II SULFUR-TREATED CATALYSTS

Introduction

An important property of improved Fischer-Tropsch synthesis (FTS) catalysts is low selectivity for the production of light alkanes (paraffin hydrocarbons), especially methane. Production of light alkanes causes several inefficiences in the production of synthetic fuels in addition to the lower yield of gasoline or middle distillate range hydrocarbons. Light alkane products require additional processing steps, such as separation and steam re-forming or thermal cracking before they can be recovered and converted into syngas for recycle or converted into higher value products. These steps necessitate operational and capital investment expenses well beyond the market value of the light alkanes. Reduction in light alkane yield therefore directly reduces the costs associated with these ancillary processing steps.

Dry[1] has described commercial FTS operation at elevated temperature and moderate pressure that gives methane yields down to 10 wt% and total light alkanes in yields from 20 to 30 wt%. As a result of our current investigation, we believe that low-level sulfur pretreatment of new catalyst formulations, such as dual-function catalysts, could directly give motor fuel range hydrocarbons and light olefins in yields well above 80 wt% with a corresponding decrease in light alkane yield. Iron FTS catalysts and other metal catalysts with desirable FTS activity can be treated with controlled amounts of sulfur to selectively inhibit the formation of methane. This approach to development of improved FTS catalysts has several advantages:

- Only selectivity characteristics of the metal crystallite surfaces would be altered; physical properties, such as pore-size distribution, and chemical properties, such as acid-base character, would remain unchanged.

- Any heterogeneous supported metal FTS catalyst can, in principle, be treated with low levels of sulfur.
- Low levels of sulfur may reduce the coking tendencies of FTS catalysts in addition to altering the product distribution.
- Since sulfur is a ubiquitous component of coal and coal processing technology, no environmental or undesirable synergistic catalytic effects would be introduced by treatment with very low levels of H_2S.

Two problems might accompany low-level sulfur treatment:

- Uniform fractional adsorption of sulfur on metal surfaces within a porous catalyst is extremely difficult because of the strong affinity of such surfaces for chemisorbed sulfur.
- Enhancement of selectivity may be offset by a large decrease in activity for the formation of desirable hydrocarbon products; indeed, high coverage by sulfur is a poison for FTS and for methanation.

Selective poisoning of methane production could result in an FTS process with a high yield of hydrocarbons in the motor fuel range. High-molecular-weight waxes can be suppressed by operating at elevated temperatures with a dual-function catalyst. Higher operating temperature could also mitigate any decline in activity caused by the sulfur treatment.

The success of selective methane poisoning depends on the actual kinetic details of the much studied FTS reaction mechanism. There is some evidence that methane and higher molecular weight FTS products are formed through parallel reaction pathways and that methane yield does not always follow the polymerization statistical distribution. Commercial FTS catalysts often follow the polymerization distribution, with the exception of methane.[1,2] The lower methane production rate may result from differences in the stability and termination rates for adsorbed methyl and alkyl species. Consequently, depending on the degree of polymerization, the product distribution can vary from 100% methane (methanation) to a predominance of high-molecular hydrocarbons weight. High temperature and low pressure operation favors the production of methane, whereas low temperature and high pressure operation favors the production of waxes. Some catalysts, such as nickel and the noble metals, favor methanation, whereas other catalysts,[3] such as ruthenium and cobalt, favor waxes. In general, all are constrained by the Anderson-Schultz-Flory (ASF) product distribution. Improved catalyst performance, e.g., suppressed methane and light alkane production, in combination with changes in operating conditions, e.g., higher temperature with low H_2/CO ratio syngas, may narrow the product distribution curve to substantially improve the yield of usable liquid fuels. Catalysts selectively poisoned by controlled quantities of sulfur may represent such improved FTS catalysts.

Background

Selective Poisoning of FTS Catalysts

Sulfur is a well-known poison for the FTS reaction. However, as pointed out in the review of Madon and Shaw,[4] unexplained observations indicate that small quantities of sulfur can enhance the activity and alter the selectivity of the catalyst. Herington and Woodward[5] reported that the light hydrocarbon yield for a thoria-promoted cobalt catalyst supported on kieselguhr declined, whereas the heavy hydrocarbon yield increased with introduction of H_2S. Increased heavy hydrocarbon production was also noted when H_2S was introduced to the potassium-promoted catalyst under methanation conditions (300°C). Similar observations were reported by Fischer and Meyer[6] for Ni and by King[7] for Co with CS_2 as the poison. Anderson et al.[8] reported an increase in the yield of hydrocarbons in the liquid fuel range after adding small quantities of sulfur to iron catalysts possessing small particle size.

These observations are supported by the more recent evidence that sulfur adsorption strongly decreases the methanation activity of metal surfaces. Dalla Betta[9] reported that 10 ppm H_2S reduced the stationary state methanation activity of Ru and Ni several orders of magnitude. In studies with more carefully controlled sulfur-poisoned metal surfaces, Bartholomew et al.[10] found that the methanation activity declined as the square of unpoisoned sites. Similar and stronger poisoning influence was reported by Goodman and Kiskinova[11] for the methanation activity of single-crystal Ni and Ru surfaces. However, these studies did not systematically measure the effect of controlled sulfur adsorption on the selectivity of metals for higher molecular weight products under more favorable FTS conditions (higher pressure and lower temperature).

The effect of sulfur poisoning on activity and selectivity during FTS has generally been systematically investigated under transport-limited sulfur poisoning conditions and at H_2S levels well above those necessary to completely cover the active metal surfaces.[4] In these selective poisoning experiments, probably only a very small portion of the total metal surface area of the catalysts was fractionally covered with sulfur, the case for which the selectivity would be most affected. The majority of the surface area would be either clean or completely covered with a monolayer of sulfur. If the entire metal surface area were uniformly covered with low levels of chemisorbed sulfur, the FTS selectivity might be significantly altered.

More recent work by Satterfield and Stenger[12] and by Matsumoto and Satterfield[13] with dibenzyl thiophene-poisoned fused iron in a slurry reactor and our own results with H_2S pretreated fused iron in a fixed-bed reactor have shown significantly decreased methane yield and increased olefin selectivity relative to clean fused iron catalysts.

Uniform Sulfur Adsorption on FTS Catalysts

Our approach was to carefully treat iron and ruthenium catalysts with sulfur so that uniform controlled adsorption could occur separately, before FTS reaction. As our own work has shown,[14,15] the great thermodynamic stability of chemisorbed sulfur ensures that the sulfur is not removed during the subsequent FTS reaction.

The essentially irreversible chemisorption of sulfur to metal surfaces results in poisoning for very low gas phase concentrations of sulfur-bearing gas. It has been long known that levels of H_2S lower than necessary for the formation of metal sulfides still result in complete poisoning, given adequate stoichiometric exposure time. Measurements of the thermodynamic properties of chemisorbed sulfur on FTS catalysts, including Ni,[16] Fe,[14] Ru,[15] and Co,[14] have shown that extremely low levels of sulfur-bearing gas are required before the adsorption process with H_2S becomes reversible (Table II-1). At FTS temperatures, the ratio of H_2S/H_2 is less than 0.001 ppb for equilibrium with chemisorbed sulfur on iron at 70% of the capacity of the surface to adsorb sulfur.[14] The reversible adsorption levels or threshold poisoning levels for the other metals is even lower. Correlations of the heat of formation of chemisorbed sulfur as a function of bulk sulfide heat of formation and the empirical relation between the coverage and chemical potential of adsorbed sulfur[17] allow an estimate to be made for sulfur coverage as a function of metal, temperature, and gas phase chemical potential of sulfur. All metal catalysts, given some uncertainty owing to the unknown effect of promoters and FTS intermediates, irreversibly chemisorb sulfur for all practical FTS conditions.

Therefore, substantial transport limitations must exist within the pores and even through a catalyst bed because of the very low levels of gas-phase sulfur. The rates of sulfur adsorption at 500 K appear adequate to quickly poison a metal crystallite surface, given any practical gas phase concentration. Thus, few metal crystallites can exist with fractional adsorbed atomic sulfur coverage under ordinary poisoning conditions. Crystallites near the exterior surface of a porous catalyst particle and those located upstream in a fixed bed are completely poisoned, whereas those downstream remain essentially free of chemisorbed sulfur. Those catalysts for which sulfur exposure caused a change in selectivity undoubtedly contained considerable gradients in the adsorbed sulfur coverage. This nonuniformity lessens the effect of sulfur coverage on FTS product selectivity.

Experimental Results

Catalyst Preparation

A doubly promoted (potassium and copper) precipitated iron catalyst was prepared from aqueous solutions of copper(II)nitrate

Table II-1

SULFUR CHEMISORPTION THERMODYNAMICS FOR IRON, COBALT, AND RUTHENIUM

Metal	Temp (K)	P_{H_2S}/P_{H_2} for Fractional Sulfur Coverage,					
		0.05	0.10	0.20	0.50	0.75	1.00
Fe	500	6.6×10^{-15}	1.3×10^{-14}	2.7×10^{-14}	5.4×10^{-11}	3.6×10^{-8}	2.1×10^{-5}
	600	6.4×10^{-13}	1.3×10^{-12}	2.5×10^{-12}	2.6×10^{-9}	8.9×10^{-7}	2.8×10^{-4}
	800	1.9×10^{-10}	3.8×10^{-10}	7.6×10^{-10}	3.2×10^{-7}	4.9×10^{-5}	6.8×10^{-3}
	1000	5.8×10^{-9}	1.2×10^{-8}	2.3×10^{-8}	5.7×10^{-6}	5.5×10^{-4}	4.7×10^{-2}
Co	500	6.1×10^{-16}	1.2×10^{-15}	2.4×10^{-15}	1.8×10^{-12}	3.5×10^{-10}	6.1×10^{-8}
	600	1.8×10^{-13}	3.6×10^{-13}	7.3×10^{-13}	2.1×10^{-10}	1.8×10^{-8}	1.4×10^{-6}
	800	2.3×10^{-10}	4.5×10^{-10}	9.0×10^{-10}	7.9×10^{-8}	2.5×10^{-6}	6.9×10^{-5}
	1000	1.6×10^{-8}	3.2×10^{-8}	6.5×10^{-8}	2.8×10^{-6}	4.8×10^{-5}	7.2×10^{-4}
Ru	500	2.3×10^{-26}	4.3×10^{-25}	1.5×10^{-22}	7.0×10^{-15}	1.7×10^{-8}	4.1×10^{-2}
	600	3.4×10^{-23}	5.1×10^{-22}	1.2×10^{-19}	1.4×10^{-12}	1.1×10^{-6}	9.0×10^{-1}
	800	3.1×10^{-19}	3.5×10^{-18}	4.7×10^{-16}	1.1×10^{-9}	2.1×10^{-4}	4.2×10
	1000	7.3×10^{-17}	7.1×10^{-16}	6.7×10^{-14}	5.7×10^{-8}	4.9×10^{-3}	4.3×10^{2}

Source: J. Chem. Phys. 74, 5877 (1981); J. Chem. Phys. 76, 1162 (1982).

[$Cu(NO_3)_2 \cdot 3H_2O$, Alfa Products, puratronic grade] and iron(III)nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Alfa Products, puratronic grade] in the required ratio at 353 K. The mixed nitrate solution was then slowly added to hot sodium carbonate solution with vigorous stirring over a period of several minutes until the pH reached 7 to 8. The precipitate was collected by centrifugation and washed with 1000 mL of deionized water. Alkali was added by stirring the precipitate with dilute potassium carbonate solution. The catalyst was then dried at 373 K for 24 h. The final weight ratio was $Fe:Cu:K_2CO_3 = 100:0.1:2$. The precipitated iron catalyst was ground and screened to 0.043-0.14 mm. The catalyst was reduced at 623 K for 16 h with hydrogen gas at a gas hourly space velocity (GHSV) of $3 \times 10^4\ h^{-1}$.

A fused iron catalyst was obtained from United Catalysts Inc. (C73-1-01) as 1.5 x 3.0 mm granules and was crushed and screened to 0.3-0.5 mm. The catalyst was reduced as recommended in 100 mL min^{-1} of flowing hydrogen and programmed from 533 K to 766 K over 29 h.

An unpromoted cobalt catalyst was prepared from an aqueous solution of cobalt(II)nitrate [$Co(NO_3)_2 \cdot 6H_2O$, Alfa Products, puratronic grade] by the method of incipient wetness on Harshaw AL-0104 alumina (BET surface area = 88 m^2/g) and crushed and screened to 0.3-0.5 mm. The catalyst was then dried in air at 400 K for 24 h. The final weight ratio was $Co:Al_2O_3 = 1:10$.

An unpromoted ruthenium catalyst was prepared from an aqueous solution of ruthenium chloride ($RuCl_3$) by the method of incipient wetness on Harshaw AL-0104 alumina crushed and screened to 0.3-0.5 mm. The catalyst was then dried in air at 400 K for 24 hours. The final weight ratio was $Ru:Al_2O_3 = 2:100$.

Sulfur Treatment of Precipitated Iron Catalyst

Sulfur treatment of the precipitated iron catalyst was performed in a gas recirculation system as shown in Figure II-1. After catalyst reduction *in situ* in 100-kPa hydrogen at 623 K for more than 16 h, aliquots of 0.96 mol% H_2S/H_2 were injected into the recirculation loop at 723 K, and the change in the gas-phase concentration of hydrogen sulfide

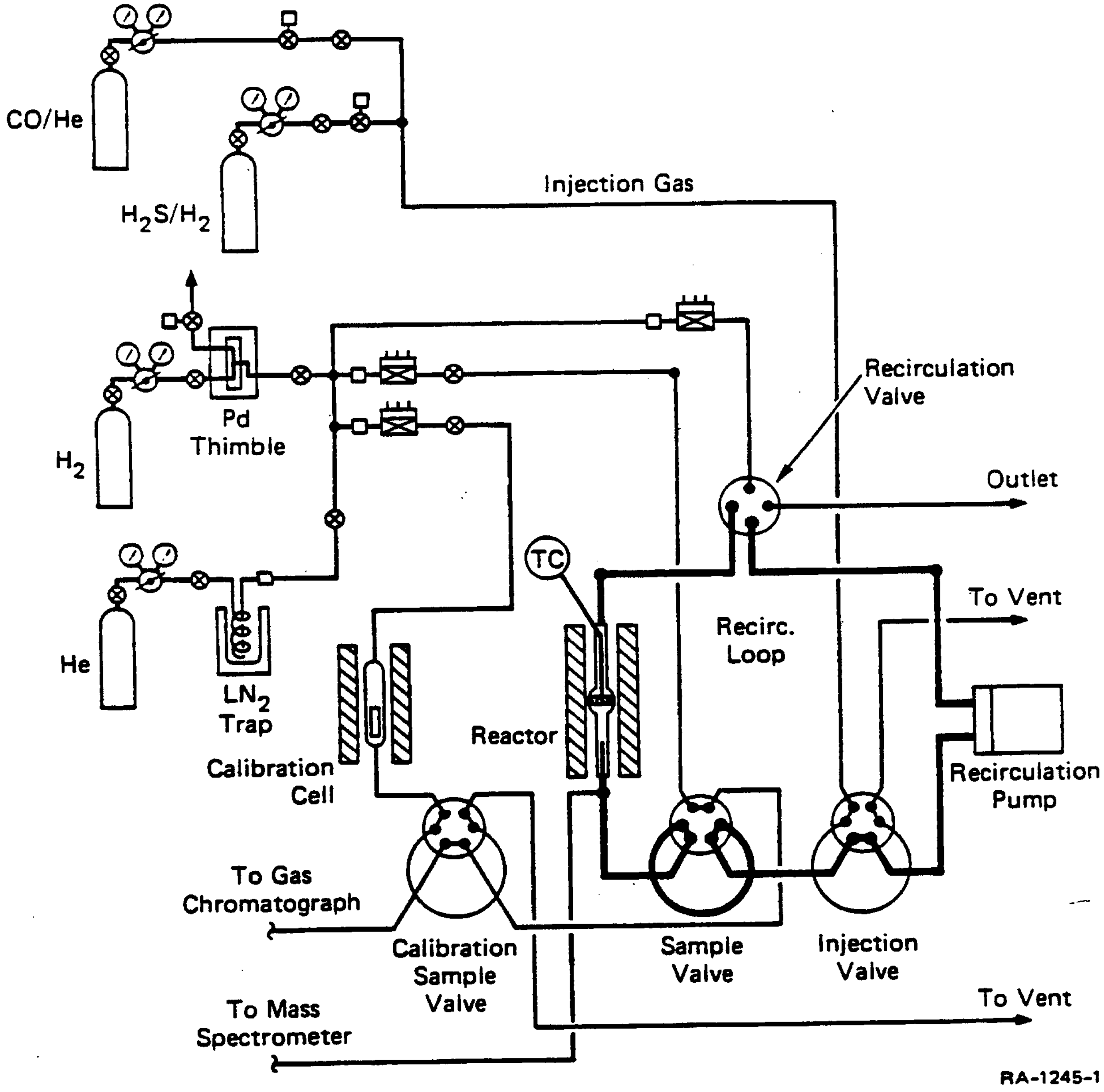

Figure II-1. FTS catalyst sulfur treatment system.

with time was closely monitored. Approximately 39.3 μmol of hydrogen sulfide was adsorbed at saturation, corresponding to a reduced metal surface area of about 6.7 m^2 g^{-1}. The catalyst was exposed to the gaseous mixture for 24 h at 723 K to ensure equilibration. The H_2S gas was flushed with pure hydrogen after cooling to 423 K. Comparison of our data with previously published isosteres on iron powder[14] indicates that our iron catalyst had reached approximately 100% of saturation coverage (i.e., about 1.0 adsorbed sulfur atoms per iron surface atom). The catalyst was then removed from the recirculation system and immediately reduced at 623 K in 100-kPa hydrogen in the FTS testing apparatus.

Sulfur Treatment of Fused Iron Catalyst

Sulfur treatment of the fused iron catalyst was performed in a gas recirculation system, as described previously. After catalyst reduction *in situ* in 100-kPa hydrogen and temperature programming to 766 K over 29 h, aliquots of 3080 ppm H_2S/H_2 were pulsed into the recirculation loop at 723 K, and the change in the gas-phase concentration of hydrogen sulfide with time was closely monitored. Approximately 140 μmol of hydrogen sulfide was injected into the system, corresponding to a reduced metal surface area of about 8 m^2 g^{-1}. The catalyst was equilibrated with the gaseous mixture for 24 h at 723 K. Gas-phase hydrogen sulfide concentrations were measured over a range of temperatures, and the isostere was plotted in Figure II-2. Comparison of our data with previously published isosteres on iron powder[14] indicates that our iron catalyst had reached approximately 100% of saturation coverage (i.e., about 1.0 adsorbed sulfur atoms per iron surface atom). The catalyst was then removed from the recirculation system and reduced at 573 K in hydrogen in the FTS testing apparatus immediately before we began the catalytic studies.

A special pretreatment procedure was developed for uniform fractional adsorption of sulfur below half saturation coverage because partial sulfur coverage on the metal surfaces within a porous catalyst is extremely difficult to produce owing to the strong affinity of such

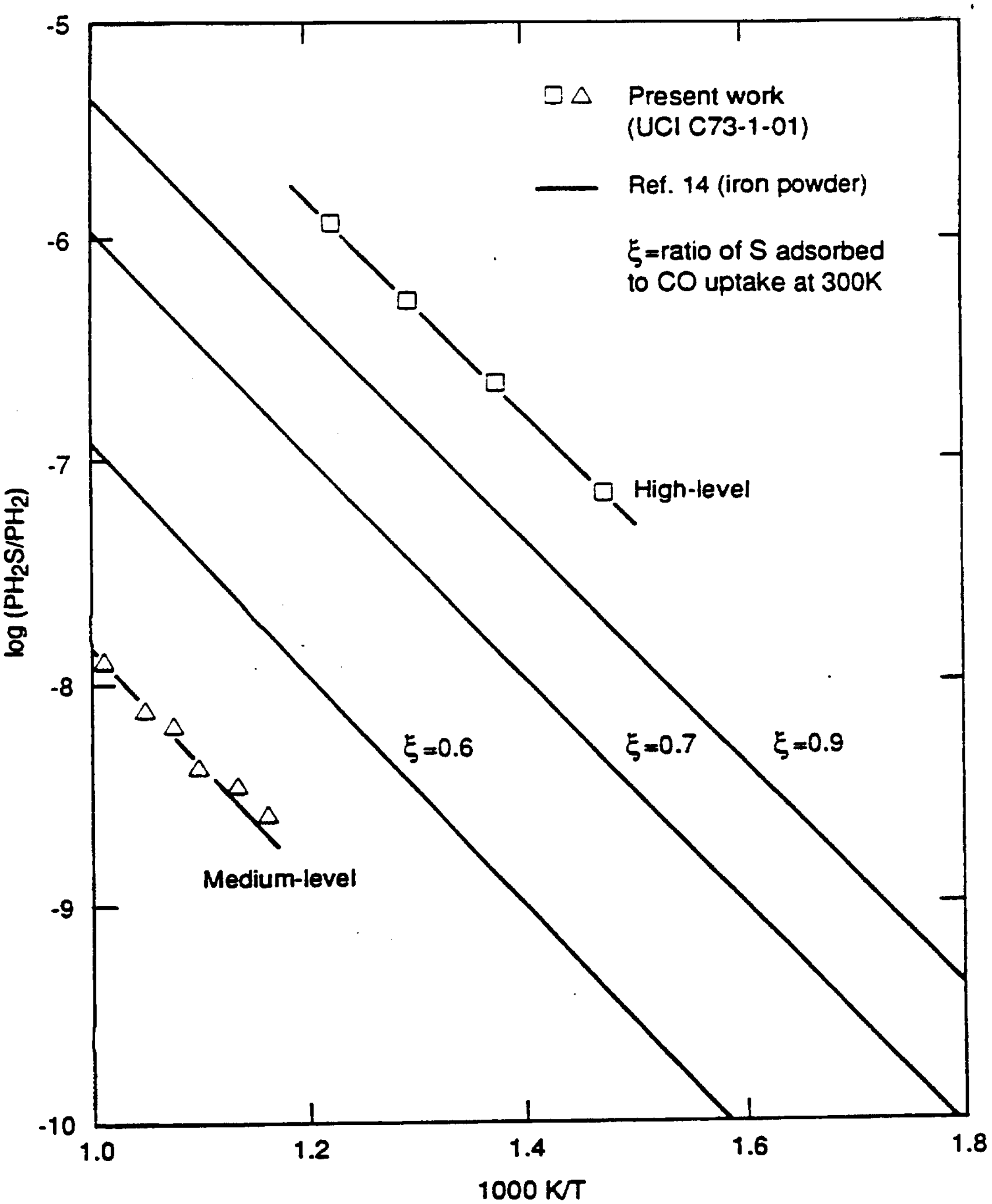

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Figure II-2. Sulfur chemisorption isosteres on fused iron and iron powder.

surfaces for chemisorbed sulfur. A low uniform level of sulfur coverage was achieved by slowing the rate of dissociative chemisorption of H_2S on the catalyst surface by the presence of a passivating layer containing a readily removed adsorbate so that surface reaction, rather than pore diffusion, limited the net rate of sulfur uptake. The reduced fused iron catalyst was passivated by CO adsorption, dissociation, and disproportionation to CO_2 at 473 K. Aliquots of 100-kPa CO were injected into the closed gas recirculation loop containing 1 g of the reduced fused iron catalyst, while the CO-CO_2 ration was followed with an on-line mass spectrometer. Approximately 200 μmol of carbon monoxide was injected, corresponding to two monolayers of adsorbed CO. Some CO_2 evolution was observed, and most of the CO was consumed during passivation.

Following passivation, aliquots of 0.96% H_2S/H_2 were injected into the closed recirculation loop at 473 K, while the gas-phase H_2S concentration was monitored with a sensitive photoionization detector. Approximately 200 μmol of hydrogen sulfide was injected into the system, representing approximately 0.4 monolayer sulfur capacity of the catalyst. The gas-phase H_2S concentration slowly fell to 15 ppm after 2 h. The system was then flushed with pure hydrogen at 343 K. The deposited carbon, iron carbide, and adsorbed CO were removed by temperature-programmed reaction (TPR) to 873 K in 100-kPa flowing hydrogen. Methane, but no hydrogen sulfide, was observed during the TPR, indicating that chemisorbed sulfur was irreversibly bound during the removal of the passivating layer.

The catalyst was held at 825 K in recirculating hydrogen for 12 h to allow local microscopic surface diffusion and equilibration. Gas-phase hydrogen sulfide concentrations were measured over a range of temperatures and the final sulfur chemisorption isostere was determined (Figure II-2). Compared with isosteres for fractional monolayer sulfur coverage on powdered iron[41], the medium-level sulfur-treated fused iron catalyst had approximately 0.5 monolayer sulfur coverage. The BET surface area of the freshly reduced catalyst (30 m^2 g^{-1}) and medium-level sulfur-treated catalyst (7 m^2 g^{-1}) showed a factor of four reduction in surface area. The catalyst was further passivated by CO adsorption at room temperature before removal from the recirculation system and transfer to the FTS testing system. The catalyst was reduced in flowing hydrogen at 523 K before FTS testing, as described below.

A low-level sulfur-treated fused iron catalyst (20% monolayer sulfur coverage) was successfully prepared by the technique used to prepare the 50% monolayer sulfur-treated catalyst. The catalyst was heated to only 873 K to avoid sintering, and no isostere was measured. The BET surface area of the low-level sulfur-treated catalyst (17 m^2 g^{-1}) showed a 20% reduction compared with the freshly reduced catalyst.

Sulfur Treatment of Cobalt Catalysts

The alumina-supported cobalt 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), the rate of sulfur adsorption at 425 K was slowed to about 0.4 monolayers per hour in a recirculating stream of 30 ppm H_2S in 100-kPa H_2. After reduction at 773 K, the catalyst was characterized by H_2 and CO chemisorption and tested for FTS performance.

A fully sulfided (100% monolayer sulfur coverage) cobalt catalyst was also prepared as a titration of the total active metal surface area. This high-level sulfur-treated cobalt catalyst was also tested for FTS activity and methane selectivity. Approximately 18 μmol of H_2S was injected into the recirculation system at 773 K, corresponding to a metal surface area of 22.5 m^2 g^{-1}. The catalyst was equilibrated overnight at 773 K, the gas-phase H_2S concentration was measured over a range of temperatures, and the isostere was plotted in Figure II-3. Comparison of our data with previously published isosteres on cobalt powder[14] indicates that our cobalt catalyst reached approximately 90% of saturation coverage.

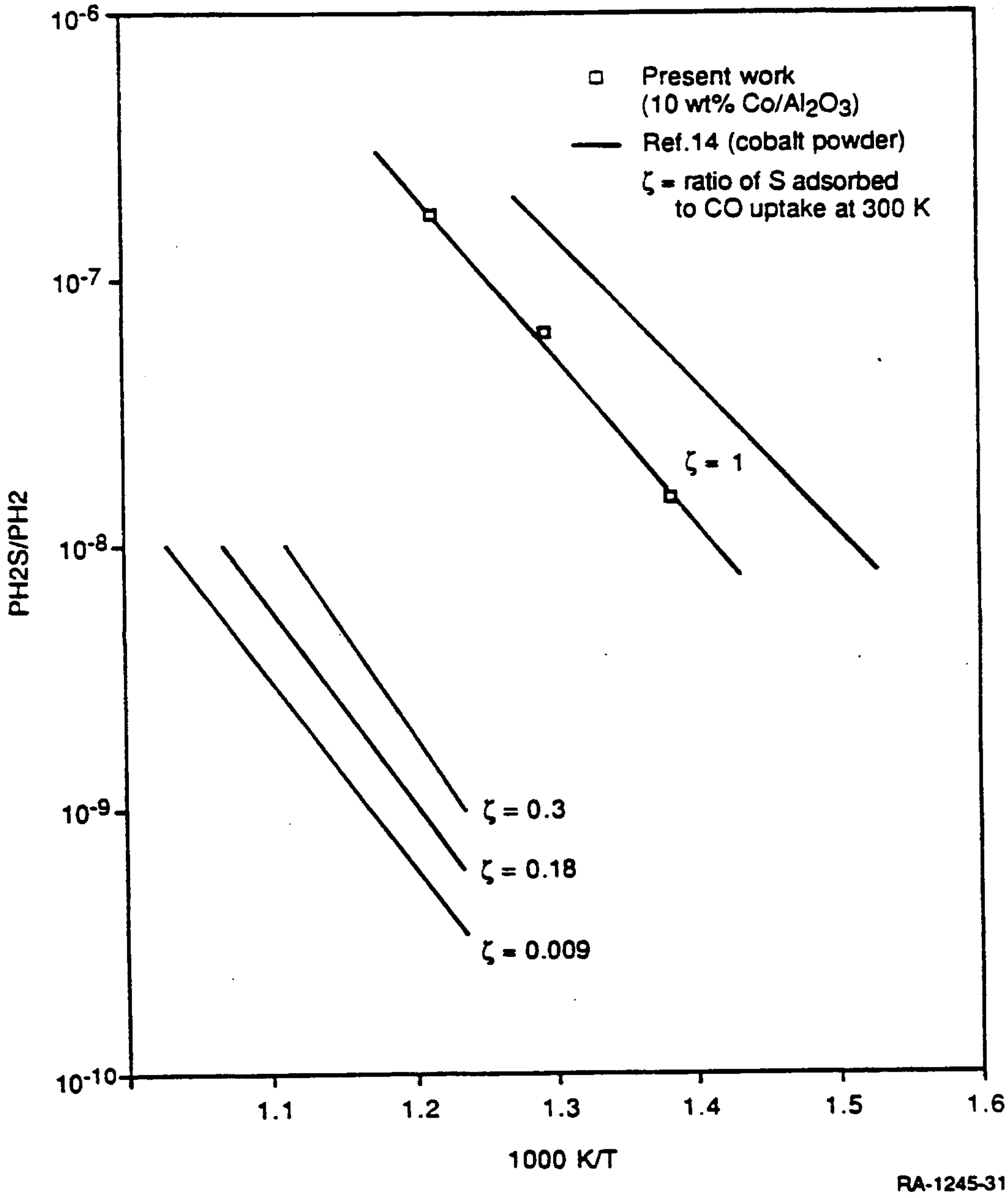

Figure II-3. Sulfur chemisorption isosteres on cobalt/Al_2O_3 and cobalt powder.

Characterization and Testing of FTS Catalysts

Experimental Procedures. The reactant gases included a 33.5% carbon monoxide in hydrogen mixture and a 50.2% carbon monoxide in hydrogen mixture, with metal carbonyls removed by passage through a molecular sieve trap cooled by dry-ice/acetone. The hydrogen used for pretreatment of the catalysts was purified by diffusion through a Pd-Ag thimble, and 99.99% pure helium was further purified with a commercial oxygen-trap.

A continuous flow quartz microreactor was used for FTS reaction studies. The catalyst sample (0.2-0.5 g) was placed on a fritted quartz disk located inside the reactor. The reactor was heated by a resistance furnace and maintained at the desired temperature by an automatic temperature controller. A Chromel-Alumel thermocouple was situated in the catalyst bed to measure the reaction temperature. A schematic diagram of the FTS testing apparatus is shown in Figure II-4.

Effluent from the reactor was continuously monitored by a quadrupole mass spectrometer and two gas chromatographs. The mass spectrometer and the automated two-column gas chromatograph (Carle) were used to follow the methane and hydrocarbon yields up to C_3 and the overall CO conversion rate. Aliquots of samples were injected into a second programmable gas chromatograph (Hewlett-Packard) equipped with a subambient control system, a wide-bore capillary column, and a flame ionization detector. Hydrocarbon products up through carbon number C_{15} were measured, and light olefins and paraffins were separated.

The entire downstream flow and sampling system were heated to about 523 K to prevent condensation of high-boiling waxy products. The experimental configuration permitted sampling of the reactor inlet and outlet gas mixtures by the mass spectrometer and gas chromatograph. The FTS product distribution and synthesis gas conversion were determined from the difference between the inlet and outlet concentrations.

All the FTS experiments were conducted under differential conditions with a maximum CO conversion of 5%. The hydrocarbon reaction rate R is defined as the number of nanomoles of carbon monoxide converted into C_1

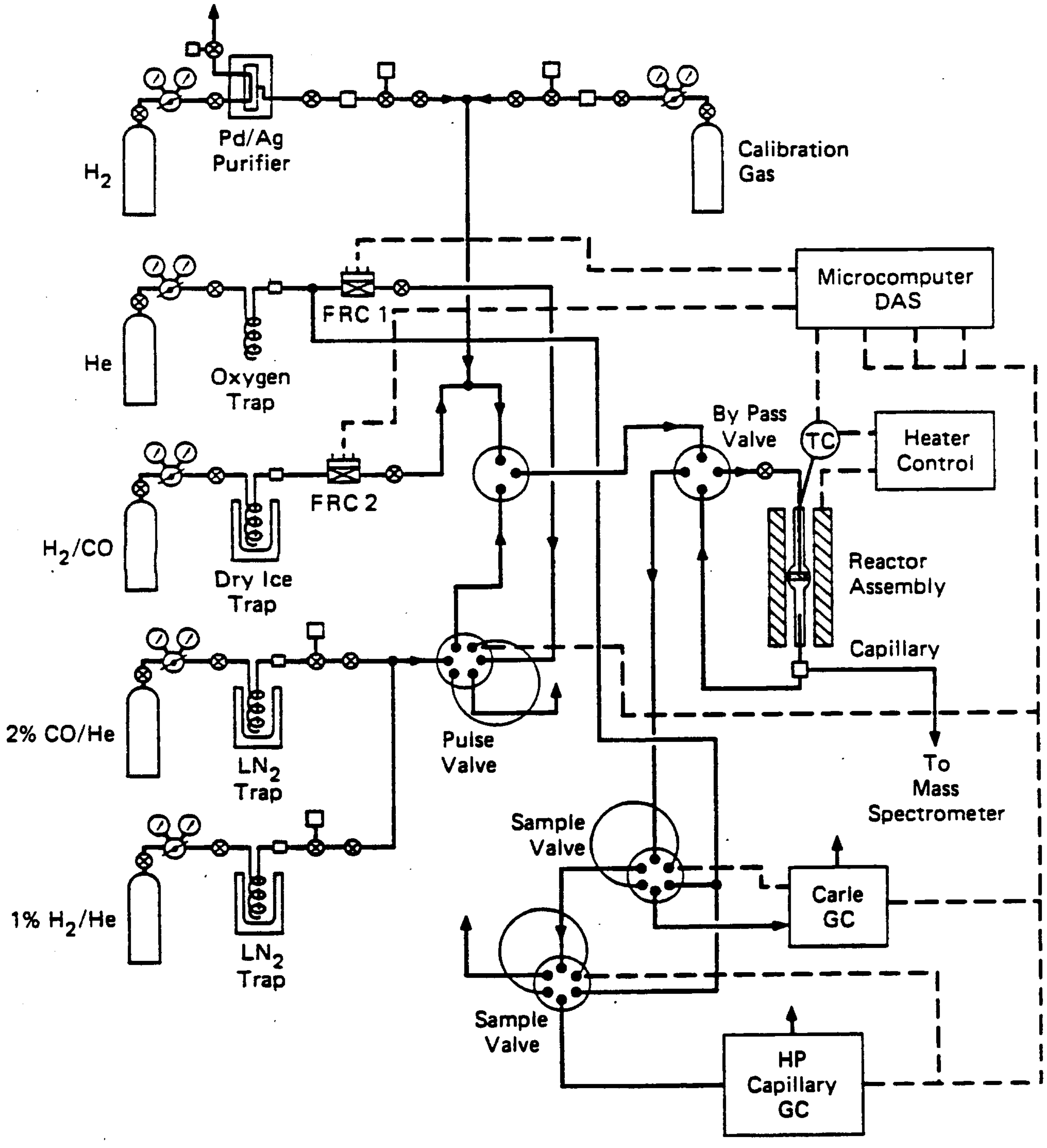

Figure II-4. Catalyst characterization and FTS testing apparatus.

through C_{10} hydrocarbon per gram of catalyst per second. The selectivity S is defined as the ratio of the rate of formation of methane relative to the overall hydrocarbon reaction rate for C_1 through C_{10} products (on a carbon-atom basis). A list of experimental parameters for FTS catalyst testing is included in Table II-2.

FTS Testing of Clean and Sulfur-Treated Fused Iron Catalysts. Fixed-bed FTS tests were performed at 1-atm (0.1 MPa) with 2:1 and 1:1 H_2:CO feedgas ratio for a series of clean and sulfur treated fused iron catalysts (Table II-3). As expected, the sulfur treatment greatly reduced the overall activity of the fused iron catalyst with 2:1 H_2:CO synthesis gas at 573 K after 22 h. The medium-level sulfur-treated showed only 8% and the high-level sulfur-treated fused iron catalysts showed only 2% of the activity of the clean catalyst. However, both sulfur treatments reduced the methane selectivity of fused iron from about 40% (C atom basis) to about 14%, thereby partially offsetting the reduced rates for C_2 and higher hydrocarbons. In addition, the high-level sulfur-treated catalyst produced almost exclusively light olefins with a chain growth factor of only approximately 0.25. These results were encouraging so additional tests were performed with 1:1 H_2:CO synthesis gas.

At 573 K and 100 kPa with 1:1 H_2:CO synthesis gas, the clean fused iron catalyst after 2 h on stream produced hydrocarbons at a rate of 26 μmol g^{-1} s^{-1} with a chain growth probability factor of 0.43 (Figure II-5) an a methane selectivity of 39% at 573 K. The methane selectivity increased to 63% as the clean catalyst deactivated after 24 h to a total hydrocarbon rate of roughly 10% of its projected initial rate (Table II-3). The activity of the clean fused iron catalyst could be restored temporarily to its original value by TPR in 1-atm hydrogen up to 773 K. This effect implicated carbon deposition as the cause for deactivation of the clean fused iron catalyst, as could be expected for low-H_2 synthesis gas; and at 548 K, the clean catalyst had a chain growth probability of 0.48 with a 27% selectivity toward methane and no obserable deactivation.

Table II-2

EXPERIMENTAL PARAMETERS FOR FTS CATALYST EVALUATION

Parameter	Range
Catalyst weight	0.5 to 1.0 g
Feed gas composition	33.51 vol% CO, bal. H_2 50.2 vol% CO, bal. H_2
Feed gas flow rate	2.5 to 20 mL/min
Pressure	0.1 to 2.0 MPa
Temperature	525, 550, 575 K
CO conversion	0.05 to 0.1 mol/mol feed
Run duration	2 to 50 h
Product analysis	CO, CO_2, H_2, CH_4, C_nH_{2n+2}, C_nH_{2n}

Table II-3

FIXED-BED FTS PERFORMANCE OF CLEAN AND SULFUR-TREATED FUSED IRON CATALYSTS AT 1-ATM

Catalyst	Clean Fused Fe					Low-Level Sulfur-Treated Fused Iron			Medium-Level Sulfur-Treated Fused Iron		High-Level Sulfur-Treated Fused Iron	
Temperature (K)	548	573	573	548	573	548	573	573	573	573	548	573
H_2/CO Ratio	1	1	1	2	2	1	1	2	1	2	1	2
Run Duration (h)	23	2	22	24	22	22	22	24	24	24	24	20
Product Rate[a] (nmol/g/s)												
C_1	5.03	9.32	4.54	11.21	57.8	1.56	3.21	10.66	1.79	1.52	0.60	0.24
C_2	2.49	3.05	0.70	5.20	24.1	0.99	2.19	4.50	2.20	1.91	0.47	0.72
C_3	1.44	1.72	0.31	2.86	5.37	0.54	1.17	2.42	1.20	0.96	0.22	0.13
C_4	0.63	0.62	0.10	1.24	2.46	0.22	0.47	0.83	0.46	0.46	0.07	0.055
C_5	0.28	0.22	0.03	0.51	1.19	0.08	0.17	0.22	0.12	0.20	0.01	0.006
C_6	0.15	0.11	0.02	0.23	0.52	0.04	0.07	0.102	0.05	0.058	--	--
C_7	0.12	0.09	0.004	0.14	0.26	0.03	0.06	0.044	0.02	--	--	--
C_8	0.05	0.02	--	0.08	--	0.01	0.02	0.025	0.01	--	--	--
C_9	0.01	0.01	--	--	--	0.003	0.003	--		--	--	--
C_{10}	0.01	0.01	--	--	--		0.002	--		--	--	--
TOTAL	20.60	25.78	7.56	40.7	139.2	6.97	14.85	21.8	12.79	11.41	2.56	2.4
Chain Growth Factor[b]	0.48	0.43	0.36	0.50	0.47	0.43	0.45	0.52	0.39	0.42	0.24	0.25
Olefin to n-Paraffin Ratio[c]	2.2	1.4	3.9	15	--	11.7	3.5	4.8	7.35	21.9	--	>20
Methane Selectivity[d]	27	39	63	30	42	25	24	35.7	15.7	14	26	18

[a] GHSV = 600 h^{-1} and P = 0.1 MPa; 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.

rate/(total rate) x 100%.

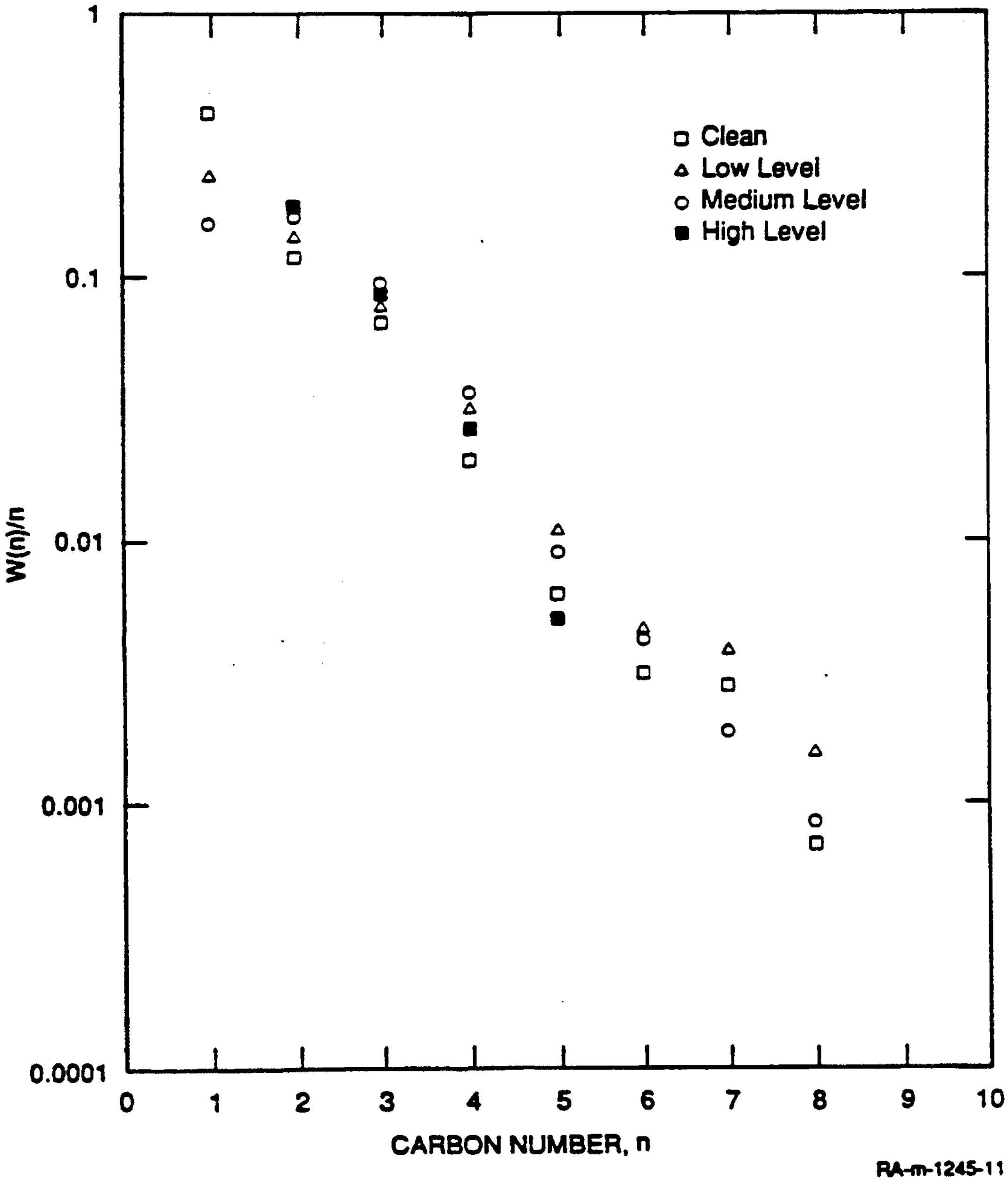

Figure II-5. Schulz-Flory plot of the hydrocarbon product distribution for clean and sulfur-treated fused iron catalysts at 573 K, 100 kPa, and $H_2/CO = 1$.

Unlike the clean catalyst, which deactivated to one-tenth of its original (after 2 h) activity with H_2:CO = 1:1 synthesis gas at 573 K, the sulfur-treated catalysts maintained their activity throughout the 24-h synthesis run. The activity of the low-level sulfur-treated catalyst was about one-third the activity of the clean catalyst at 548 K, but at 573 K under steady state conditions (24 h), it was twice as active as the clean catalyst with superior reduced methane selectivity. The medium-level sulfur-treated catalyst showed about the same activity as the low-level catalyst at 573 K in 1:1 H_2:CO synthesis gas but with a further reduction in methane selectivity. The high-level sulfur-treatment substantially reduced the activity of the fused iron catalyst with a very poor chain growth factor.

The sulfur-treated catalysts demonstrated preferential suppression of methane formation and preferential olefin production. Compared with the early (2 h) FTS performance of the clean catalyst, the low-level sulfur-treated fused iron catalyst demonstrated nearly a twofold (Figure II-6) and the medium-level sulfur-treated catalyst, nearly a threefold reduction in methane selectivity at 573 K (Figure II-7). The selectivity toward methane at 14% for the medium-level sulfur-treated catalyst (50% monolayer sulfur coverage) and 18% (Figure II-8) for the high-level sulfur-treated catalyst (100% monolayer sulfur coverage) as compared with 39%, initially (after 2 h) and 63% at steady-state (after 22 h) for the untreated catalyst. The ratio of alkenes to alkanes was very high at about 20 for both sulfur-treated catalysts (Figures II-7 and II-8). The chain growth probability for C_2 to C_{10} hydrocarbons was reduced slightly as the amount of sulfur chemisorbed on the catalyst's surface increased (Figure II-5).

The series of sulfur-treated fused iron catalysts showed a minimum in methane selectivity (Figure II-9) at roughly 50% saturation coverage. The olefin production rate showed little change from that of the clean catalyst, but the paraffin production rate (including methane) dropped significantly. If only C_2 to C_{10} total hydrocarbon rates were considered, the activity of the medium-level sulfur-treated catalyst in H_2:CO = 2:1 synthesis gas at 573 K was 11% of the clean catalyst, and the activity of the high-level sulfur-treated catalyst was 1.3%; with H_2CO = 1:1 synthesis

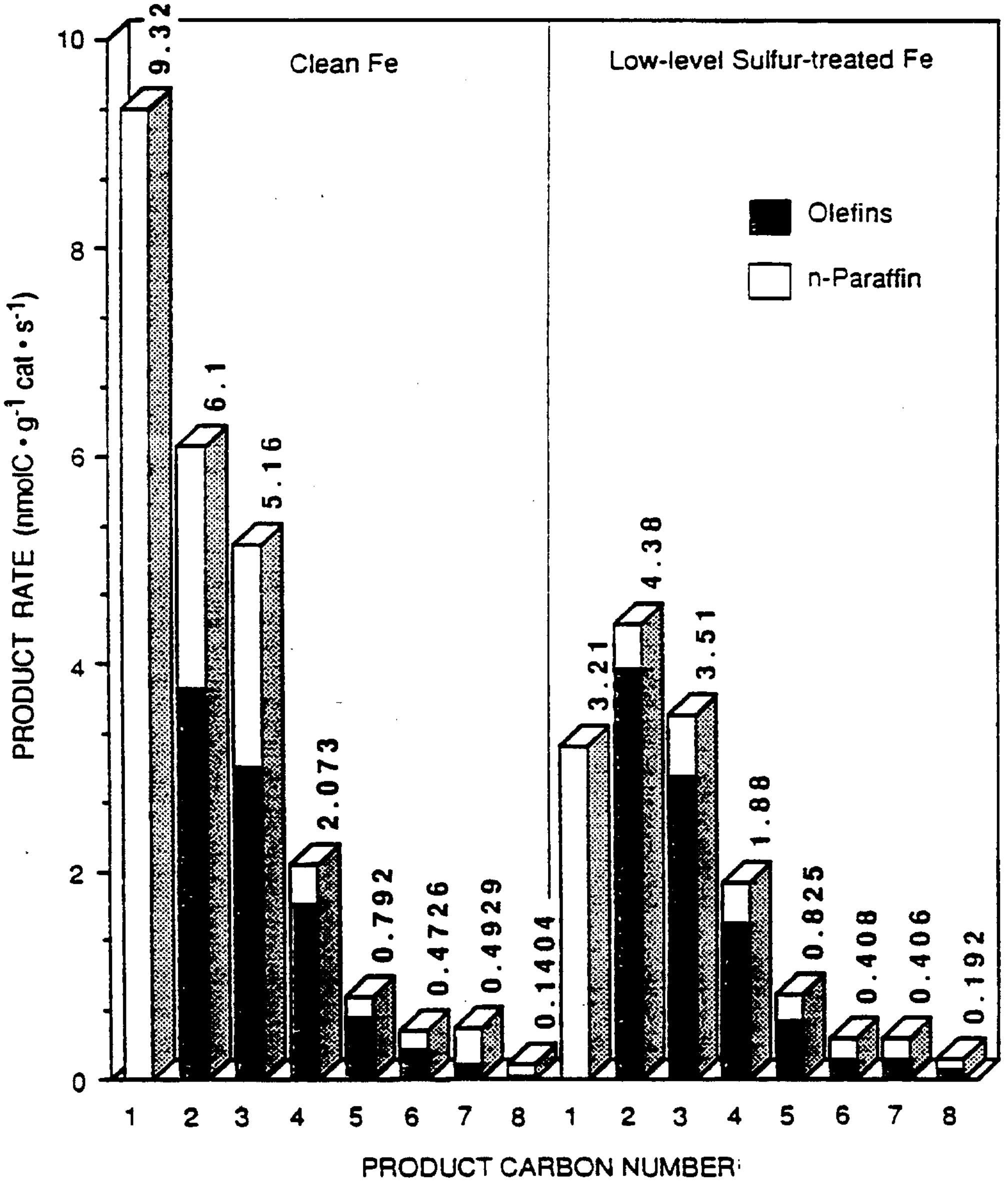

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Figure II-6. Fischer-Tropsch synthesis at 573 K, 100 kPa, and H_2/CO ratio = 1, on clean and low-level sulfur-treated fused iron catalysts after 22 h. Rates are in nmoles carbon per gram catalyst per second.

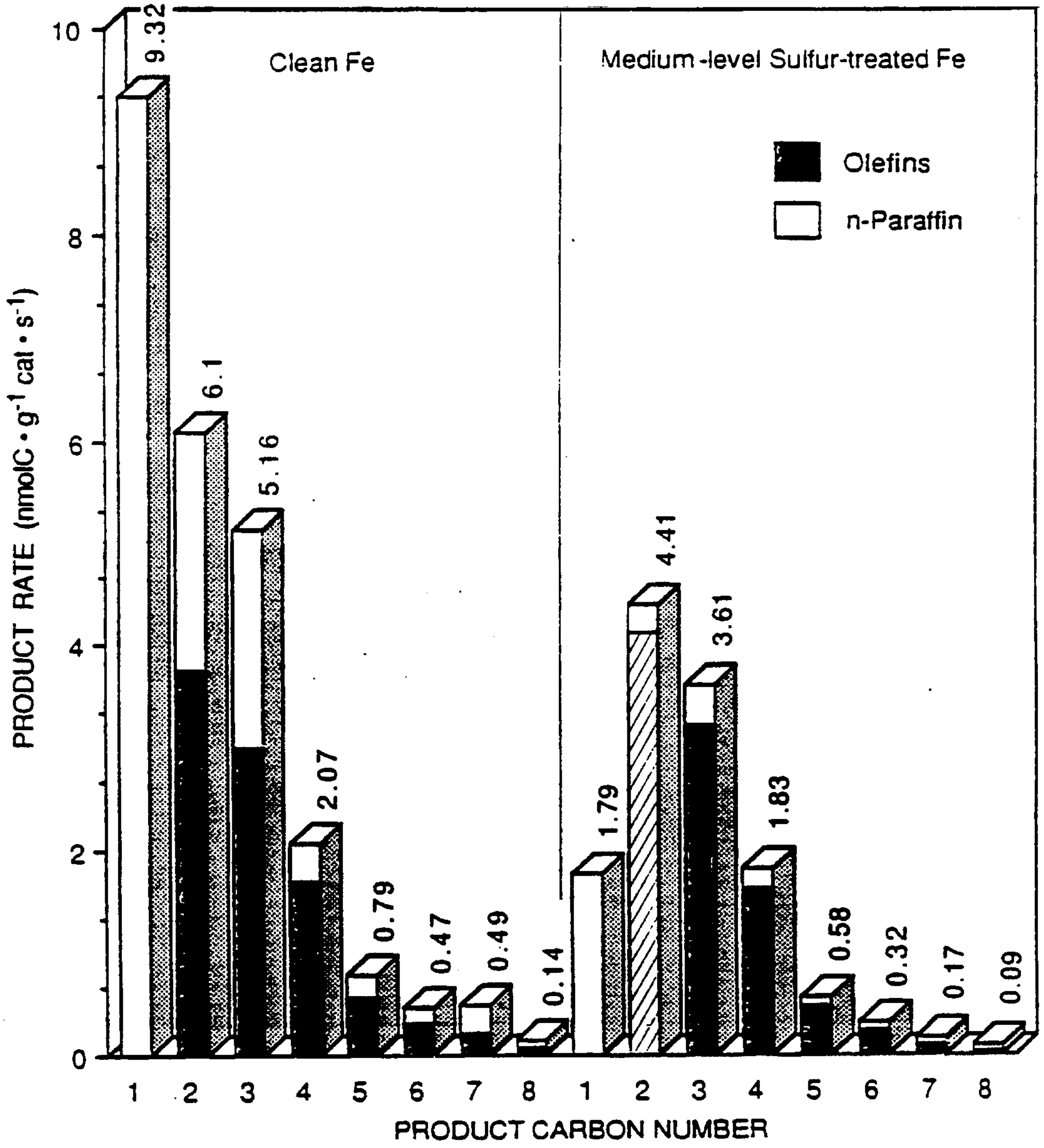

Figure II-7. Fischer-Tropsch synthesis at 573 K, 100 kPa, and H_2/CO ratio = 1, on clean and medium-level sulfur-treated fused iron catalysts after 24 h. Rates are given in nmoles carbon per gram catalyst per second.

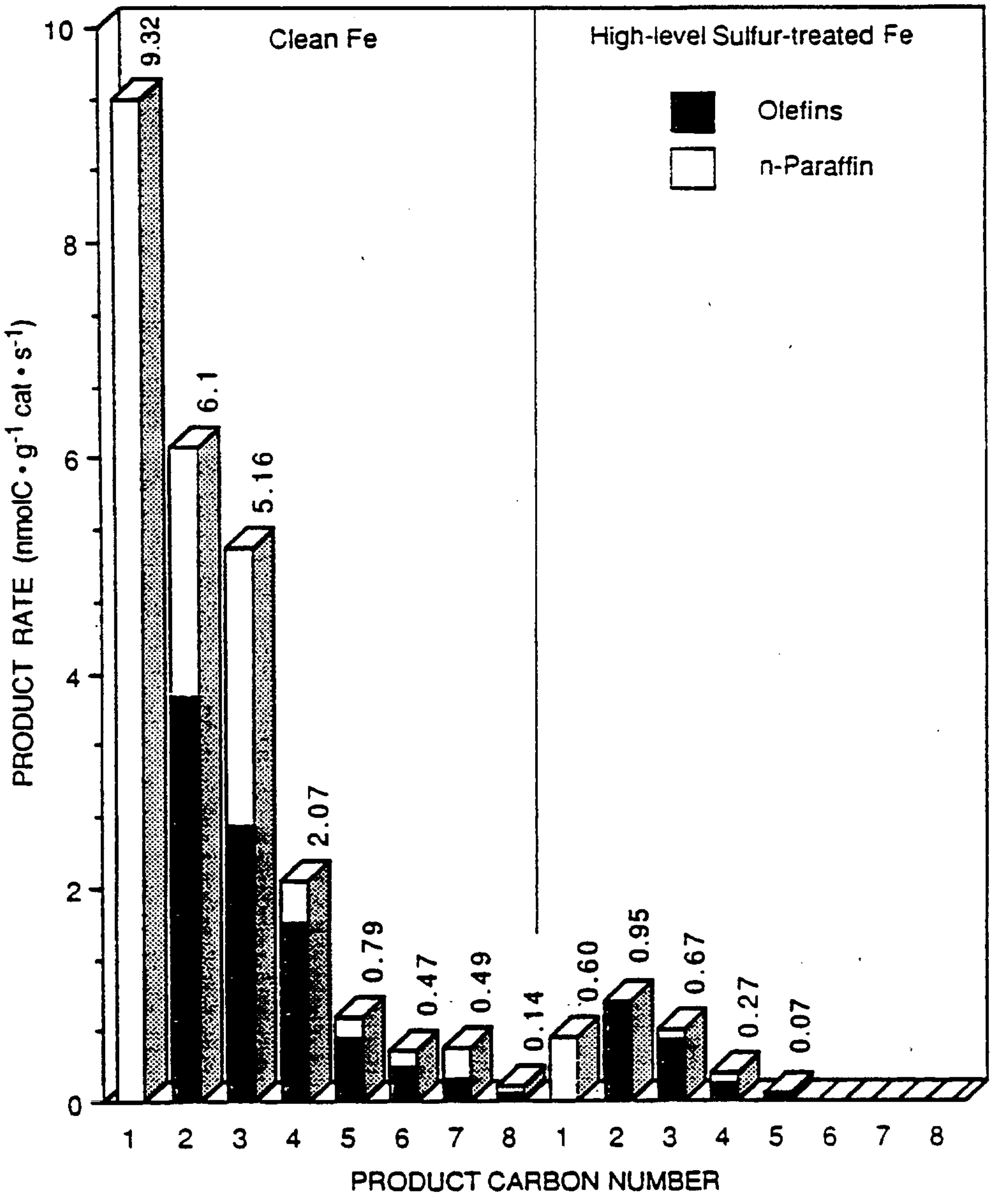

Figure II-8. Fischer-Tropsch synthesis at 573 K, 100 kPa, and H_2/CO ratio = 1, on clean and high-level sulfur-treated fused iron catalysts after 24 h. Rates are given in units nmoles carbon per gram catalyst per second.

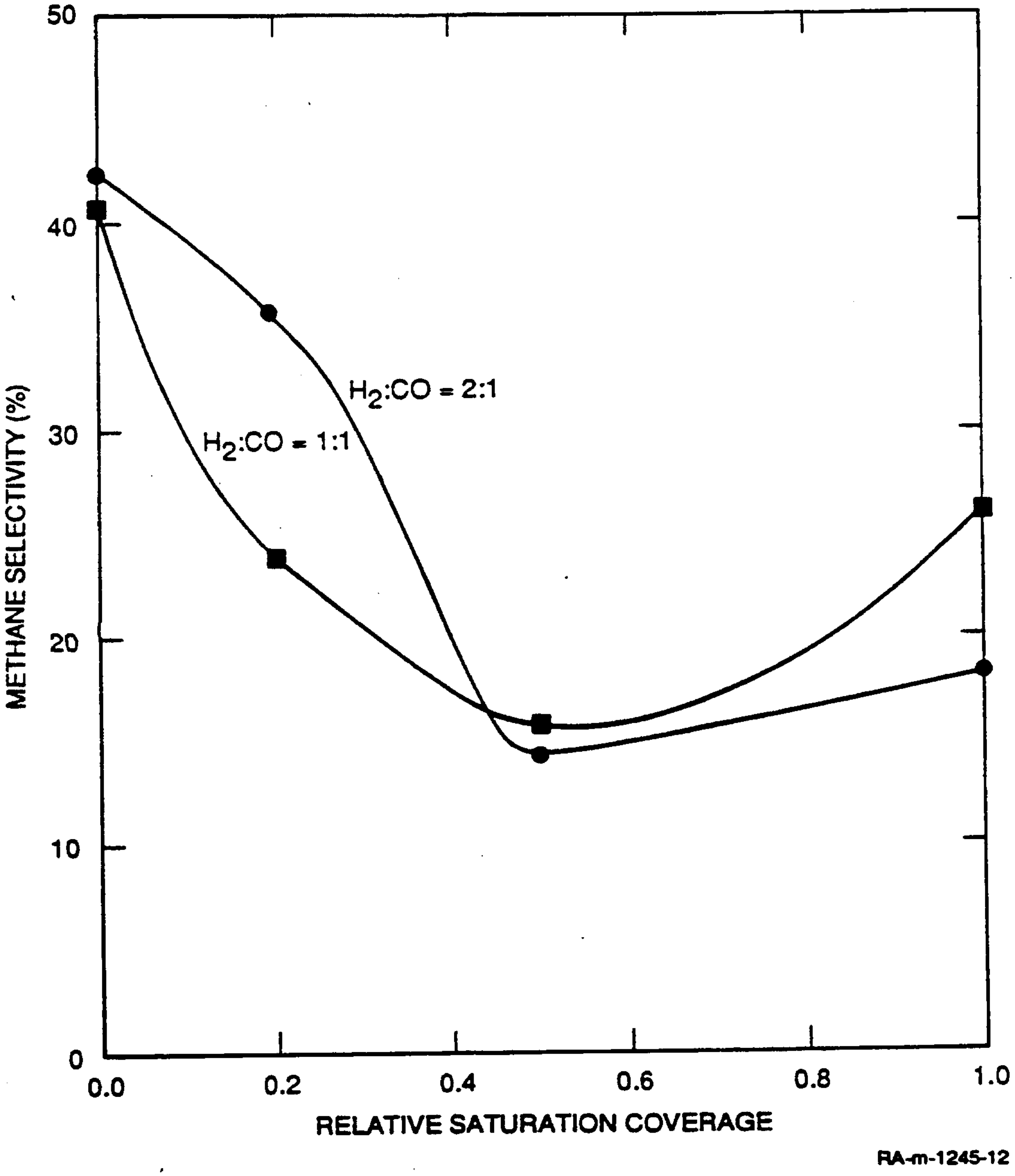

Figure II-9. Fischer-Tropsch synthesis at 573 K and 100 kPa on fused iron catalysts.

gas, the low- and medium-level sulfur-treated catalysts were comparable or superior to the deactivating clean fused iron (Figure II-10).

FTS Testing of Clean and Sulfur-Treated Cobalt Catalysts. The clean cobalt catalyst had higher FTS activity than the fused iron catalyst (Table II-4). The clean cobalt catalyst was 30 times higher in FTS activity initially than the fused iron catalyst at 548 K and 10 times higher at steady state (after a 24-h synthesis run). The clean cobalt catalyst produced hydrocarbons with a chain growth probability factor of 0.47 and a methane selectivity of 43% at 548 K. The chain growth probability factory increased slightly to 0.54 (Figure II-11), but the methane selectivity remained unchanged as the catalyst deactivated after a 24-h run. (At 523 K, the clean catalyst had a chain growth probability of 0.58 with 45% selectivity towards methane and showed no change with time.) The activity of the clean cobalt catalyst could be restored temporarily to its original value by TPR in 1-atm hydrogen up to 773 K. This effect implicated carbon deposition as the cause of deactivation of the clean cobalt catalyst, as could be expected from low-H_2 synthesis gas. The cobalt catalyst may have deactivated at a lower temperature than fused iron (548 K for cobalt and 573 K for fused iron) because of its greater rate of olefin production under low hydrogen conditions.

Figure II-12 shows the similarity of hydrocarbon product distribution between the clean fused iron and clean cobalt catalysts at 573 K and 548 K, respectively. It is most encouraging that the cobalt catalyst possesses a high olefin to paraffin selectivity (alkene/alkane ratio = 10) for light hydrocarbons and a ten-fold higher activity in its uncontaminated state and at lower temperature than the clean fused iron catalyst.

The medium-level sulfur-treated cobalt catalyst was examined for FTS activity and product distribution with $H_2/CO = 1$ synthesis gas at 100 kPa and 525 K. It showed reduced activity relative to the fresh cobalt catalyst but, unlike the sulfur-treated fused iron catalyst, only a moderate decrease in methane selectivity (Table II-4). The olefin-to-paraffin ratio for light hydrocarbons for the sulfur-treated cobalt

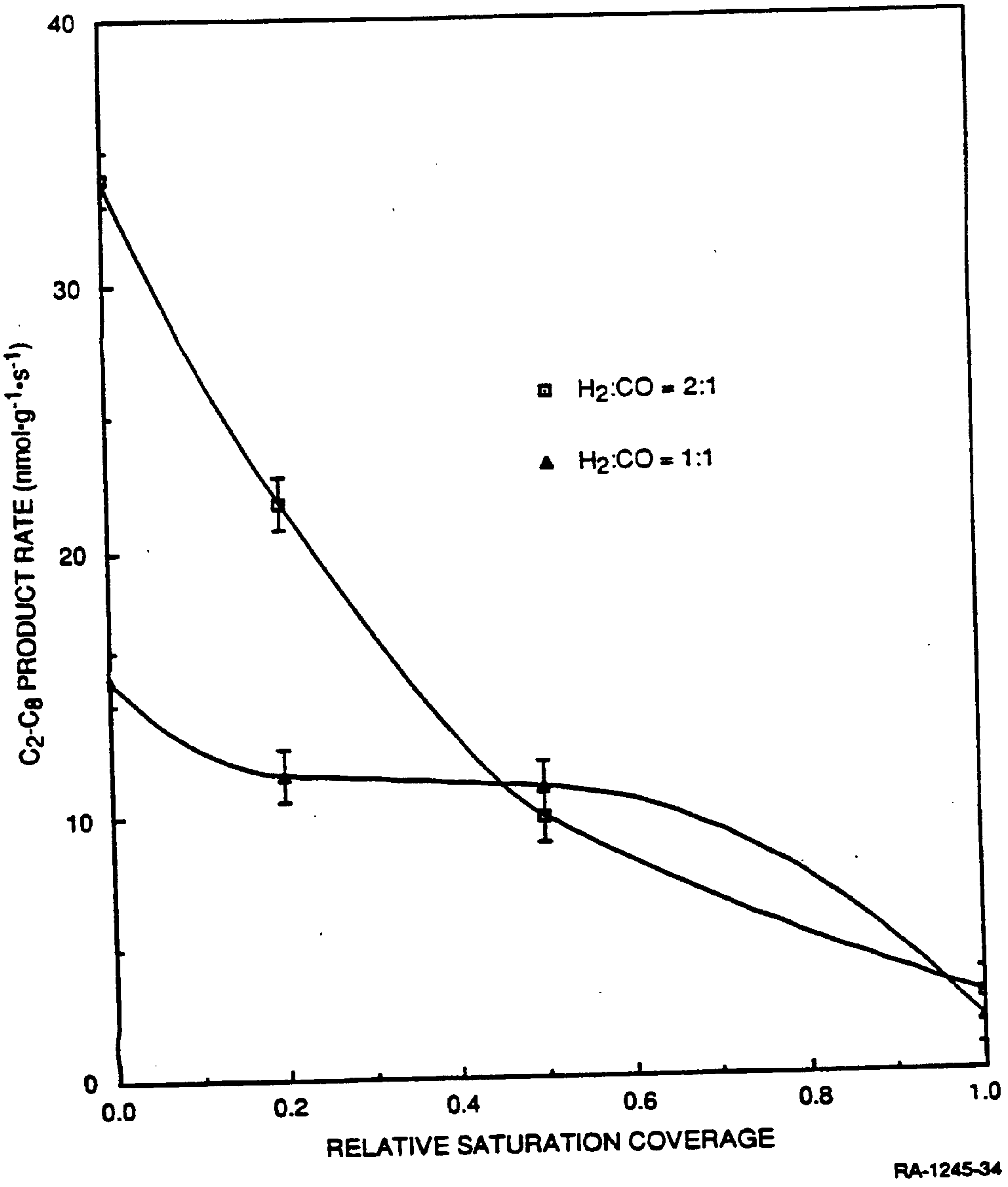

Figure II-10. Effect of sulfur treatment on light hydrocarbon product rate during Fischer-Tropsch synthesis at 573 K and 100 kPa on fused iron catalysts.

Table II-4

FIXED-BED FTS PERFRORMANCE OF CLEAN FUSED IRON AND CLEAN AND SULFUR-TREATED COBALT CATALYSTS

Catalyst	Clean Fused Iron		Clean 10 wt% Co/Al_2O_3			High-Level Sulfur-Treated 10 wt% Co/Al_2O_3	Medium-Level Sulfur-Treated 10 wt% Co/Al_2O_3	
Temperature	548	548	523	548	548	548	523	523
Pressure (MPa)	0.1	2	0.1	0.1	0.1	0.1	0.1	2
H_2/CO Ratio	1	1	1	1	1	1	1	1
Run Duration (h)	23	24	20	2	24	21	23	24
Production Rate[a] (nmol/g/s)								
CO_2	33.53	608.35	33.79	78.75	29.99	2.75	21.64	28.05
C_1	5.03	90.41	113.44	261.97	86.67	2.86	103.57	124.36
C_2	2.49	25.43	9.66	24.41	15.17	1.02	9.42	7.95
C_3	1.44	27.22	14.67	39.86	12.82	0.69	16.65	15.63
C_4	0.63	17.72	8.94	18.95	6.47	0.28	9.54	13.14
C_5	0.28	10.87	4.56	7.32	2.91	0.14	5.44	10.19
C_6	0.15	7.49	2.81	3.55	1.76	0.08	3.15	8.75
C_7	0.12	5.36	1.54	1.62	0.93	0.06	1.73	7.71
C_8	0.05	3.77	0.90	0.75	0.52		1.00	7.06
C_9	0.02	2.99	0.51	0.35	0.26		0.49	7.08
C_{10}	0.01	3.12	0.34	0.22	0.16		0.29	
TOTAL	20.60	518.08	278.09	586.76	221.12	9.69	284.03	517.3
Chain Growth Factor[b]	0.48	0.72	0.58	0.47	0.54	0.49	0.56	0.85
Olefin to Paraffin Ratio[c]	2.2	1.6	3.6	4.2	10.6		0.21	0.93
Methane Selectivity[d]	27	19	45	43	43	32	39	26

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[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%.

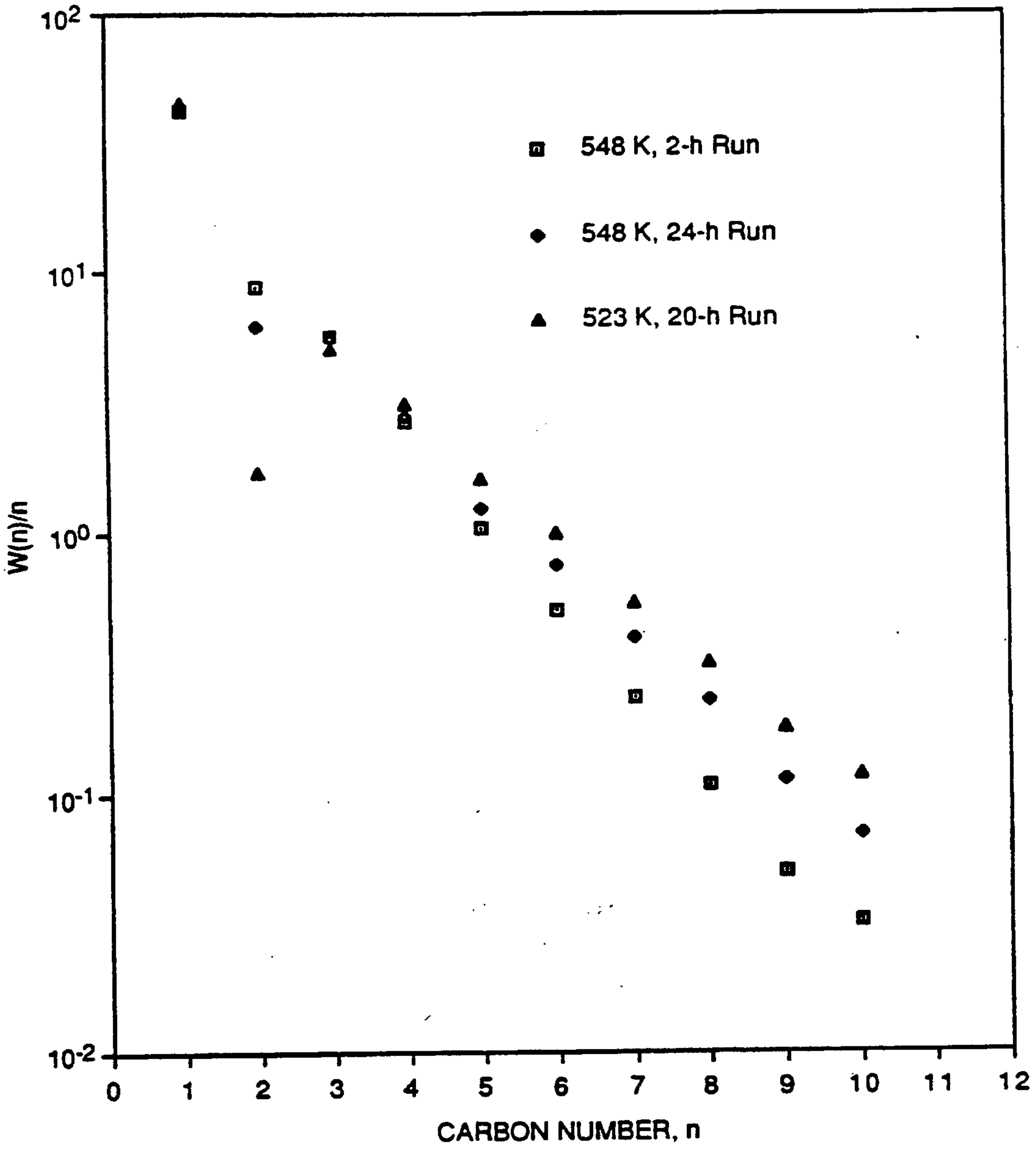

Figure II-11. Schulz-Flory plot of the hydrocarbon product distribution for cobalt on alumina catalyst at 100 kPa and $H_2/CO = 1.0$.

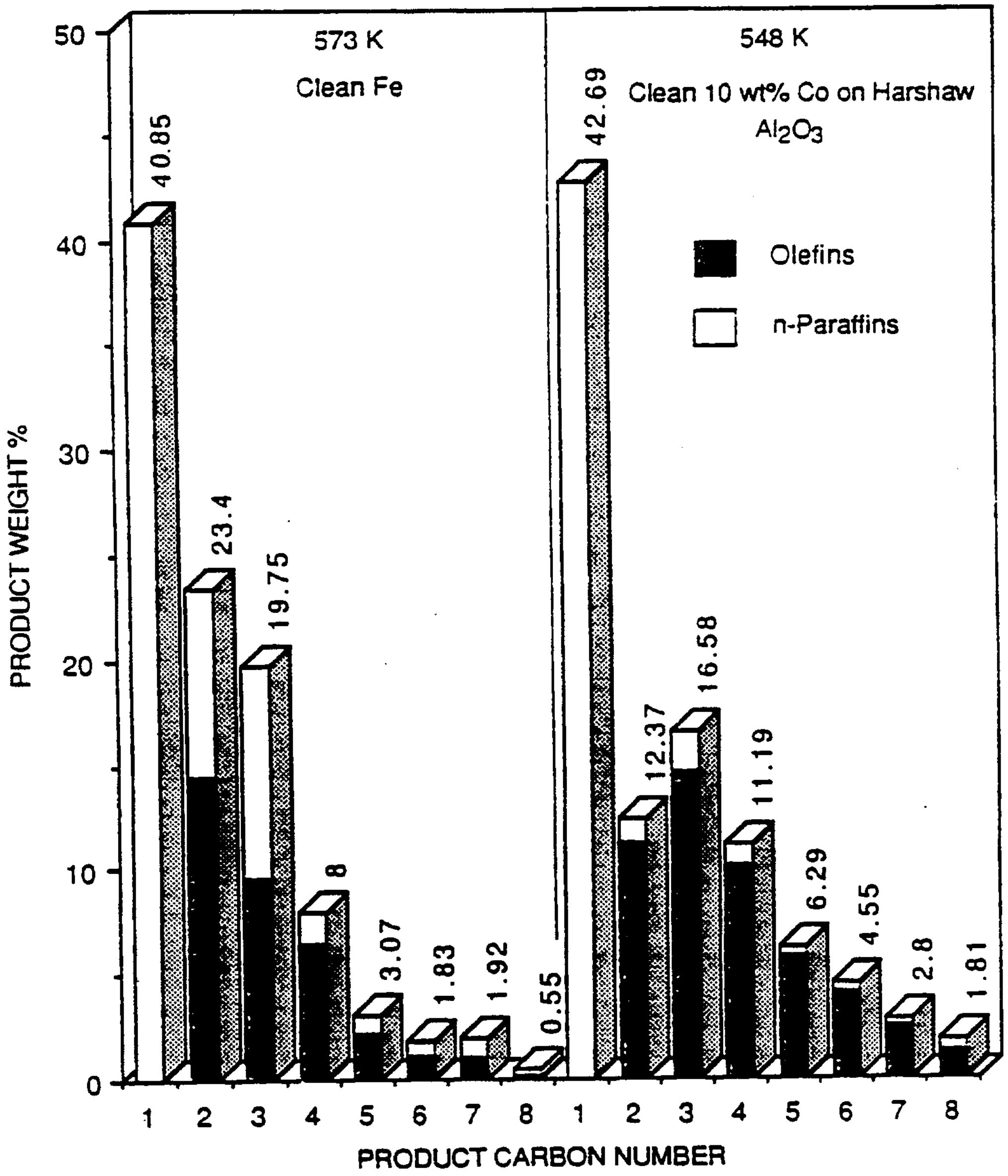

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Figure II-12. Fischer-Tropsch synthesis at 100 kPa and H_2/CO ratio = 1 on clean fused iron and clean cobalt catalysts at 573 K and 548 K, respectively.

catalyst was also low (3:1) relative to that of the medium-level sulfur-treated fused iron catalyst (20:1). Unlike the sulfur-treated fused iron catalyst, which showed an increase in olefin selectivity relative to the clean iron catalyst, the sulfur-treated cobalt catalyst showed a decrease in light olefin selectivity compared to that of the clean cobalt catalyst under similar conditions.

Clean and Sulfur-Treated Precipitated Iron Catalysts. The clean and sulfur-treated K- and Cu-promoted precipitated iron catalysts were tested for FTS activity and found to be 68% and 48%, respectively, selective toward methane at 573 K and steady-state conditions. Preparing a sulfur-treated precipitated iron FTS catalyst at a desirable fractional monolayer coverage was difficult because we had no reliable measure of true metal surface area of the potassium-promoted precipitated catalyst. Even at what appeared to be full-saturation sulfur coverage ($\Theta_S = 1.0$), the sulfur-treated precipitated iron catalyst remained more selective toward methane (48%) than fused iron catalysts. No further testing was done on the promoted precipitated iron catalyst because of its instability during sulfur treatment and its high selectivity for methane compared with that of the standard fused iron catalyst.

Evaluation of Improved FTS Catalysts

FTS performance of the medium-level sulfur-treated fused iron catalyst and the fused iron standard catalyst was examined in a fixed bed reactor at 2 MPa and 525 to 575 K. Typically, the CO conversion was about 20%. After 24 h at 575 K, the methane yield of the sulfur-treated fused iron catalyst was 15 wt% at low conversion, whereas the clean fused iron catalyst showed nearly 28 wt% CH_4 under the same reaction conditions (Table II-5). The chain growth parameter (for C_3-C_9) decreased from 0.65 to 0.52 with increased sulfur treatment (Figures II-13 and II-14).

The results for the fixed-bed FTS performance of the medium-level sulfur-treated fused iron FTS catalyst are encouraging. After 24 h, the total hydrocarbon rate at 573 K for the medium-level sulfur-treated catalyst was about 49.6% of the rate of the untreated catalyst. If only C_2 through C_{10} total hydrocarbon rates were considered, the activity of the

Table II-5

FIXED-BED FTS PERFORMANCE OF CLEAN AND SULFUR-TREATED FUSED IRON CATALYSTS AT 20-ATM

Catalyst	Clean Fused Fe		Medium-Level Sulfur-Treated Fused Iron			
Temperature (K)	573	548	573	548	573	548
H_2/CO Ratio	1	1	1	1	2	2
Run Duration (h)	24	24	24	24	24	24
Product Rate[a] (nmol/g/s)						
C_1	332.36	90.41	53.86	7.75	32.55	11.58
C_2	42.44	25.43	43.07	8.27	22.82	9.75
C_3	79.45	27.21	34.70	6.24	16.58	7.04
C_4	47.77	17.72	17.30	3.57	7.81	3.59
C_5	24.56	10.87	6.81	1.27	2.89	1.32
C_6	16.91	7.49	3.80	0.78	1.53	0.75
C_7	10.98	5.36	1.86	0.42	0.77	0.38
C_8	7.28	3.77	1.04	0.24	0.42	0.23
C_9	5.37	2.98	0.65	0.14	0.24	0.13
C_{10}	4.71	3.12	0.37	0.09	0.11	0.09
TOTAL	1201.43	518.08	401.16	75.34	194.85	84.21
Chain Growth Factor[b]	0.65	0.72	0.52	0.54	0.50	0.53
Olefin to n-Paraffin Ratio[c]	1.67	1.58	3.67	5.23	3.34	4.69
Methane Selectivity[d]	28	19	15	11.6	18.6	15.4

[a] GHSV = 600 h^{-1} and P = 20 MPa; 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%.

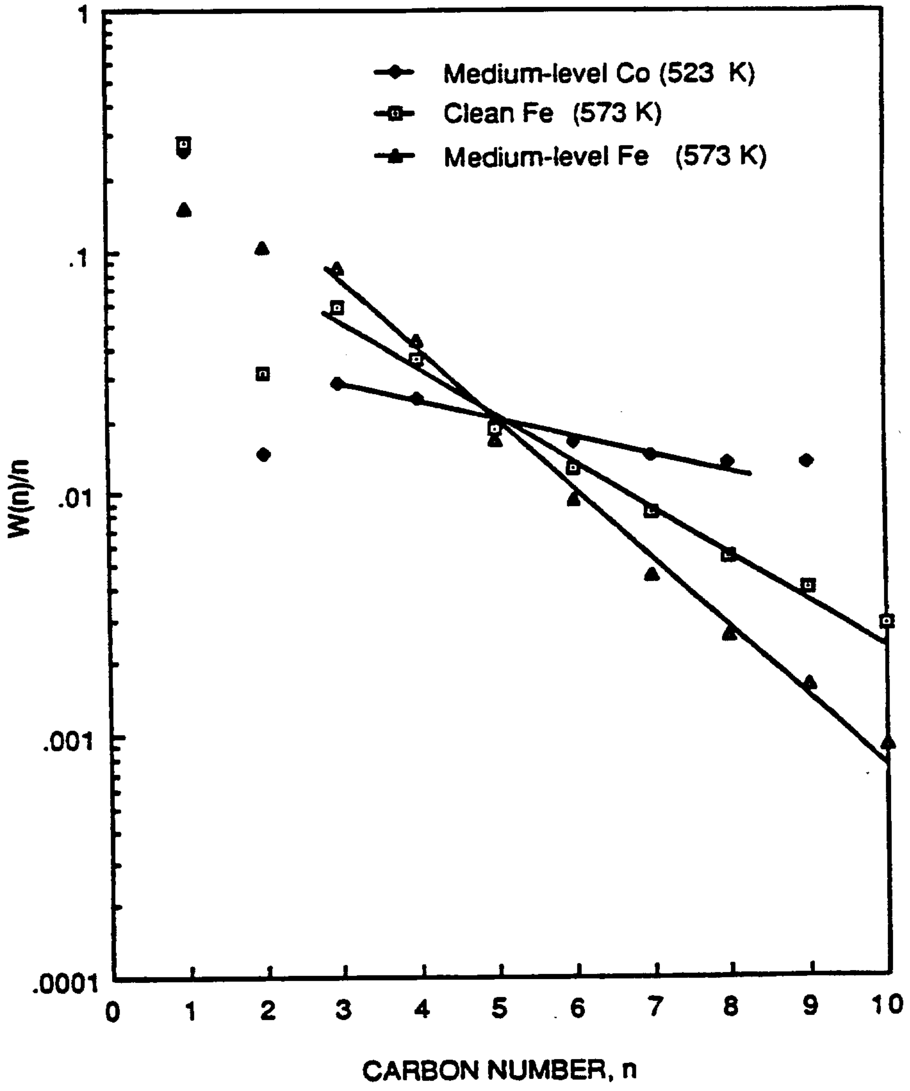

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Figure II-13. Schulz-Flory-Anderson plot of the hydrocarbon product distribution for fused clean iron, medium-level sulfur-treated iron, and medium-level sulfur-treated cobalt catalysts at 2 MPa, $H_2/CO = 1$, and 573 K and 523 K, respectively.

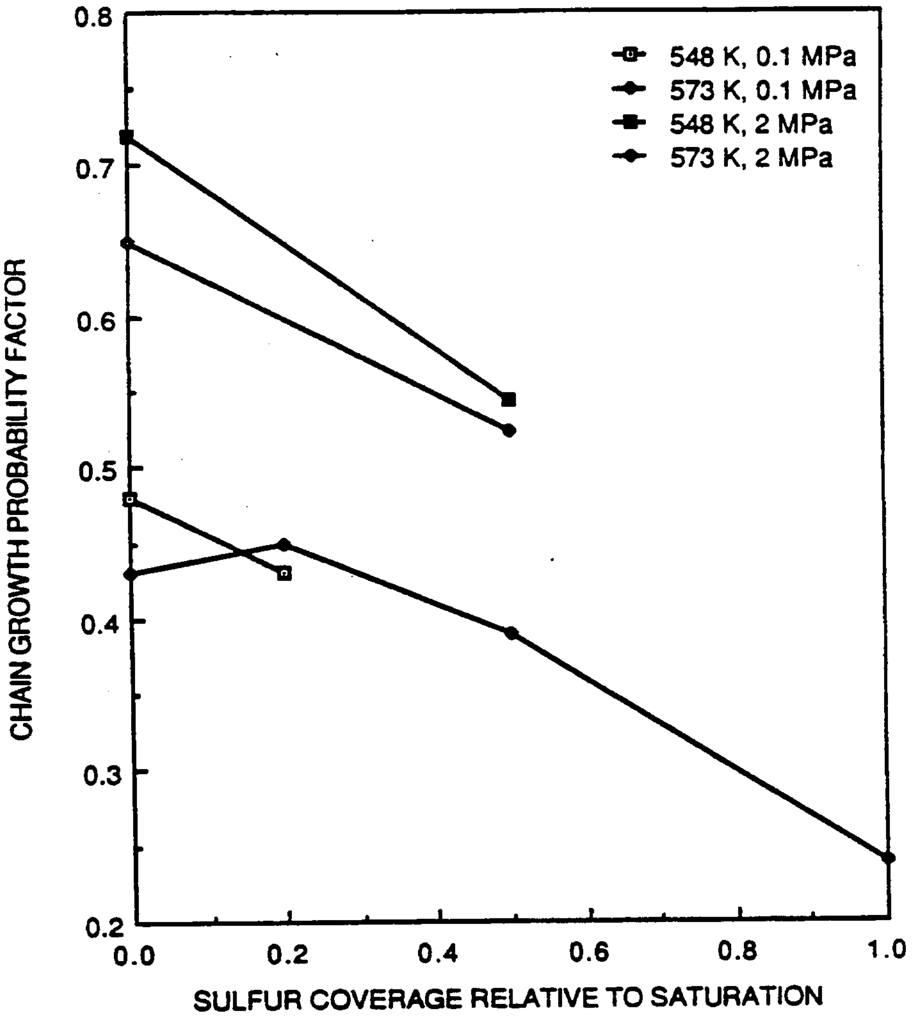

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Figure II-14. Chain growth probability factor for clean and sulfur-treated fused iron catalysts with H_2/CO ratio = 1.

medium-level sulfur-treated catalyst was 66.8% of the clean catalyst. The sulfur-treated catalyst shows nearly the same level of improvement in methane selectivity (decreased by a factor of about 2) at 2 MPa as previously found at 100 kPa, with roughly a factor of three decline in overall rate at 575 K.

A hot-wax trap was installed at the exit of the FTS reactor. The trap was designed to collect C_{12+} hydrocarbons when operated at 393 K. The condensed wax was dissolved in toluene and analyzed by FIMS to determine the distribution and chain growth probability factor of higher hydrocarbons. Hydrocarbon wax contains both paraffins and olefins and exhibits chain growth probability of up to carbon number C_{50}. Samples from slurry reactor runs using cobalt and fused iron catalysts were kindly provided by Professor Satterfield of MIT and were used as the comparative standard and calibration for our FIMS data. In using the FIMS technique to analyze the MIT cobalt sample, which was composed almost entirely of normal paraffins, we obtained results (weight %) for C_{30} through C_{45} very similar to the data in the accompanying analysis.[18] Therefore, we were able to obtain the weight fractions of C_{30} and C_{40} in the sample from the hot wax trap for the fixed-bed synthesis run with clean fused iron at 573 K, 2 MPa, and H_2/CO ratio of 1 (Table II-6).

Table II-6

FIMS ANALYSIS OF FTS WAX

Carbon Number	FIMS Result (weight %)	Predicted Value (weight %)
30	3.07×10^{-4}	1.32×10^{-3}
40	4.34×10^{-5}	2.36×10^{-5}

We compared the FIMS results in Table II-6 to the values predicted by extrapolating to the wax range using the calculated (for C_3 through C_9) chain growth probability factor ($\alpha = 0.649$). The FIMS results indicated that a higher probability factor ($\alpha \cong 0.8$) existed for the wax range than for the light hydrocarbon range.

Discussion

The selectivity of the medium-level sulfur-treated fused iron catalyst with two to threefold reduction in methane yield and nearly 80% olefin selectivity for light hydrocarbons is most encouraging. The two to threefold decrease in activity can be offset by the higher operating temperature; i.e., the sulfur-treated catalyst operating at 573 K has about the same activity for C_{2+} hydrocarbon production as the untreated catalyst at 523 K. The adequate activity, low selectivity for methane, and high selectivity for light olefins make this catalyst a good candidate for FTS in a fluid-bed or fixed-bed reactor operating above 550 K to suppress wax production by lowering the Anderson-Schulz-Flory chain growth parameter.

Matsumoto and Satterfield[13] (at MIT) reported, in a study similar to our high-pressure fixed-bed studies, FTS results with sulfur-treated fused iron catalyst. They used liquid dibenzothiophene as the poison in a slurry reactor operating at 536 K, 1.48 MPa, and H_2/CO ratio of 0.7:1.0, and they observed that methane selectivity of the poisoned fused magnetite catalyst was significantly lower than that of the unpoisoned catalyst and that the olefin to paraffin ratio was higher on the poisoned catalyst than on the clean catalyst. They also reported that methane selectivity increased and olefin to paraffin ratio decreased with increased CO conversion and that neither parameter was substantially affected by temperature or pressure for a given sulfur-treated catalyst.

Comparison of the results of Matsumoto and Satterfield with our results (respectively) is complicated by differences in sulfur treatment methods (injection of dibenzyl-thiophene to the wax solution of freshly reduced and used carburized catalysts versus H_2S exposure to reduced and passivated catalysts), in extent of sulfur adsorption (approximately 1-10 monolayers determined by bulk elemental analysis versus submonolayer measured adsorption), and in reactor configuration (integral continuous stirred slurry reactor versus fixed-bed reactor, differential with respect to reactants). Since the MIT studies of sulfur-exposed freshly reduced catalysts probably resulted in formation of bulk sulfides, we compare only the results for the used carburized catalyst. The amount of sulfur adsorbed was approximately one monolayer, based on the elemental analysis and the leveling of sulfur loading with increased sulfur exposure. This average sulfur loading was about twice the level of our medium-level sulfur-treated catalyst and probably was less uniform. However, the similar change (roughly 50% decrease) in activity suggests comparable local sulfur coverage.

Our study showed that methane selectivity decreased from about 20 wt% to 12 wt% for the medium-level sulfur-treated fused iron catalysts compared with a 30 mol% to 15 mol% decrease in the MIT study, and the methane selectivity was not affected by increasing pressure (Figure II-15). However, in our study, the olefin to paraffin ratio was increased by the sulfur treatment but decreased with increasing pressure (Figure II-16). Their smaller pressure range (from 0.79 to 1.48 MPa compared to our 0.1 to 2 MPa) may explain why Matsumoto and Satterfield observed no pressure effect for methane selectivity or olefin to paraffin ratio. At 548 K and 2 MPa, our methane selectivities were in the same range for the clean C-73 iron catalyst as that reported for slurry reactor studies, e.g., Dictor and Bell,[19] Pennline et al.,[20] and Huff and Satterfield,[21] as well as Matsumoto and Satterfield.[13] Our study showed that the primary products were linear 1-olefins and paraffins with the majority of the olefins being terminal (i.e., α- versus β-olefins). We also observed that the β-olefin/α-olefin ratio increases with increasing carbon number and the olefin to paraffin ratio remains high (unity) in the wax range. These observations are in agreement with slurry results reported by Dictor and Bell.[19]

Sulfur-treated iron FTS catalysts may have beneficial properties in addition to improved product selectivity. One possibility is that the

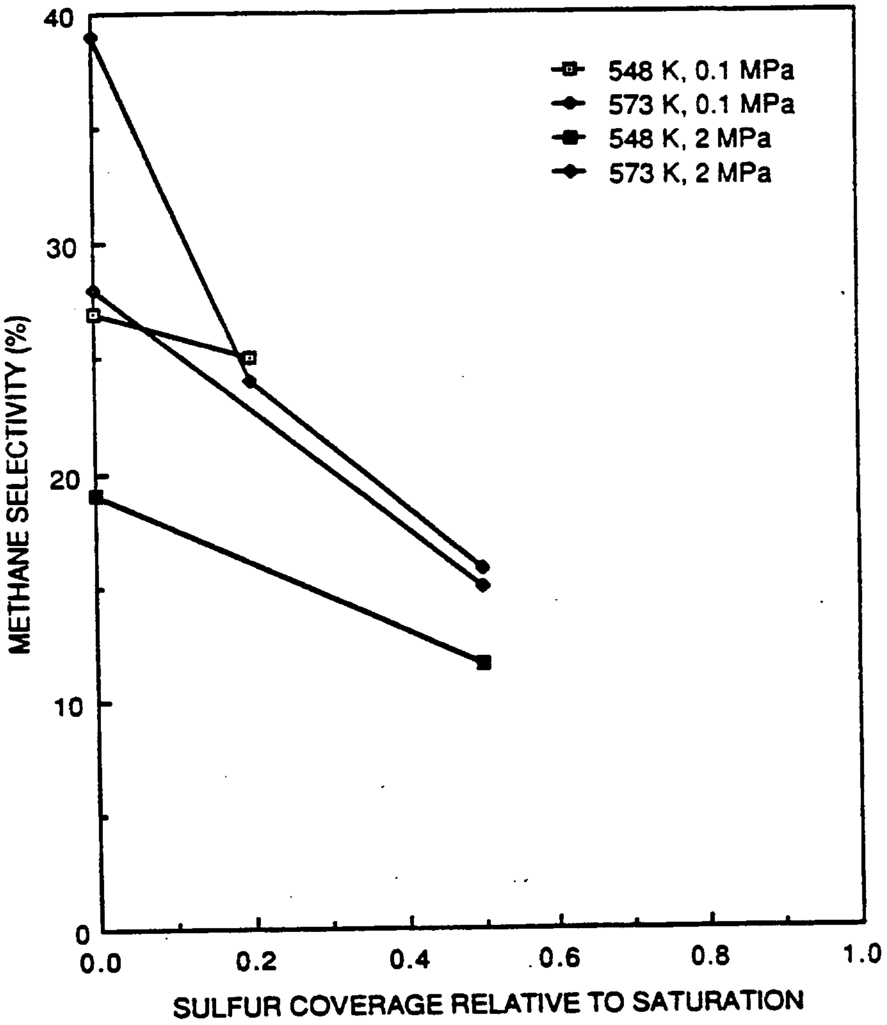

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Figure II-15. Methane selectivity for fixed-bed FTS by clean and sulfur-treated fused iron catalysts with H_2/CO ratio = 1.0.

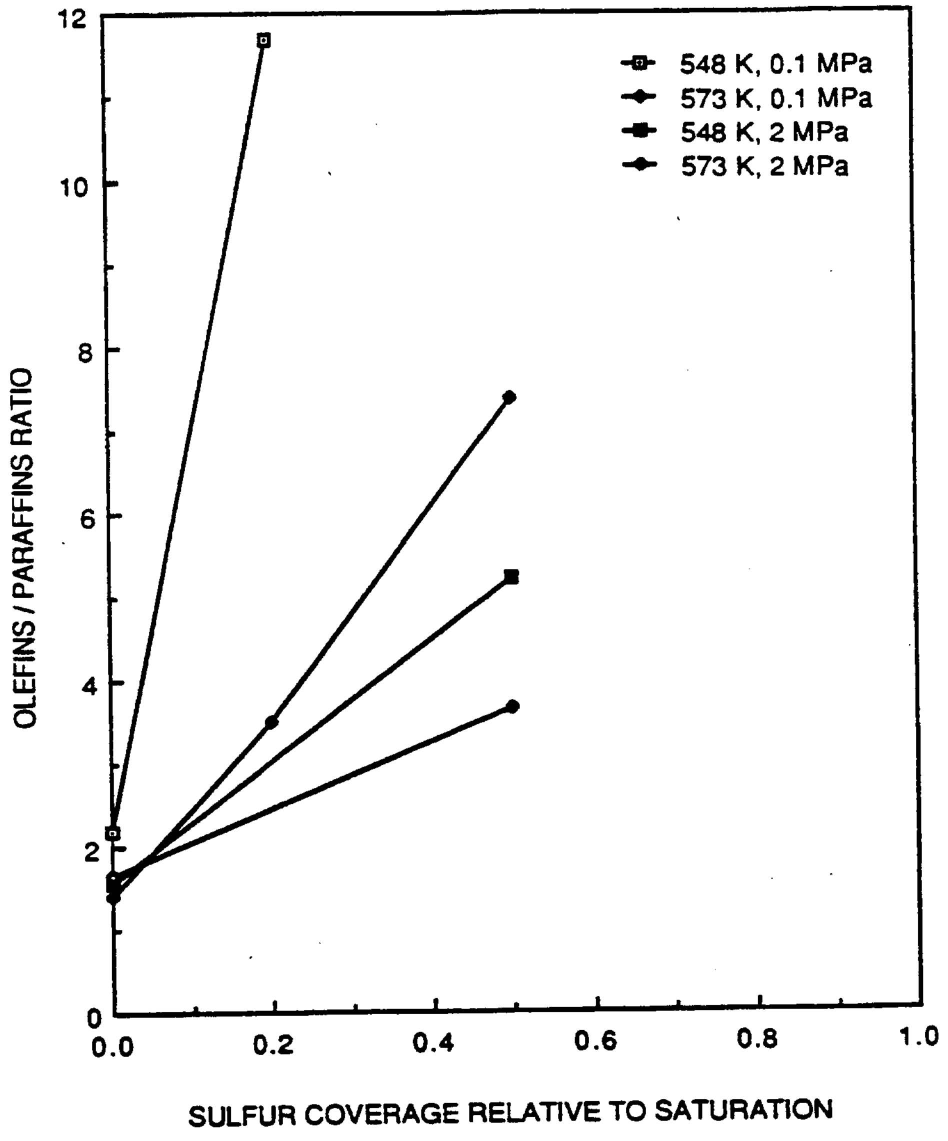

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Figure II-16. Light olefin selectivity for fixed-bed FTS by clean and sulfur-treated fused iron catalysts with H_2/CO ratio = 1.0.

activity is more strongly dependent on pressure than for the untreated catalyst. The increased pressure dependence is due to the decreased binding strength of both chemisorbed hydrogen and carbon monoxide because of the presence of uniformly distributed surface sulfur. The reaction order for production of hydrocarbons (dependence of the log FTS rate on log partial pressure) is typically less than 1 for H_2 and less than 1 for CO, indicating that the active surfaces are nearly fully occupatied by adsorbed intermediates. Weakened CO and H adsorption could free reaction sites, thereby increasing the synthesis rate.

Another possible desirable property could be increased coking resistance. Steam re-forming catalysts are known to have increased resistance to coke formation owing to fractional adsorption of (low-level) sulfur. Deposition of catalyst carbon is associated with surface planes of high coordination (those containing steps and ledges), which may be responsible for methane formation and are known to preferentially bind adsorbed sulfur atoms on nickel surfaces. Increased coking resistance could allow FTS reaction with a higher CO-to-hydrogen ratio, perhaps 1:1 or greater, thereby increasing olefin and higher hydrocarbon yields while using less expensive synthesis gas processes following the gasifier.

Recommendations

The effect of increased conversion on methane and olefin selectivity of sulfur-poisoned fused iron must be examined in future work. Matsumoto and Satterfield[13] report that the initial improvements in selectivity noted at low conversion declined with higher CO conversion and at 80% conversion no enhancement in selectivity was observed. They offered no explanation. However, since the CO and especially H_2 levels (with $H_2/CO = 0.7$ in the feed gas) decline considerably at 80% CO conversion, the actual H_2 levels in the exit gas may have varied owing to the presence of sulfur. Perhaps the change noted[13] in the effect of water vapor on the activity, because of the sulfur treatment, is responsible for the change in selectivity with high CO conversion. Additional work with sulfur-in selectivity with high CO conversion. Additional work with sulfur-treated C-73 fused iron catalysts at high CO conversion should clarify this phenomenon.

Sulfur treatment with stable manganese-promoted iron catalysts in the absence of alkali promoters should be examined further. The coking resistance of the sulfur treatment also warrants further study.

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