

5.2.6 STEM ANALYSIS: HIGH COBALT CATALYST PRECURSOR

A sample of the pre-reduced material used in Runs 102 and 104 was analyzed by STEM. Metal oxide crystallites ranging from 30 (the smallest the STEM instrument can see) to 2000 Å were found, the average being 500 Å. Some of the crystallites were associated with the zeolite, some were not. Crystallite composition varied. There was a tendency for the zirconium and ruthenium not to be found together. Ruthenium was rarely seen in crystallites smaller than 100 Å, whereas zirconium was mostly noted in crystallites smaller than 200 Å. Manganese content varied among the crystallites examined but seemed to increase in the smaller crystallites. Representative STEM photographs are attached as Figures 114 and 115. Additionally, tables containing representative STEM elemental analyses of various-sized crystallites are attached as Figure 116.

The pre-reduction precursor of the catalysts used in Runs 110 and 121 had similar 30 to 2000 Å crystallites by STEM. There were, however, more crystallites. Crystallites were again observed which were free of the zeolite. Zirconium was again associated with the smaller particles and again tended to be associated with the zeolite.

The STEM work indicates that this high cobalt level catalyst contained at least some metals exterior to the 50-100 Å pores of the steamed zeolite. In fact some of the metal crystallites existed entirely free of the zeolites. Others appeared to have grown attached to the zeolite such as those in the bottom left of Figure 115. The performance data indicates that the external cobalt is active for F-T synthesis, and, since the lowest methane selectivities were found for the highest cobalt-level catalysts, the external cobalt must not have been extremely selective for methane.

The STEM work indicates, additionally, that further work must be done to understand the affect of the trace metals. They do not seem to be evenly distributed throughout the crystallites!

5.2.7 VERY HIGH COBALT CATALYSTS

Catalysts containing approximately 27 wt% cobalt were prepared. The first of these was evaluated in Run 101; it was prepared on the second lot of 3 hour hydrochloric acid-washed support (Figure 86). A fresh sample of the steamed Y-zeolite used for the first hydrochloric acid wash was used for the second washing. Performance during Run 102 is summarized as a series of plots of conversions and selectivities vs. hours on stream (Figures 117 to 122). The high activity of the catalyst can be further illustrated by the temperature profiles in Figure 123.

A second catalyst with a cobalt level similar to that of the Run 101 catalyst was prepared. This catalyst was supported on material resulting from the third three hour hydrochloric acid wash of the original steamed Y-zeolite sample (Figure 86). It was also screened in the fixed-bed pilot plant (Run 110) but less catalyst and more diluent were used to decrease the intensity of the catalyst bed exotherm. Performance during this run is summarized as a series of plots of conversions and selectivities vs. hours on stream in Figures 124 to 129. The feed rate per gram of cobalt was the same as in Run 101; this resulted in less heat being generated on the catalyst bed as evidenced by the temperature profiles in Figure 130.

The conversions after the usual initial high rate of catalyst deactivation were still quite high (carbon monoxide conversion = 82% at 100 hours on stream). Therefore, the earlier high conversions with this very high cobalt-type catalyst were not just due to the high temperature of operation resulting

from the intense exotherm. The maximum temperature on the catalyst bed during Run 110 was, in fact, very close to that on the bed during Run 97 (compare Figures 130 and 131).

At 100 hours on stream the feed rate was reduced by half. This initially resulted in an increase in conversion some of which was rapidly lost, in part at least, due to continued loss in catalyst activity. However, it is also likely that the system required some time to equilibrate at the new feed rate. The conversions did appear to approach line out after the feed rate change (carbon monoxide conversion = 85% at 140 hours on stream). The catalyst bed maximum temperature before and after the feed rate change was the same. Although less feed was going into the plant, the higher conversion no doubt resulted in approximately the same amount of heat being produced.

Operating the 27% cobalt catalyst with less catalyst and more diluent produced the desired effect, namely high conversions at 211° C inlet temperature with a low exotherm on the catalyst bed. A tabular summary of the performance during Runs 97, 101 and 110 is attached as Figure 132. The lowest methane selectivity of any of the catalysts developed under this contract resulted during Run 110

5.2.8 ADDITIONAL VERY HIGH COBALT CATALYSTS

The initial sample of commercial steamed Y-zeolite was consumed prior to these experiments. A second sample was obtained, but it was from a different commercial lot. An aliquot of it was washed for three hours with hydrochloric acid before being used as a support for the catalysts below.

Two catalysts were prepared from this support, each contained slightly more than 28 wt% of cobalt. Support and catalyst analyses for these two catalysts are summarized in Figure 133. Each catalyst was reduced for two hours at 350° C with hydrogen prior to use in fixed-bed pilot plant Runs 122 and 123. The ruthenium-containing catalyst (Run 122) was inferior to the earlier similar composition catalyst evaluated in fixed-bed pilot plant Run 110. The performance difference between the two catalysts can be illustrated through comparison of the temperature profiles during the two runs (Figures 130 and 134). In Run 110 the initial catalyst bed maximum temperature was slightly over 220° C; at 132 hours on stream the profile had hardly changed. During Run 122, however, the maximum temperature decayed from slightly over 220° C to about 217° C at 138 hours on stream. The temperature decay continued throughout the run. Loss of catalyst activity witnessed by decay of temperature in this fashion is characteristic of deactivation mechanisms such as covering over the reactive sites with reaction by-products such as coke (in this case perhaps wax) or destruction of these sites, for instance, by a thermal mechanism such as sintering. Loss of activity due to feed impurities, on the other hand, causes loss of active sites from the inlet of the reactor where feed impurities first adsorb. In such cases the temperature maximum usually is constant but moves further and further away from the inlet.

The difference between the two ruthenium-containing catalysts is also apparent in the plots of conversion and selectivity vs. hours on stream in Figures 135 to 139. The rate of loss of activity during Run 122 was severe and never slowed, whereas in Run 110 the rate of activity loss slowed and the catalyst appeared to be approaching activity line out by run's end.

The least stable ruthenium catalyst was prepared on the second support. However, a ruthenium-free catalyst was also prepared on this support. It was activated and tested in a similar fashion to

the two ruthenium-containing catalysts (Run 123). It was more active and more stable than either of these catalysts. It is possible that something, as yet not understood, went wrong during preparation of the Run 122 catalyst. It is also possible that the initial activity of the Run 122 catalyst was very high but that it suffered a very rapid deactivation.

The ruthenium-free catalyst was evaluated in Run 123. Temperature profiles during this run are summarized in Figure 140. The initial catalyst activity was so high that the catalyst bed maximum temperature was at the inlet with heat being transferred back to the incoming feed. A little deactivation occurred at the beginning of the run causing the maximum temperature to move a bit down from the inlet. A slight increase in the catalyst bed maximum temperature was noted, perhaps due to slight upward adjustments in the reactor heaters to maintain the target inlet temperature which previously had been maintained, in part, by the reaction heat. However, after the slight change at the beginning of the run the catalyst bed maximum was stable. It was higher and more stable than the corresponding temperature during the two runs with the ruthenium-containing catalysts; it was 232° C at 219 hours on stream.

The two best runs (110 and 123) are compared in summary fashion in Figure 141. The conversion and methane selectivity were higher in Run 123. Normally with cobalt catalysts the methane selectivity decreases at higher conversion. That the opposite is true in the present comparison is probably at least in part due to the higher effective temperature during Run 123; methane selectivity increases with increasing temperature. The higher temperature during Run 123 also partially accounts for the higher conversions noted during this run. Conversions and selectivities as a function of hours on stream are summarized in Figures 142 to 145.

The Run 122 and 123 catalysts were evaluated in slurry autoclave tests. In both cases the catalysts were activated at 350° C in a fixed-bed reactor prior to loading into the autoclave reactor. Catalysts were moved to the autoclave under a nitrogen atmosphere. The Run 123 catalyst was activated by a somewhat different procedure than was used for any of the other catalysts. During its activation there was a calcination and second reduction with hydrogen after the first hydrogen reduction. However, in both cases the catalysts were used without being bound. In the earlier slurry autoclave evaluation of a lower cobalt catalyst, the catalyst was bound with silica before being evaluated. Both of the autoclave runs with the very high cobalt catalysts were disappointing. In both cases very low conversions were obtained, although the ruthenium-free catalyst seemed to line out at a better conversion than the ruthenium-containing one. Conversions, selectivities and operational conditions vs. hours on stream for these two runs are summarized in Figures 146 to 155.

The second slurry autoclave evaluation (Run 74) provided information that was unexpected but enlightening from the standpoint of further catalyst development. The catalyst was very active initially at 200° C operating temperature. The initial high conversions decayed rapidly over a ten hour period. At twenty-five hours on stream the operating temperature was increased to 210° C. Normally such a temperature increase would provide an increase in conversion. In this case it didn't, probably due to the continuing high rate of activity loss. It is possible that binding would have provided a more activity stable catalysts under the conditions of liquid phase processing. For instance, the powdery catalyst could have been splashed to the sides of the autoclave during use. Obviously, the high initial activity of the Run 74 catalyst was close to that expected.

5.2.9 STEM ANALYSIS OF A REDUCED VERY HIGH COBALT CATALYST

STEM-wise, reduced and pre-reduced catalysts were similar. For instance, STEM analysis of a reduced high cobalt catalyst similar to the ruthenium-free catalyst of Run 123 showed the same wide range of crystallite sizes as earlier such analyses of pre-reduced catalysts. The reduced catalyst contained small crystallites within a zeolite matrix (dark spots in light gray, zeolite, particle mid-center of Figure 156) and large amorphous cobalt particles (entire Figure 157). The latter particles were extraneous to the zeolite. Both types of cobalt were also present in pre-reduced (high) cobalt catalysts.

Atomic analysis of the crystallites by STEM showed most of the zirconium associated with the large rather than small cobalt crystallites (Figure 158). This was also observed with pre-reduced catalysts analyzed by STEM earlier in this work. Zirconium is added to the catalyst composition to promote activity stability, therefore, it is possible that the activity loss noted with high cobalt catalysts is due to deactivation of the large crystallites.

6. CONCLUSIONS

Cobalt-based F-T catalysts from a reverse micelle impregnation route have, so far, exhibited low activity and excessive methane selectivities. Various compositions of metals have been tried, some with cobalt and others with cobalt and ruthenium. Three supports have been used. The reverse micelle approach was abandoned when it appeared that nothing attempted had promise of producing a catalyst superior to the one which resulted from two previous contracts to the Union Carbide Corporation. This catalyst was prepared on a modified Y zeolite support.

The Union Carbide catalyst resulted from impregnation of about 8 wt% cobalt on a steamed, acid-washed Y zeolite. This support is unique in a way that makes it a good fit as a F-T catalyst support. Steaming produces 50-100 Å amorphous pores or "cages" linked by crystalline channels. Metal crystallites, 50-100 Å in diameter and stable to agglomeration, may formed in these pores.

It has now been found that catalysts more active than the reference catalyst may be formed by the simple expedient of impregnating more cobalt. Catalysts with cobalt levels as high as 27 wt% have been prepared. Activity gains going from 8 wt% to 16 wt% and from 16 wt% to 27 wt% have been documented.

Although more active, the high cobalt catalysts were not as stable as the Union Carbide one. This is possibly due to a maldistribution of zirconium which was added to the original composition as a stabilizing agent. STEM analysis indicates that the zirconium tends to remain associated with cobalt

that is actually within the pores of the zeolite. Some of the cobalt in the high cobalt catalysts is external to the zeolite pores.

Small amounts of ruthenium have been added to the high activity compositions. However, the ruthenium rate enhancement expected from earlier work by Gulf/Chevron and Exxon could not be documented. Additional experiments are warranted because Gulf/Chevron and Exxon have employed special activation procedures to insure good ruthenium distribution and these techniques have not yet been evaluated.

Quite a bit of characterization work has been done. STEM has proven to be a particularly useful method of analysis. For instance, with the high cobalt, zeolite-supported, catalysts it has shown that some of the cobalt is present external to the pores of the zeolite as fairly large crystallites with a porous or "Raney" type of structure.

7. FUTURE DIRECTIONS

Experimental evidence that a small amount of ruthenium can promote Y-zeolite-supported cobalt F-T catalysis is lacking. For instance, the catalysts for Runs 122 and 123 were similar in composition except the Run 122 catalyst contained a low level of ruthenium. The Run 122 catalyst lost activity fastest. Because of the very high initial activity of these catalysts it was not possible to tell which was initially more active. Additional work with ruthenium-promoted catalysts is warranted.

STEM analysis of a reduced high cobalt catalyst similar to the ruthenium-free Run 123 catalyst above showed a wide range of crystallite sizes (Figures 164 and 165). Earlier STEM analyses before reduction had given same result. This is a different observation than expected from the previously-developed low cobalt level catalyst of Union Carbide. In this catalyst the cobalt exists mainly as 50-100 Å crystallites within the pores of the steamed Y-zeolite support. The high cobalt catalyst had particles that were definitely too big to be within the pores of the steamed zeolite.

Atomic analysis of the crystallites (by STEM) showed that most of the zirconium was associated with the small rather than large cobalt crystallites (Figure 166). This was also observed with pre-reduced catalysts analyzed by STEM earlier in this work. Zirconium is added to the catalyst composition to promote activity stability, therefore, it is possible that the activity loss noted with high cobalt catalysts was due to deactivation of the large crystallites. Future work should be directed toward obtaining a better zirconium distribution, perhaps by simply adding more zirconium to the composition. Interestingly, STEM analysis showed that the other trace metal, manganese, was more

evenly distributed through the small and large particles.

Once the stability issue has been addressed, the ruthenium vs. ruthenium-free problem should be settled. Initially high space velocity data will be required in order to reduce initial conversions and allow an assessment of whether or not the ruthenium catalyst is more active. If not, methodology similar to that described by Gulf/Chevron⁴⁵ and Exxon^{46, 47} should be used, i.e. multiple oxidation/reduction cycles to enhance ruthenium distribution.

Additional attempts should be made to develop a method for low temperature catalyst reductions. Reasonable approaches would be longer reduction times at the lower temperatures and/or incorporation of a reduction promoting metal into the catalyst composition.

Finally, additional experiments with surfactant salts are warranted. The initial experiment reported herein was similar to ones performed during development of a precipitated iron catalyst under Contract No. DE-AC22-90PC90055 (final report pending). In such experiments potassium surfactant was added during slurry processing and startling changes in the activity and selectivity of the iron catalyst were noted. Similar changes were not noted with a similar addition to a cobalt catalyst (above experiment). However, potassium is known to be a better promoter for iron than cobalt whereas manganese, ruthenium and zirconium are among those useful for cobalt, perhaps surfactant salts of these metals would promote the cobalt catalyst.

It is also possible that suitable surfactants, perhaps even metal-free ones, might be useful to accelerate the rate of the Fischer-Tropsch reactions during slurry processing by accelerating the rate of mass transfer from the gas bubbles to the wax/catalyst surface.

REFERENCES

1. V.Rao, G.Stiegel, G.Cinquegrane and R.Srivastava, Fuel Processing Technology, 1992, 30, 83-107.
2. M.Dry, *Catalysis: Science and Technology* (J.Anderson and M. Boudart, eds.) Vol. 1, Chapter 4. Springer Verlag, Berlin and New York, 1981.
3. The three volume BMFT-Research Report on Fischer-Tropsch Synthesis prepared by Schering A.G. in cooperation with the Technical University in Munich and the Engler-Bunte Institute at the University of Karlsruhe, 1983.
4. C.Rofer-DePoorter, Chem. Rev., 1981, 81, 447.
5. P.Biloen and W.Sachtler in *Advances in Catalysis* (D.Eley, H.Pines and P.Weisz, eds.), Vol. 30, Academic Press, 1981, 165.
6. F.Fischer and H.Tropsch, Brennst.-Chem., 1926, 7, 97.
7. M.Poutsma, L.Elek, P.Ibarbia, A.Risch and J.Rabo, J. Catal., 1978, 52, 157.
8. J.Rabo, A.Risch and M.Poutsma, J. Catal., 1978, 53, 295.
9. M.Araki and V.Ponec, J. Catal., 1976, 44, 439.
10. P.Wentrcek, B.Wood and H.Wise, J. Catal., 1976, 43, 3363.
11. P.Biloen, J.Helle and W.Sachtler, J. Catal., 1979, 58, 95.
12. G.Low and A.Bell, J. Catal., 1979, 57, 397.
13. J.Ekerdt and A.Bell, J. Catal., 1979, 58, 170.
14. J.McCarty, P.Wentrcek and H.Wise, personal communication cited in ref. 20.
15. R.Brady III, R.Petit, J. Am. Chem. Soc. 1980, 102, 6181.
16. R.Brady III, R.Petit, J. Am. Chem. Soc. 1981, 103, 287.
17. H.Bock, G.Tschmutova and H.Wolf, J. Chem. Soc. Chem. Commun., 1986, 1068.
18. G.Henrici-Olive and S.Olive, J. Mol. Catal., 1982, 16, 111.
19. G.Henrici-Olive and S.Olive, J. Mol. Catal., 1983, 18, 367.

20. M.Smutek, J. Mol. Catal., 1984, 24, 257.
21. C.Zheng, Y.Apeloig and R.Hoffmann, J. Am. Chem. Soc., 1988, 110, 749.
22. G.Schulz, Z. Physikal. Chem., 1935, B30, 379.
23. P.Flory, J. Am. Chem. Soc., 1936, 58, 1877.
24. I.Yates, Ph.D. Thesis, Massachusetts Institute of Technology, 1990.
25. L.Koenig and J.Gaube, Chem.-Ing. Tech., 1983, 55, 14.
26. R.Dictor and A.Bell, J. Catal., 1986, 97, 121.
27. C.Satterfield, R.Hanlon, S.Tung, Z.-M.Zou and G.Papaefthymiou, Ind. Eng. Chem. Prod. Des. Dev., 1986, 25, 401.
28. S.Novak, R.Madon and H.Suhl, J. Chem. Phys., 1981, 74(11), 6083.
29. S.Novak and R.Madon, Ind. Eng. Chem. Fund., 1984, 23, 274.
30. H.Schulz, B.Rao and M.Elstner, Erdol and Kohle, 1970, 23, 651.
31. H.Pichler and H.Schulz, Chem.-Ing. Tech., 1970, 42, 1162.
32. E.Iglesia, S.Reyes and R.Madon, 1991, 12th North American Meeting of the Catalysis Society, Lexington, KY.
33. E.Gibson and R.Clarke, J. Appl. Chem., 1961, 11, 293.
34. C.Kibby, R.Pannell and T.Kobylinski, ACS Pet. Chem. Preprints, 1984, 29(4), 1113.
35. R.Summerhayes, S.Thesis, Massachusetts Institute of Technology, 1982.
36. J.Donnely, I.Yates and C.Satterfield, Energy and Fuels, 1988, 2, 734.
37. A.Lapidus, M.Savel'yev and M.Tsapkina, Petrol. Chem., 1991, 31, 502.
38. R.Anderson, *The Fischer-Tropsch Synthesis*, Academic Press, Inc., New York, 1984, 140.
39. R.Fiato, E.Iglesia and S.Soled, U.S. Patent 5,248,701, 1993.
40. R.Fiato, E.Iglesia and S.Soled, U.S. Patent 5,162,284, 1992.
41. G.Ansell, R.Fiato, E.Iglesia and S.Soled, U.S. Patent 5,169,821, 1992.
42. H.Beuther, T.Kobylinski, C.Kibby and R.Pannell, U.S. Patent 4,585,798, 1986.

43. H.Beuther, C.Kibby, T.Kobylinski and R.Pannell, U.S. Patent 4,413,064, 1983.
44. H.Beuther, C.Kibby, T.Kobylinski and R.Pannell, U.S. Patent 4,493,905, 1985.
45. T.Kobylinski, C.Kibby, R.Pannell and E.Eddy, U.S. Patent 4,605,676, 1986.
46. R.Fiato, European Patent Application Publication No., 0 414 555 A1, filing date 8/23/90.
47. E.Iglisia, S.Soled, R.Fiato and G.Via, *J. Catal.*, 1993, 143, 345.
48. A.Lapidus, A.Krylova, J.Rathousky, A.Zukal and M.Jancalkova, *Applied Catal. A: General*, 1992, 80, 1.
49. M.Hu, European Patent Application Publication No. 0 533 228 A1, filing date 8/17/92.
50. T.Kobylinski, C.Kibby, R.Pannell and E.Eddy, U.S.Patent 4,670,414, 1967.
51. T.Ishihara, N.Horiuchi, T.Inoue, K.Eguchi, Y.Takita and H.Arai, *J. Catal.*, 1992, 136, 232.
52. J.Haggin, *Chem. and Eng. News*, Oct 26, 1981.
53. D.Jones, AIChE Spring National Meeting, Houston, Texas, April, 1991.
54. H.Koebel and M.Ralek, *Catalysis Reviews Science and Engineering*, 1980, 21(2), 225.
55. H.Koebel, German Patent 1,060,854.
56. U.S. Bureau of Mines, Report of Investigation 5043, 1954, 56-62.
57. J.Kuo, "Two-Stage Process for Conversion of Synthesis Gas to High Quality Transportation Fuels", Final report prepared by Mobil Research and Development Co. under U. S. DOE Contract No. DE-AC22-83PC60019, October, 1985. Report No. DOE/PC/60019-9.
58. W.Deckwer, *Reaktionstechnik in Blasensäulen*, Salle + Sauerlander, Frankfurt/Main(D), Germany (1985). English Translation: *Bubble Column Reactors*, Wiley, Chichester, England (1992).
59. H.Bi and L.-S.Fan, *A.I.Ch.E. Journal*, 1992, 38, 297.
60. S.Kumar, K.Kusakabe, K.Raghunathan, and L.-S. Fan, *A.I.Ch.E. Journal*, 1992, 38, 733.
61. J.-W.Tzeng, R.Chen and L.-S.Fan, *A.I.Ch.E. Journal*, 1993, 39, 733.
62. S.Kumar, K.Kusakabe, and L.-S.Fan, *A.I.Ch.E. Journal*, 1993, 39, 1399.
63. P.Stenius, International Patent Application, PLT/SE81/0091, 1981.