V.4. Binder / Support Effect Research

Supported catalyst systems with high support-to-metal ratios have not been overly effective in yielding good Fischer-Tropsch synthesis performance. In the slurry phase process, supported catalysts reduce the bulk concentration of metal and thus may hinder mass transfer from gas to liquid as solids loadings are increased to maintain metal concentrations. On the other hand, supported systems may actually increase the concentration of active metal sites by maintaining higher metal dispersions. The nature of the support is also important, since acidic sites on the support can render basic promoters like potassium ineffective, preventing interaction between promoter and metal. Previous work at SASOL (Dry, 1981) in fixed bed reactors, examined the effects of promoters and supports on the performance of Ruhrchemie-type precipitated Fe catalysts. In one set of experiments, a series of Fe/Cu/K_2O precipitates was prepared using Cr_2O_3, MgO, Al_2O_3 or ZnO in place of silica. None of these catalysts was as active as the standard SiO_2- containing material. An unsupported composition was also less active. Compositions containing both SiO_2 and a second support material also showed lower performance. Of all the supports, small amounts of added Al_2O_3 resulted in the lowest wax selectivity without excessive deactivation. This concept could be used to control selectivity to some extent.

In our study we have used the Ruhrchemie-type catalyst with the nominal composition of 100 Fe/5 Cu/4.2 K/24 SiO_2 as the base case, and then varied amounts of silica (0, 8 and 100 parts of SiO_2 per 100 parts of iron) while keeping promoter levels constant. Also, we synthesized two catalysts containing alumina in place of silica as binder (8 and 20 parts Al_2O_3/ 100 parts Fe). The impregnation technique used to prepare the alumina-containing catalysts was limited to a maximum concentration of about 30 parts Al_2O_3/100 parts Fe, so a catalyst with high alumina concentration (i.e., 100 parts) was not available for testing. A sample of commercial Ruhrchemie catalyst, designated LP 33/81, was made available to us through Dr. Cornelius Frohning of Ruhrchemie . This catalyst was used originally at SASOL's fixed bed (ARGE) reactors and its average composition (as per Dr. Frohning) is : 100 Fe/4.3 Cu/4.1 K/25 SiO_2. Professor Satterfield of M.I.T. has also obtained a sample of Ruhrchemie catalyst and has reported the following composition, determined by Galbraith Laboratories: 100 Fe/5 Cu/4.1 K/27 SiO_2 (Satterfield, 1988; Donnelly and Satterfield, 1989). Both of these compositions are similar to that reported by Dry (1981, p.176) for the Ruhrchemie catalyst. The actual composition of our baseline catalyst (100 Fe/5.4 Cu/4.6 K/28 SiO_2) is similar to that of the Ruhrchemie catalyst.

Catalytic tests were conducted in fixed bed reactors, at different process conditions (Table V.4-1) using synthesis gas with an H_2:CO molar ratio of about 1. Approximately 3.5 g of calcined catalyst was crushed to 30/60 mesh, and mixed with glass beads (1:7 volume ratio, catalyst:inert particles) of the same mesh size range before loading the reactor. All catalysts were activated with CO at 280°C and atmospheric pressure for 12 hours. The first mass balance was conducted after about 40 hours on stream at operating conditions.

V.4.1. Results and Discussion

A summary of the selectivity and activity results is given in Table V.4-2 for the three silica-containing catalysts (Runs FA-63-0418, FA-66-0548, and FA-69-0668), the two alumina-containing catalysts (Runs FA-73-0828, and FA-76-0968), the unsupported catalyst using supported catalyst promoter levels (Run FA-31-1118), and the calcined Ruhrchemie LP 33/81 catalyst (Run FB-99-1348).

Catalyst activity, as measured by (H_2—CO) conversion, decreases as the binder concentration increases (Figure V.4-1). The 8 parts SiO_2 and the unsupported catalysts had the highest activities, and on a per Fe basis, gave essentially the same (H_2—CO) conversions. The 8 parts Al_2O_3 catalyst also had high activity. The similarity in conversions for the unsupported and 8 parts supported catalysts show that the high activity is not due to surface area alone. The very high potassium concentrations are responsible for the increase in catalyst activity over previous unsupported catalyst tests. While the BET surface areas of the reduced SiO_2-containing catalysts increase from 94, 148, and 250 m^2/g at 8, 25, and 100 parts SiO_2/100 parts Fe, the (H_2—CO) conversions decrease at all conditions tested. The unsupported catalyst has a BET surface area of 38 m^2/g. The increased BET surface areas are caused by the addition of high surface area binder, and do not necessarily reflect a large increase in active metal surface area. Our measurements by H_2 temperature programmed desorption showed that the fractional metal exposures of CO reduced, silica-containing catalysts are the same as for unsupported catalysts (~2.3%), thus crystallite size is constant. When alumina is added to the catalyst, the exposure roughly doubles. Egiebor and Cooper (1985) measured the BET surface areas of both fresh and used silica supported catalysts, with compositions of 100 Fe/4.2 Cu/6.7 K with 21, 50, and 73 parts SiO_2. Prior to use, these catalysts had surface areas of 151, 252, and 275 m^2/g, which agree with our values, but after use the surface areas decreased to 71, 17 and 28 m^2/g, respectively. The authors attributed the decrease in surface areas to carbon deposition on the

Table V.4-1. Summary of fixed bed tests and testing conditons for binder/support reseach.[a]

Test ID	Catalyst	220°C 1.48 MPa 2 Nl/g-cat.h	235°C 1.48 MPa 2 Nl/g-cat.h	235°C 1.48 MPa 4 Nl/g-cat.h	250°C 1.48 MPa 2 Nl/g-cat.h	250°C 1.48 MPa 4 Nl/g-cat.h	235°C 2.86 MPa 4Nl/g-cat.h
FA-31-1118	100/5/4.2	120(4)	48(1),144(5)[b]	72(2)		95(3)	169(6)[b]
FA-63-0418	100/5/4.2/8SiO_2	121(4)	46(1),169(6)[b]	72(2)		96(3)	145(5)[b]
FA-66-0548	100/5/4.2/25SiO_2	120(4)	40(1)	73(2)	96(3)		145(5)[b]
FB-99-1348	Ruhrchemie LP 33/81	144(5)	48(1),96(3)	72(2)	114(4)		169(6)[b]
FA-09-0608	100/5/4.2/100SiO_2	119(4)	41(1),143(5)[b]	72(2)	96(3)		169(6)[b]
FA-73-0828	100/5/4.2/8Al_2O_3	119(4)	48(1),144(5)[b]	72(2)		96(3)	168(6)[b]
FA-76-0908	100/5/4.2/20Al_2O_3	120(4)	48(1),144(5)[b]	72(2)	96(3)		168(6)[b]

[a] Time on stream, h (balance period) are indicated; $H_2/CO=1$ for all tests

[b] Catalyst had partially deactivated

Table V.4-2 Summary of Binder / Support Catalysts Tests

Catalyst	Run	Bal	Conditions TOS (*h*)	T (°C)	P (*MPa*)	SV[a]	H_2/CO	STY[b]	% Conversion CO	H_2+CO	Usage	Wt % Hydrocarbons CH_4	C_2-C_4	C_5-C_{11}	C_{12}+
100 Fe/5 Cu/4.2 K	FA-31-1118	1	47.5	235	1.48	2.00	1.03	0.070	93.6	78.3	0.70	6.4	21.8	22.2	49.6
		2	71.5	235	1.48	3.99	1.03	0.097	65.6	54.8	0.69	4.8	19.2	19.2	56.8
		3	94.5	250	1.48	3.99	1.03	0.116	78.8	65.4	0.69	5.8	22.3	22.0	49.9
		4[c]	119.8	220	1.48	1.99	1.03	0.029	37.3	33.0	0.80	5.7	23.6	23.2	47.5
		5[c]	143.7	235	1.48	1.99	1.03	0.042	54.7	47.2	0.75	6.0	23.6	24.4	46.0
		6[c]	168.5	235	3.00	3.99	1.03	0.091	55.6	51.3	0.87	4.6	23.1	19.5	52.8
100 Fe/5 Cu/4.2 K/8 SiO_2	FA-63-0418	1	49.0	235	1.48	2.00	1.10	0.069	93.8	76.7	0.71	3.5	16.4	20.1	60.0
		2	72.0	235	1.48	4.01	1.10	0.094	64.5	52.8	0.71	3.2	16.9	20.3	59.6
		3	96.0	250	1.48	4.01	1.10	0.116	80.5	65.1	0.70	3.7	16.0	12.4	67.9
		4	121.0	220	1.48	2.00	1.10	0.055	73.6	62.1	0.77	2.8	16.0	15.4	65.8
		5[c]	145.0	235	3.00	4.01	1.10	0.076	46.4	42.7	0.93	2.8	17.5	16.7	63.0
		6[c]	169.0	235	1.48	2.00	1.10	0.040	52.9	44.8	0.78	3.4	18.8	16.5	61.3
100 Fe/5 Cu/4.2 K/25 SiO_2	FA-66-0548	1	40.0	234	1.48	2.00	1.00	0.049	59.8	55.0	0.85	5.7	22.7	15.2	56.4
		2	72.5	235	1.48	4.01	1.00	0.069	39.4	38.5	0.95	5.0	22.4	17.7	54.9
		3	95.5	250	1.48	2.01	1.00	0.061	78.2	67.6	0.73	8.1	30.0	19.9	42.0
		4	120.0	220	1.48	2.01	1.00	0.028	29.7	31.1	1.09	4.8	23.2	20.7	51.3
		5	144.5	235	2.96	4.01	1.00	0.086	49.5	48.1	0.94	4.0	22.8	15.5	57.7
100 Fe/5 Cu/4.2 K/100 SiO_2	FA-69-0668	1	40.5	234	1.48	1.99	1.00	0.026	24.3	29.1	1.39	5.2	17.2	20.4	57.2
		2	72.0	235	1.48	3.99	1.00	0.039	17.5	22.0	1.51	4.4	14.9	16.5	64.2
		3	96.0	250	1.48	1.99	1.00	0.031	30.8	35.2	1.29	5.8	18.6	25.9	49.7
		4	119.0	220	1.48	2.01	1.00	0.014	11.3	15.8	1.79	4.5	15.8	18.3	61.4
		5	143.0	235	1.48	1.99	1.00	0.023	20.1	25.7	1.56	5.2	16.8	18.5	59.5
		6	169.0	235	2.96	3.99	1.00	0.052	22.4	29.4	1.63	4.5	15.6	15.5	64.4
100 Fe/5 Cu/4.2 K/8 Al_2O_3	FA-73-0828	1	47.5	235	1.48	2.01	1.00	0.067	90.3	75.1	0.66	4.8	18.4	19.3	57.5
		2	72.0	234	1.48	4.02	1.00	0.084	56.0	47.0	0.68	4.2	17.4	18.4	60.0
		3	96.0	250	1.48	4.02	1.00	0.104	69.8	57.8	0.66	4.9	19.2	20.2	55.7
		4	118.5	220	1.48	2.01	1.00	0.028	36.9	31.7	0.72	4.1	17.9	18.9	59.1
		5[c]	143.5	235	1.48	2.01	1.00	0.038	50.8	42.9	0.69	4.9	19.6	18.3	57.2
		6[c]	168.0	235	2.96	4.01	1.00	0.071	42.2	40.0	0.90	4.6	21.9	19.3	54.2
100 Fe/5 Cu/4.2 K/20 Al_2O_3	FA-76-0968	1	47.5	235	1.48	2.03	1.00	0.062	82.2	68.3	0.66	3.6	16.7	19.2	60.5
		2	71.8	235	1.48	4.03	1.00	0.063	41.2	35.3	0.71	3.7	16.9	17.4	62.0
		3	95.5	250	1.48	2.03	1.00	0.066	88.8	73.4	0.65	4.8	21.0	21.5	52.7
		4	120.0	220	1.48	2.03	1.00	0.020	24.7	22.1	0.79	4.0	19.5	21.8	54.7
		5[c]	143.5	235	1.48	2.03	1.00	0.028	37.1	31.5	0.70	5.1	21.5	20.2	53.2
		6[c]	168.0	235	3.00	4.03	1.00	0.055	33.0	30.5	0.87	4.8	21.9	19.2	54.1
Ruhrchemie LP 33/81 (100 Fe/5 Cu/4.2 K/24 SiO_2)	FB-99-1348	2	48.0	235	1.48	4.06	0.98	0.061	30.8	33.8	1.18	3.8	14.5	17.1	64.6
		3	96.0	234	1.48	1.99	0.98	0.044	46.9	49.1	1.07	4.3	17.6	17.0	61.1
		4	120.0	250	1.48	1.99	0.98	0.054	64.5	60.3	0.85	5.3	20.8	19.2	54.7
		5[c]	144.0	220	1.48	1.99	0.98	0.023	22.9	25.9	1.24	4.7	18.8	19.6	56.0
		6[c]	168.5	235	2.96	3.99	0.98	0.065	33.4	36.7	1.17	3.9	17.1	16.1	62.0

[a] Space Velocity (SV) [=] *Nl*/*g*-cat·*h*

[b] Space Time Yield (STY) [=] *mols*(H_2 + CO)/*g*-cat·*h*

[c] Balance made with partially deactivated catalyst

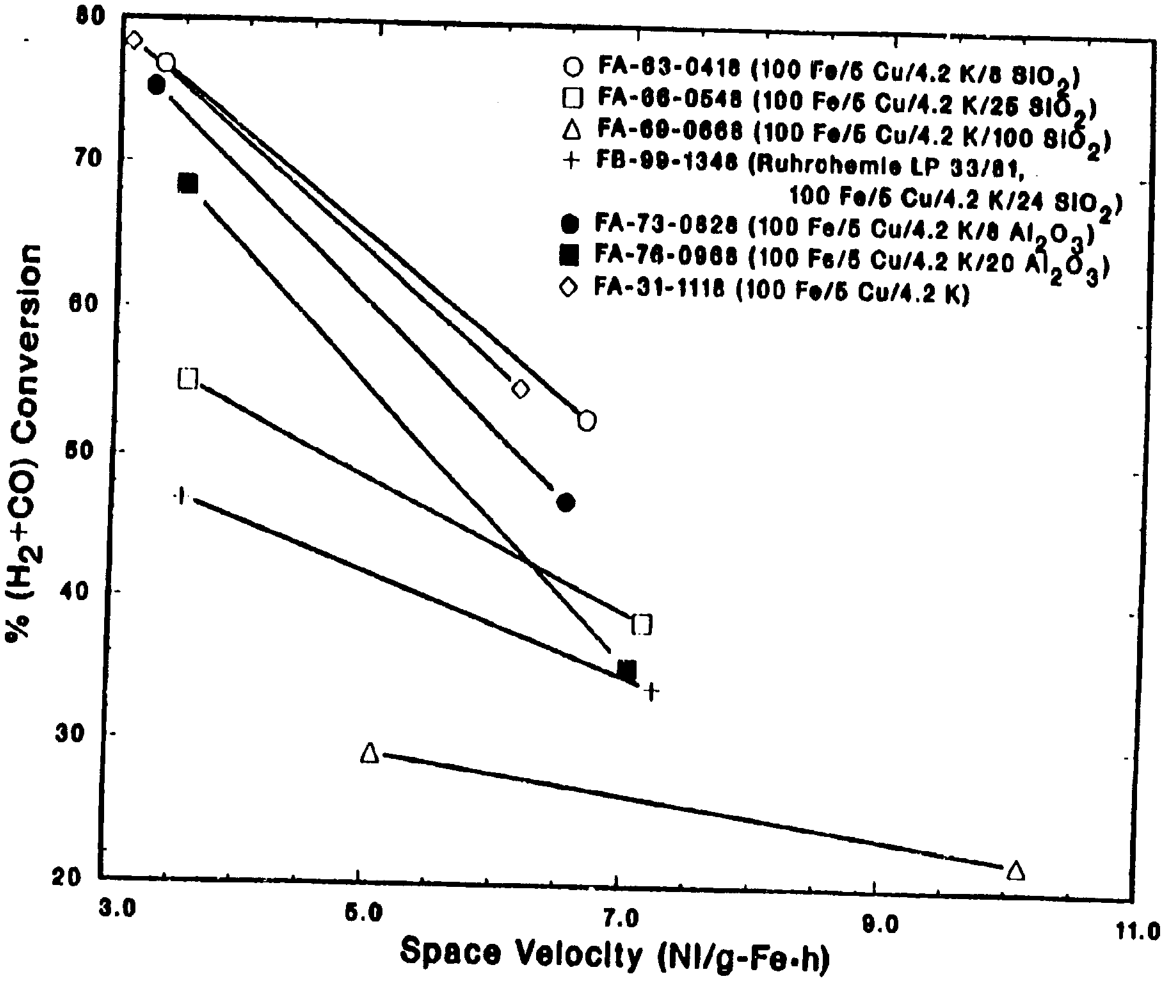

Figure V.4-1 Comparison of (H_2+CO) conversions for the binder/support catalysts and Ruhrchemie LP 33/81: 250 °C, 1.48 *MPa*, (H_2/CO) = 1.0.

catalyst during synthesis. Wax accumulation in catalyst pores may also contribute to low used catalyst surface areas. The high surface area catalysts have smaller pore diameters, increasing intraparticle diffusional limitations. Also, the catalysts with high support concentrations show stronger resistance to reduction and may not be fully activated.

The increase in silica concentration improves catalyst stability as can be seen from Table V.4-3. In this table, values of (H_2+CO) conversion obtained at the baseline conditions in the early part of the test (40-49 h) and near the end of the test (143-169 h on stream) are listed. Between these two periods of time the process conditions were varied. Catalysts containing 25 and 100 parts of SiO_2 (per 100 parts of Fe) had a rather small loss in activity, whereas the catalysts with 8 parts or less of a binder (SiO_2 or Al_2O_3) had a more significant loss in activity. Alumina containing catalysts were less stable than the corresponding silica containing catalysts.

The WGS activity, measured by CO_2 selectivity (percent of CO converted to CO_2), of different catalysts as a function of reaction temperature is shown in Figure V.4-2. The unsupported catalyst, the two alumina containing catalysts, and the catalyst containing 8 parts of SiO_2 per 100 parts of Fe have high WGS activity even at low reaction temperatures (220 and 235°C), whereas the catalysts with higher silica content (25 or more parts of SiO_2 per 100 parts of Fe) have low WGS activity which increases with temperature. The lower WGS activity of the silica containing catalysts may be explained by the fact that silica reacts with the potassium and thereby reduces its promotional effect, i.e., the catalyst behaves as if it had a lower potassium loading (see Section V.2.1.3). Apparently, the interactions between the potassium and alumina were much weaker, and therefore there was no loss in the WGS activity with increase in the alumina concentration.

The weight % hydrocarbon distributions of the supported catalysts and Ruhrchemie LP 33/81 (run FB-99-1348) are compared in Figs. V.4-3 (235°C, 1.48 MPa, 2 Nl / g-cat·h) and V.4-4 (250°C, 1.48 MPa, 2 or 4 Nl / g-cat·h). The addition of a small amount of support (8 parts/100 parts Fe) had a minor effect on conversion, but improved the selectivity by decreasing methane and C_2-C_4 formation. The calcined Ruhrchemie catalyst showed good $C_{12}+$ selectivity as well. An increase in the alumina concentration from 8 to 20 parts/100 parts Fe had no significant effect on the hydrocarbon distribution at any of the conditions tested. The selectivity of the catalyst with 8 parts SiO_2/100 parts Fe was better than (low methane, high $C_{12}+$) or comparable to the selectivities of all the supported catalysts, calcined

Table V.4-3. Catalyst stability comparison - before and after process variable studies[a]

Catalyst	TOS (h)	% Conversion (H_2+CO)	TOS (h)	% Conversion (H_2+CO)
100 Fe/5 Cu/4.2 K	48	78.3	148	47.2
100 Fe/5 Cu/4.2 K/8 SiO_2	49	76.7	169	44.8
100 Fe/5 Cu/4.2 K/24 SiO_2	40	55.0	145[b]	48.1[b]
Ruhrchemie LP 33/81	48	50.5	109[b]	31.0[b]
100 Fe/5 Cu/4.2 K/100 SiO_2	41	29.1	143	25.7
100 Fe/5 Cu/4.2 K/8 Al_2O_3	48	75.1	144	42.0
100 Fe/5 Cu/4.2 K/20 Al_2O_3	48	68.3	144	31.5

[a] tests made at 235°C, 200 psig, SV = 2 Nl/g-cat.h, (H_2/CO) = 1.0
[b] SV = 4 Nl/g-cat.h, P = 417 psig for these tests

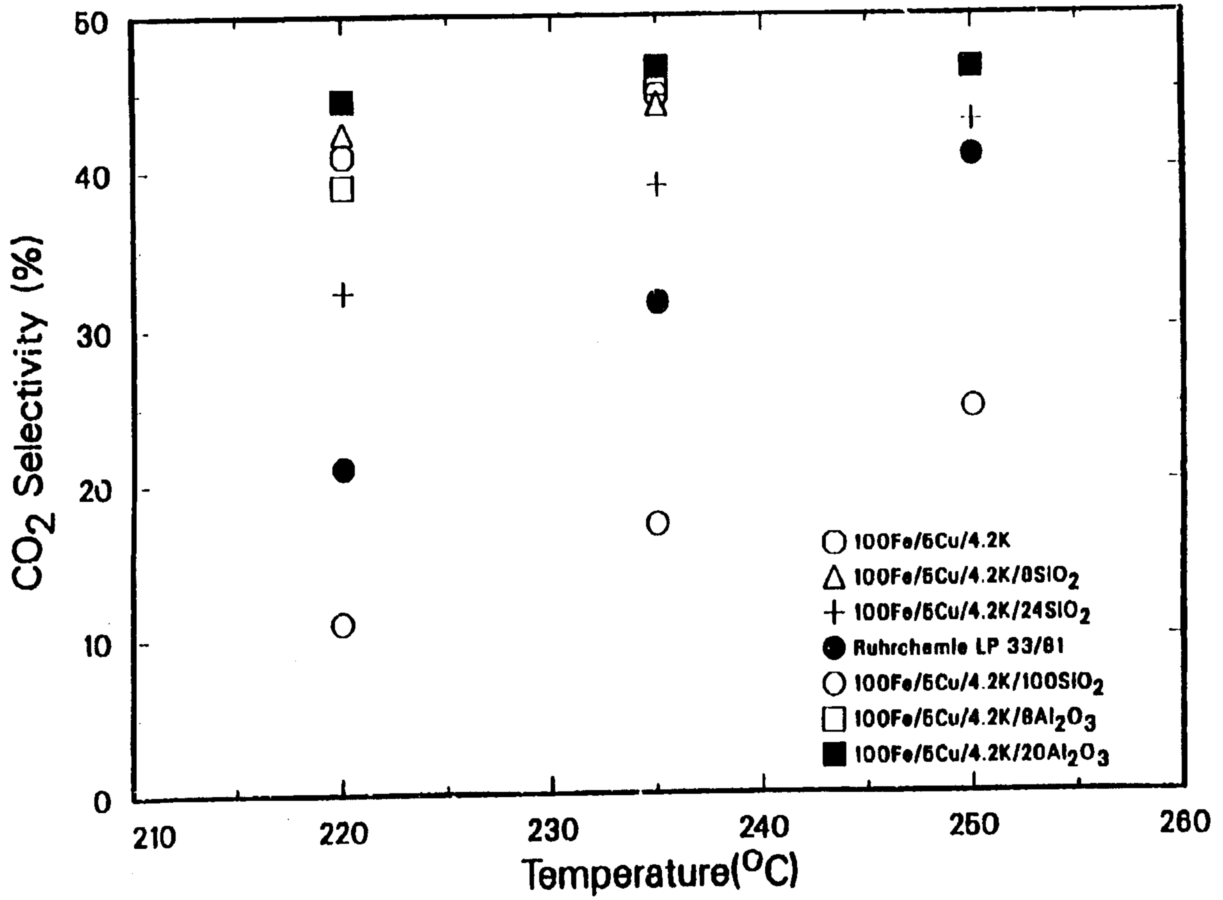

Figure V.4.2 Effect of Binder / Support and Temperature on Water - Gas - Shift Activity (1.48 MPa , 2 Nl/g-cat.h , $H_2/CO=1$)

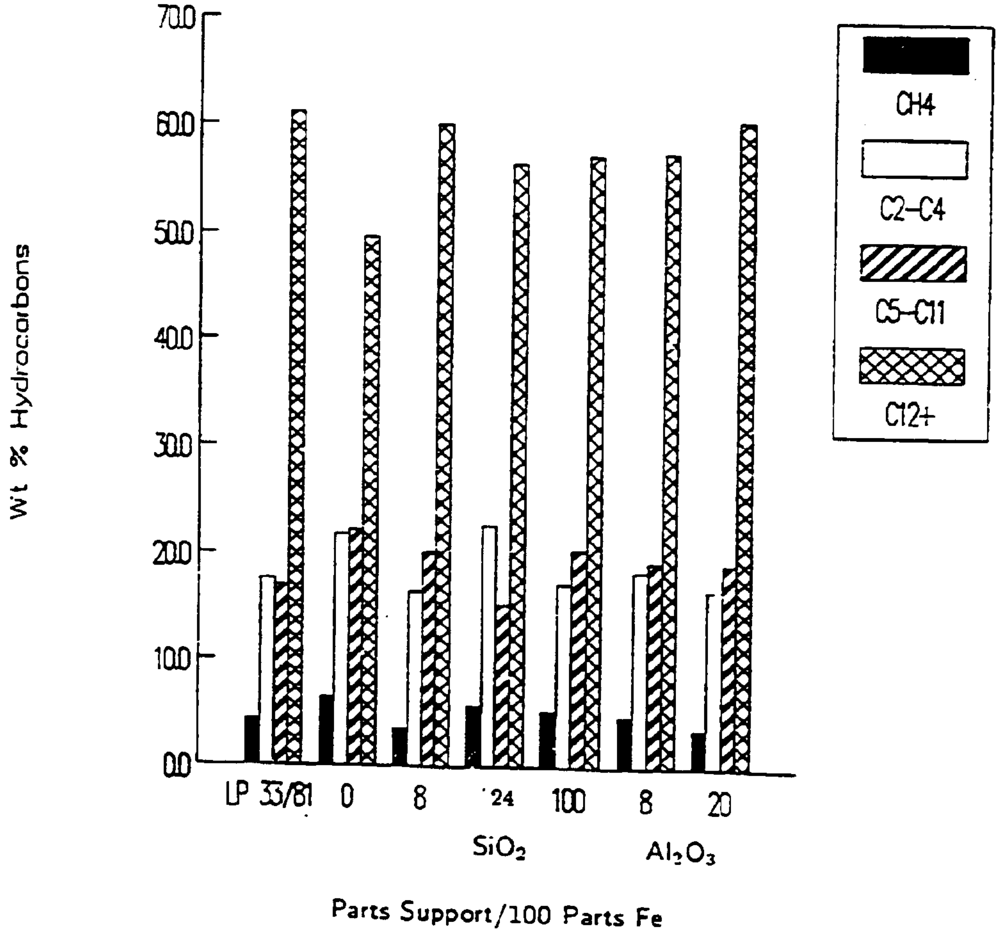

Figure V.4-3 Weight percent hydrocarbon distribution of binder/support catalysts and Ruhrchemie LP 33/81: 235 °C, 1.48 *MPa*, 2 *Nl/g*-cat·*h*, $(H_2/CO) = 1.0$.

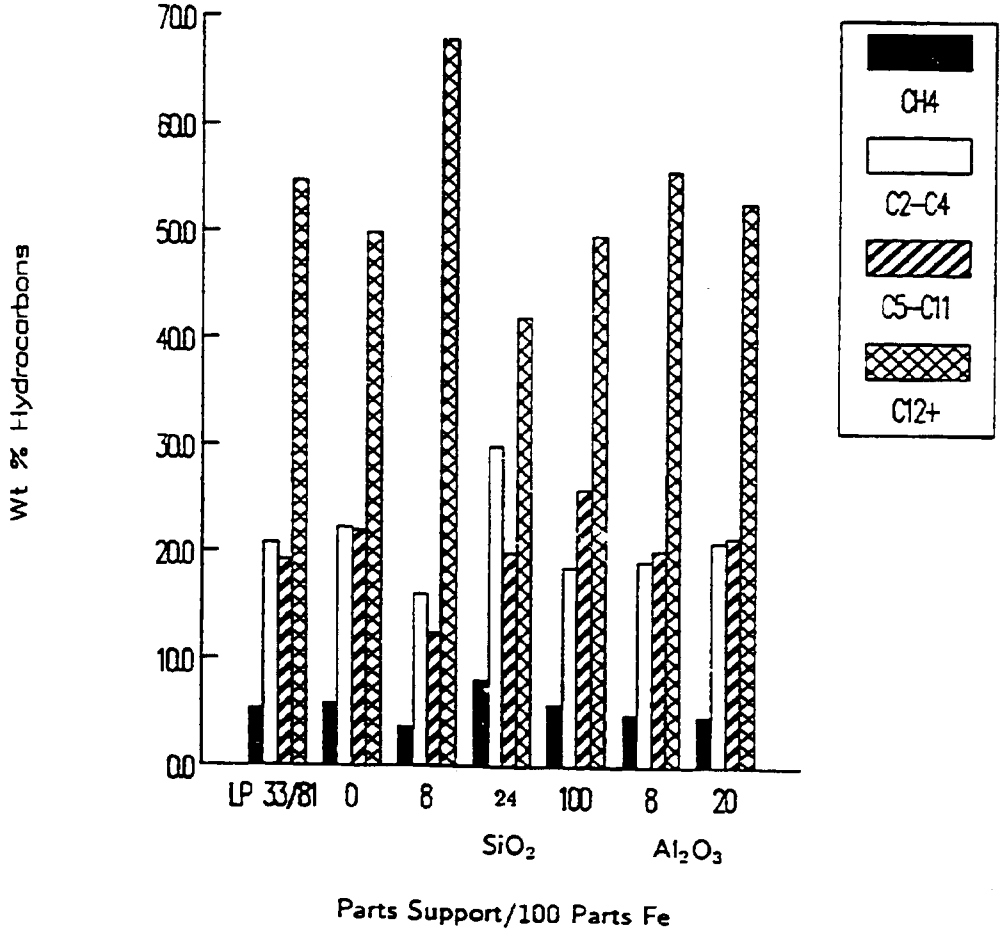

Figure V.4-4 Weight percent hydrocarbon distribution of binder/support catalysts and Ruhrchemie LP 33/81: 250 °C, 1.48 *MPa*, 2 *Nl/g*-cat-*h*, $(H_2/CO) = 1.0$.

Ruhrchemie LP 33/81, and unsupported catalyst. This catalyst is also one of the most active of all the catalysts tested in our laboratory.

Our 100 Fe/5.4 Cu/4.6 K/28 SiO_2 catalyst and the Ruhrchemie LP 33/81 catalyst (100 Fe/5 Cu/4.1 K/27 SiO_2) have similar compositions, yet showed some differences in activity and selectivity at the same operating conditions. Our catalyst was more active than the Ruhrchemie catalyst, but produced more gaseous hydrocarbons. At 235°C, 2.0 Nl / g–cat·h, the (H_2+CO) conversions were 55.0 % for our catalyst and 49.1 % for the Ruhrchemie catalyst, while the methane was 5.7 and 4.3 % and the C_2–C_4 was 22.7 and 17.6 %, respectively. Similar differences were present at other conditions, as shown in Table V.4-2. The 24 parts SiO_2 catalyst was also somewhat more selective towards lighter products than either of our 8 or 100 parts SiO_2 catalysts, regardless of differences in catalyst activity. Alumina containing catalysts had hydrocarbon selectivities similar to that of the silica containing catalysts. In general, they produced less CH_4 and C_2-C_4 hydrocarbons than the unsupported catalyst.

Dry (1981) discusses the results obtained at SASOL with supported catalysts. It is not possible to make quantitative comparisons between our work and SASOL, as Dry reports only relative values for potassium content, activity and hard wax selectivity, but some qualitative comparisons can be made. Using an Fe/Cu catalyst containing a relative K_2O concentration of 10 with 24 parts SiO_2/100 parts Fe (by weight), he reported a relative activity of 45 and a relative hard wax selectivity (i.e., high molecular weight products) of 34. This was the most active catalysts of the series reported and had the highest hard wax selectivity. With an alumina supported catalyst (100 parts Al_2O_3) with a similar potassium loading (12), the activity decreased to 18 while the hard wax selectivity remained constant. With a second alumina catalyst, containing 23 parts Al_2O_3 and a potassium level of 3, activity increased to 35 and hard wax selectivity decreased to 10. Since higher potassium loading should increase activity at the levels reported, the decrease in activity with 23 and 100 parts Al_2O_3 can be attributed to the increase in support concentration, which is what we have observed for both alumina and silica supported catalysts. (Dry shows that high potassium concentrations, above 12, cause decreases in activity for SiO_2 supported iron). The decrease in hard wax selectivity is due to the change in potassium loading.

The work of Egiebor and Cooper (1985) with 100 Fe/4.2 Cu/6.7 K and 21, 50, and 73 parts SiO_2 catalysts can also be compared to our results. They did not report their hydrocarbon distribution per se, but they noticed that the C_5–C_{11} fraction remained constant regardless of support concentration at a fixed set of conditions (300°C, 0.71 MPa, $H_2/CO = 1.0$, 240 h^{-1}) and was 40–50 weight % of the total condensed products. They found that the reactant conversions changed only slightly as the support concentration increased, with no significant difference between the three catalysts, which is not what we have experienced in our studies of supported catalysts.

V.4.2. Summary

Major findings from binder/ support studies are summarized below.

(1) The FT activity of silica (or alumina) containing catalysts decreased with increasing concentration of binder.

(2) The addition of binder improved catalyst stability (lower rate of deactivation).

(3) The WGS activity decreased with the addition of silica due to its interaction with potassium. As a result the overall "basicity" of the catalyst decreased and the promotional effect of potassium on the WGS activity was reduced.

(4) Catalyst with composition 100 Fe/5 Cu/4.2 K/8 SiO_2 displayed high activity and excellent hydrocarbon selectivity (low CH_4 and high C_5+ content), but its stability needs to be improved.

(5) Catalyst with nominal composition 100 Fe/5 Cu/4.2 K/24 SiO_2 displayed about 25% higher activity and had better stability than the Ruhrchemie LP 33/81 catalyst, but the Ruhrchemie catalyst produced less gaseous hydrocarbons.

(6) The yield of methane and gaseous hydrocarbons decreased upon addition of small amounts of binder (either silica or alumina). Hydrocarbon selectivity did not change markedly upon further addition of alumina (8 vs. 20 parts of Al_2O_3). With silica binder the yield of CH_4 and C_2-C_4 increased initially (8 vs. 24 parts of SiO_2) but then decreased again upon further addition of silica (24 vs. 100 parts of SiO_2).