 hydrocarbons.

[d] C_1 rate/(total rate) x 100 %.

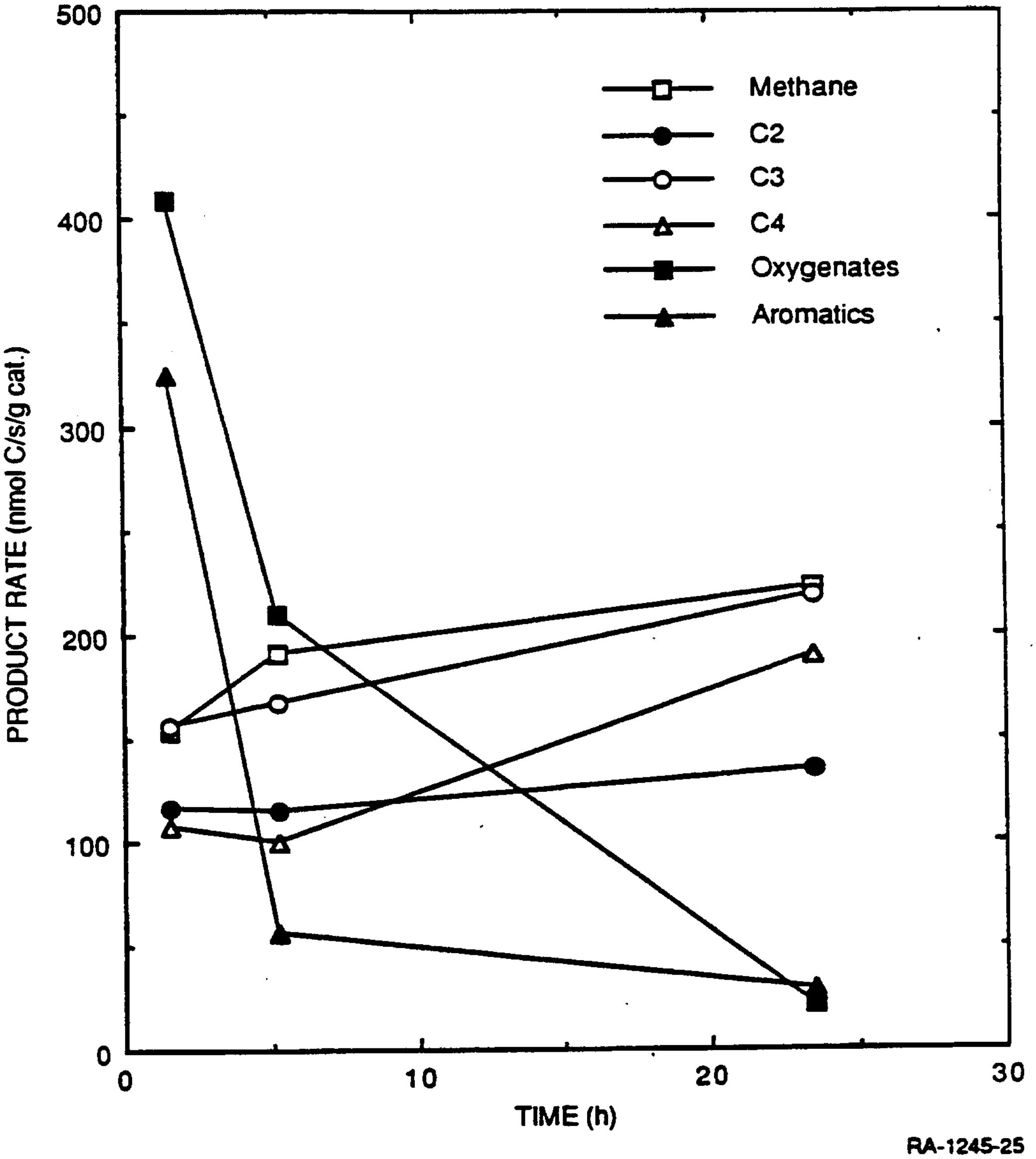


Figure III-1. Aromatic synthesis at 573 K, 2 MPa, H_2/CO ratio = 0.5 on medium-level sulfur-treated fused iron catalyst and LZY-52 zeolite (1:10 wt ratio).

loading. However, the catalysts could be regenerated by reacting the deposited carbon with pure hydrogen at 773 K and 100 KPa for 2 h. To prolong the useful life of the catalyst, especially at higher temperatures, we used a larger amount (10:1 versus 4:1) of a less acidic (higher sodium content, LZY-52) zeolite in combination with the sulfur-treated iron catalyst. This zeolite combination also showed evidence for deactivation in the form of decreased oxygenate and aromatic yields at 650 K (Table III-1).

The mixed catalyst with low sodium (LZY-82) produced predominantly oxygenates, with high conversion of the light olefins. The mixed catalyst with high sodium (LZY-52) produced a mixture of oxygenates and aromatics of roughly equal proportion, with correspondingly lower conversion of the light olefins (Figure III-2). The mixed catalyst with (LZY-62) had a product distribution similar to that of the LZY-52 mixed catalyst (Figure III-3).

The activity of the sulfur-treated alumina-supported ruthenium/Na-Y zeolite catalyst was a factor of ten lower than that of the sulfur-treated fused iron/Na-Y zeolite catalyst at 573 K. However, the oxygenates and aromatics selectivities (28 wt% and 17 wt%, respectively) of the ruthenium/Na-Y zeolite mixed catalysts were roughly the same as that of the fused iron mixed catalyst. The lower activity of the ruthenium mixed catalyst (per unit weight FTS catalyst) was primarily due to its much lower metal weight loading (2.4 wt% Ru) compared to that of the bulk fused iron mixed catalyst. The sulfur-treated ruthenium mixed catalyst showed 50% decreased methane and a factor of two increased oxygenates and aromatics yields at both 573 and 598 K when compared to the clean ruthenium mixed catalyst (Table III-2).

Discussion

The synthesis of aromatic hydrocarbons was performed under differential reactor conditions because of the constraints of maximum catalyst bed volume and minimum controllable syngas flow rate at elevated pressure. As a result, overall conversion of the syngas was limited to

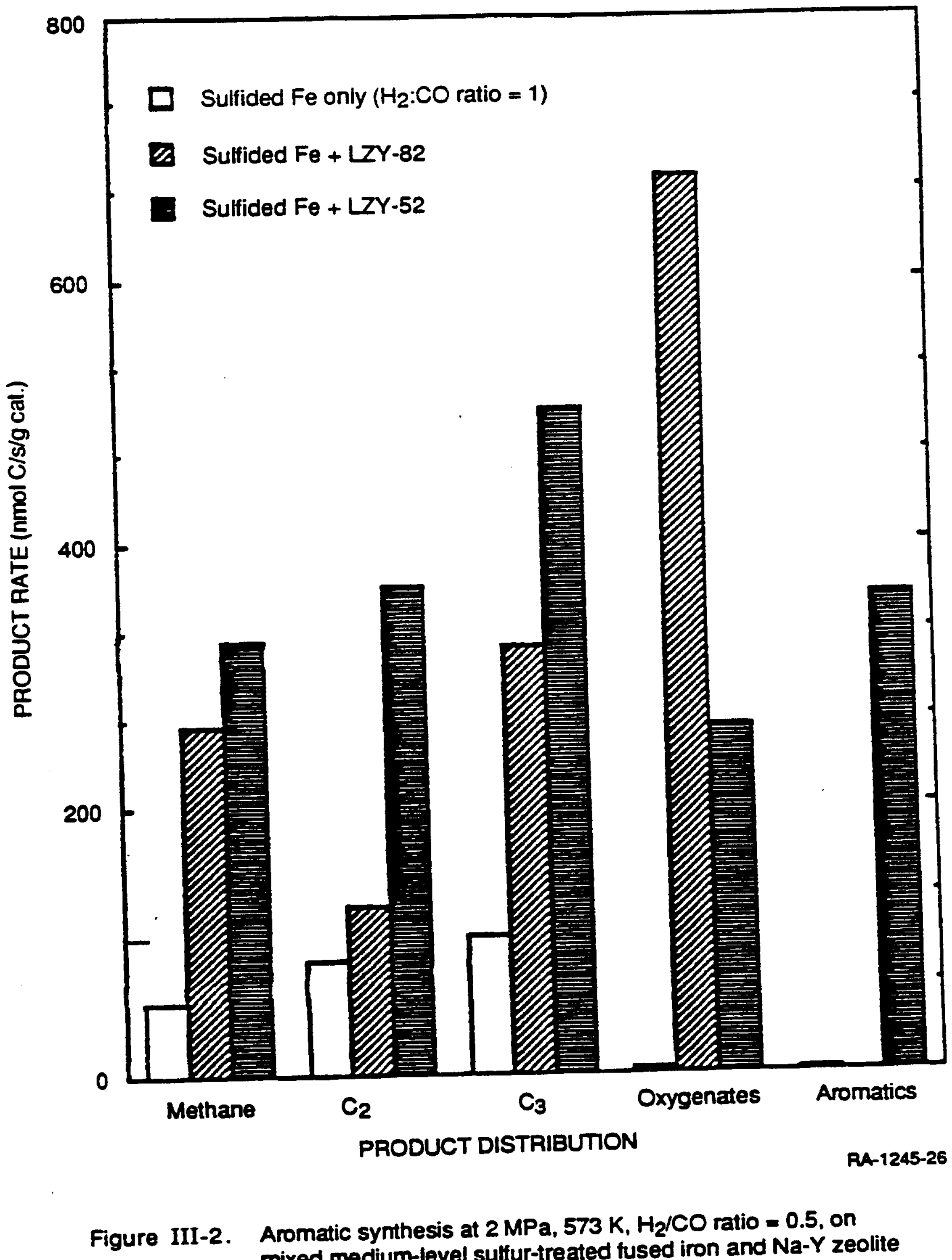
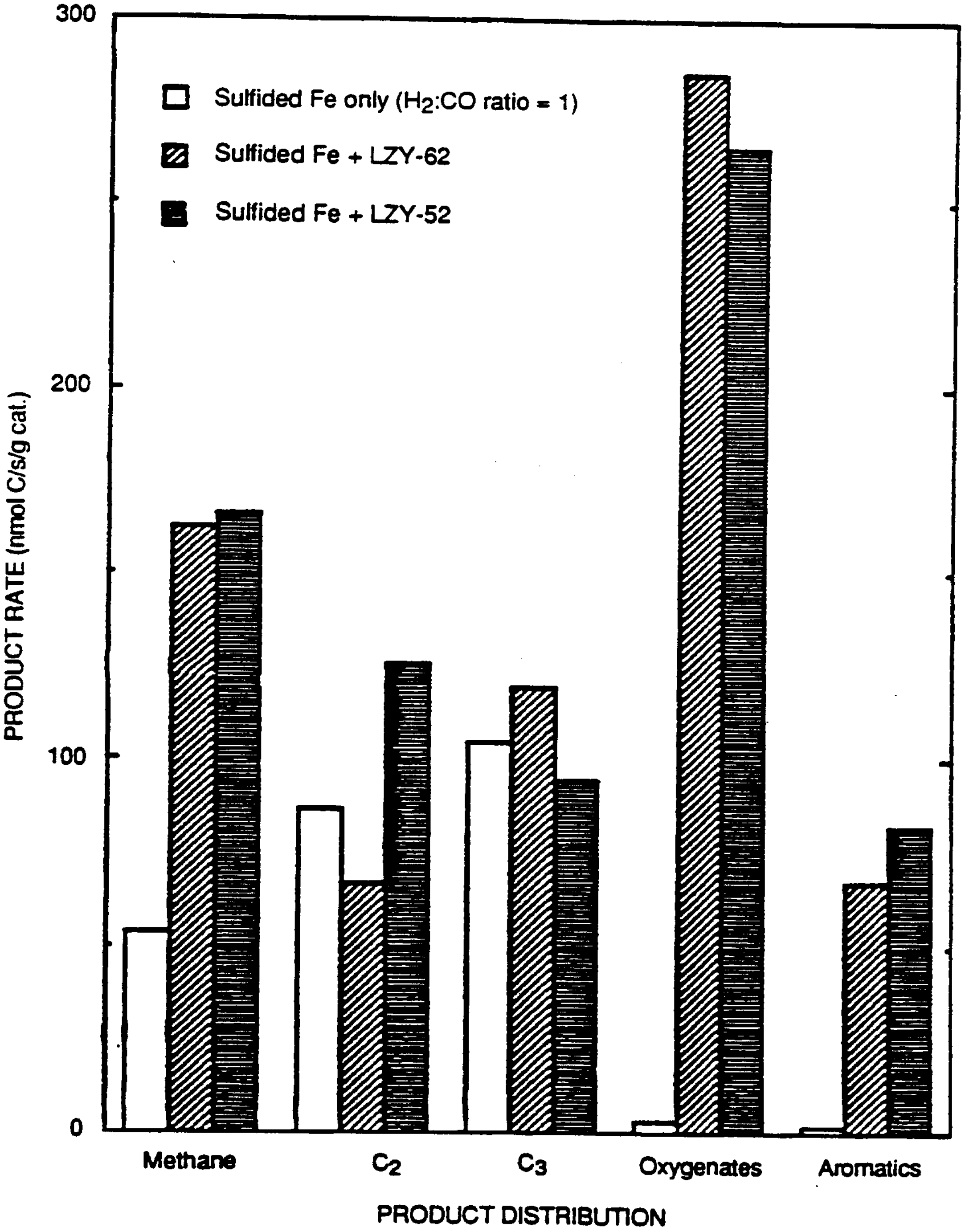


Figure III-2. Aromatic synthesis at 2 MPa, 573 K, H_2/CO ratio = 0.5, on mixed medium-level sulfur-treated fused iron and Na-Y zeolite catalysts (1:4 weight ratio).



RA-1245-27

Figure III-3. Aromatic synthesis at 2 MPa, 573 K, H_2/CO ratio = 0.5 on medium-level sulfur-treated fused iron catalyst and Na-Y zeolites (1:10 wt ratio).

Table III-2

SYNTHESIS OF AROMATICS AND OXYGENATES BY MIXTURES OF SULFUR-TREATED RUTHENIUM AND ZEOLITE CATALYSTS

Catalyst	Clean 2.4 wt% Ru/Al_2O_3 + LZY-52 Zeolite (1 to 10 wt ratio)		Medium-level Sulfur-treated 2.4 wt% Ru/Al_2O_3 + LZY-52 Zeolite (1 to 10 wt ratio)	
Temperature (K)	598	573	598	573
Pressure (MPa)	2	2	2	2
H_2/CO ratio	0.5	0.5	0.5	0.5
Duration (h)	2	2	2	2
Product rate[a] (nmol/s/g cat)				
C_1	22.96	5.20	23.44	10.32
C_2	2.37	0.55	2.55	1.14
C_3	1.72	0.89	2.33	1.56
C_4	1.11	0.84	1.56	1.42
Oxygenates	1.83	1.31	4.63	7.27
Aromatics	0.20	0.54	0.89	2.03
TOTAL				
Chain Growth Factor[b]	0.48	0.55	0.50	0.66
1-Butenes to Butane Ratio[c]	0.44	0.73	0.52	0.62
Methane Selectivity[d]	50.90	26.30	37.90	16.10
Oxygenates Selectivity	9.70	15.60	17.80	27.50
Aromatics Selectivity	2.10	13.50	7.64	16.80

---

[a] GHSV = 600 h^{-1}; Product rate for each carbon number includes n-paraffins and α- and β-olefins; total product rate is on a carbon-atom basis.

[b] Average chain growth parameter (α) for C_{3+} hydrocarbons.

[c] Average olefin to paraffin ratio for C_2 to C_6 hydrocarbons.

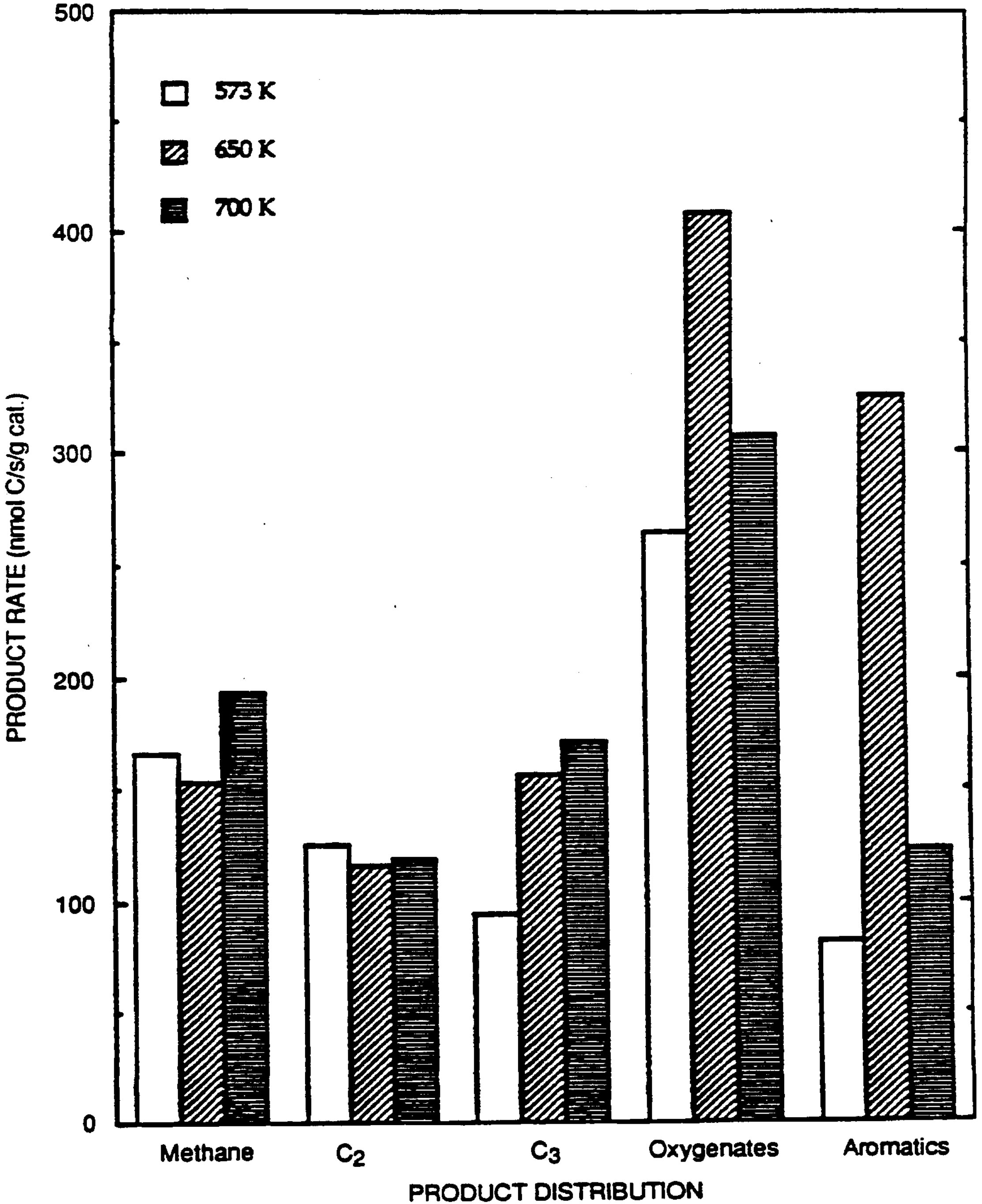
[d] C_1 rate/(total rate) x 100%.

20% and was relatively insensitive to temperature (Table III-1). The aromatics yield increased threefold with a corresponding decrease in methane yield by increasing the reactor temperature from 573 K to 650 K (Figure III-4). However, an additional increase in reactor temperature to 700 K resulted in more rapid deactivation of the zeolite catalyst without additional enhancement in aromatics selectivity or syngas conversion.

The yield of aromatics in the synthesis product using the mixed sulfur-treated iron and zeolite catalyst may have been limited by low conversion of the syngas. The presence of unreacted hydrogen and product water vapor perhaps inhibited the dehydrocyclization reaction and favored the formation of dimethylether and methanol, which can be considered intermediates for aromatic hydrocarbons on zeolite catalysts such as HZSM-5.[1,2] The acidic properties of the low-sodium zeolite enhanced oxygenate and aromatic hydrocarbon formation but also enhanced cracking and led to more rapid deactivation of the catalyst.

Since the strong acidic sites in the zeolite are responsible for the formation of aromatics by the dehydrocyclization of the C_6 olefins, the observed decrease in oxygenates and aromatics selectivity with time can be attributed to the progressive deactivation of these sites by coking. The deactivation of the zeolite component of the catalyst resulted in loss of isomerization and dehydrocyclization activity to formed aromatics and isoparaffins. Using of a higher weight ratio of zeolite to FTS catalyst in the mixed bed mode prolonged the activity and increased oxygenates and aromatics selectivity.

The consumption of light olefins, which are essential building blocks for aromatics, to form oxygenates effectively decreased the selectivity of aromatics in the product. The formation of aromatics may be the rate-limiting step of overall conversion of methanol to aromatics on HZSM-5.[1] The cracking and hydrogenolysis of intermediate olefin products apparently led to low aromatics yield and to carbon deposition on the zeolite components of the mixed catalyst.



RA-1245-28

Figure III-4. Effect of temperature on the synthesis of oxygenates and aromatics at 2 MPa and $H_2/CO = 0.5$ with medium-level sulfur-treated fused iron catalyst and LZY-52 zeolite (1:10 wt ratio).

Conclusions and Recommendations

Combinations of low and moderate sodium exchanged Y zeolites with a coking-tolerant sulfur-treated fused iron catalyst readily convert FTS product olefins into alcohol and aromatic products in a fixed-bed reactor at 2 MPa pressure, 573 to 650 K temperature, and low CO conversion (<10%). Similar results have been obtained at lower temperature and higher H_2/CO ratio (1.0). We had expected coking of the FTS component of the catalyst to be important at the higher temperatures and lower hydrogen syngas used in our study. Despite the high coking conditions at $H_2/CO = 0.5$ and 650 K, the FTS component did not deactivate and continued to produce relatively high FTS rates. Deactivation of the sodium Y-zeolite function was observed, however.

Our selection of the zeolite component was not optimal, and a more systematic search for a coking-tolerant acid catalyst is recommended. The addition of Na to the acidic Y zeolite we used was apparently insufficient to prevent moderately rapid coke formation (around 2 h). The sodium may also have contributed to the high selectivity for oxygenates, since it has been recently shown that Pd with an alkali exchanged ZSM-5 support generates high oxygenate yields in syngas.[23]

Clearly, shape selectivity is important in reducing coking rates. A small-pore high-silica zeolite that can reject coke precursors is a more desirable choice than Y or X silica-alumina zeolites. ZSM-5 is generally regarded as having low coking tendency because of its low Al content and its small pore sizes. Rare earth exchanged ZSM-5 class zeolites may have more optimal coking resistance and acidity sufficient to effect rapid rates of conversion of olefins to aromatics. The CO and, especially, hydrogen conversion must also be increased to improve the hydrocarbon selectivities. Producing high yields of aromatics without rapid acid deactivation may not be possible because of coking. Coke formation may simply parallel aromatics production. Acceptable rates of conversion of olefin intermediates to aromatics may simply require high acidity (which generally means greater Al content in the zeolite), which in turn results in unacceptable deactivation rates.

References

1. C. D. Chang, W. H. Lang, and A. J. Silvestry, J. Catal. <u>56</u>, 268 (1979).

2. C. D. Chang and W. H. Lang, Mobil Oil, U.S. Patent 4180516 (1979).

3. W. H. Seitzer, Suntech, U.S. Patent 4139550 (1979).

4. U.S. Rao, R. J. Gormley, H. W. Pennline, L. C. Schneider, and R. Obermyer, ACS Div. of Fuel Chem. Preprints <u>25</u>(2), 119 (1979).

5. A. Shamsi, U. Rao, R. J. Gormley, R. T. Obermyer, R. R. Schehl, and J. M. Stencel, Ind. Eng. Chem. Prod. Res. Dev. <u>23</u>, 513 (1984).

6. L. Bruce, G. T. Hope, and J. F. Mathews, Appl. Catal. <u>9</u>, 351 (1984).

7. R. L. Varma, K. Jothimurugesan, N. N. Bakhshi, J. F. Mathews, and S. H. Ng, Can. J. Chem. Eng. <u>64</u>, 141 (1986).

8. R. L. Varma, D.-C. Liu, J. F. Mathews, and N. N. Bakhshi, Can. J. Chem. Eng. <u>63</u>, 72 (1985).

9. H. W. Pennline, V.U.S. Rao, R. J. Gormley, and R. B. Schehl, ACS Div. Fuel Chem. Preprints <u>28</u>, 164 (1983).

10. T. J. Huang and W. O. Haag, ACS Symposium Series <u>152</u>, 307 (1981).

11. R. L. Varma, N. N. Bakhshi, J. F. Mathews, and S. H. Ng, Ind. Eng. Chem. Res. <u>26</u>, 183 (1987).

12. T. Inui, T. Hagiwara, and Y. Takegami, Sekiyu Gukkaishi, <u>27</u>, 228 (1984).

13. K. Fujimoto, Y. Kndo, and H.-O. Tominaga, J. Catal. <u>87</u>, 136 (1984).

14. B. Bussemeier, C. D. Frohring, G. H. Horn, and W. Kluy, German Offen. 2,518,964 and 2,536,488 assigned to Ruhrchemie AG (1976).

15. R. Malessa and M. Baerns, Ind. Eng. Chem. Res. <u>27</u>, 279 (1988).

16. J. Abbot, N. J. Clark, and B. G. Baker, Appl. Catal. <u>26</u>, 141 (1986).

17. W. D. Deckwar, Y. Serpemen, M. Ralek, and B. Schmidt, Ind. Eng. Chem. Process Des. Dev. <u>21</u>, 222 (1982).

18. S. Schechter and H. Wise, J. Phys. Chem. 83, 2107 (1979).

19. M. P. Manning and R. C. Reid, Ind. Eng. Chem. Process Des. Dev. 16, 358 (1977).

20. M. E. Dry, Applied Industrial Catalysis 3, 167 (1983).

21. J. Rostrup-Nielsen, presention at the 10th North American Meeting of the Catalysis Society (to be published in Appl. Surf. Sci., 1987).

22. B. J. Wood, C. M. Ablow, and H. Wise, Appl. Surf. Sci. 18, 429 (1984).

23. R. T. Thomson and E. E. Wolf, Appl. Catal. 41, 65 (1988).