

https://dspace.org/

The effect of low level sulfide addition and the performance of precipitated- iron Fischer-Tropsch catalysts

Bromfield, Tracy Carolyn

2016-08-31
http://hdl.handle.net/10539/20979

Downloaded from a DSpace repository. https://dspace.org/

No less important than catalyst composition, is the activation procedure giving rise to the active catalyst. The oxidative removal of surface contaminants is achieved by calcination in air at elevated temperatures. However, the temperature regime is relatively narrow, since sintering must be minimised, yet surface adsorbates do not all desorb at low temperatures. In addition, the surface segregation of species initially contained within the bulk is known to occur during calcination [207]. This alters both the bulk and surface composition of the catalyst. The effect of calcination temperature on the performance of sulfided catalysts was therefore to be investigated.

Finally, the high olefinity of hydrocarbons synthesised by low-level sulfided catalysts may result from the higher syngas conversion exhibited by these catalysts. Olefinity is noted to increase with increasing CO conversion [177], and it was therefore instructive to establish whether the product slate is an artifact of high conversion.

11.2. Experimental

11.2.1. Incipient wetness as a mode of sulfidation

A dried, unsulfided precipitated-iron catalyst was impregnated with 500 ppm Na_2S (dissolved in 0.5 ml deionised water per gram of catalyst) using the incipient wetness procedure. After dehydration in a fan-oven at 120°C overnight, this sulfided catalyst was subjected to various characterisation techniques.

To assess its efficacy in the Fischer-Tropsch reaction, the impregnated catalyst was monitored for hydrocarbon synthesis over a period of eight days at 250°C and 8 bar pressure (GHSV = 400 h^{-1}) in a 2:1 H_2:CO mixture. Product analysis was done using a gas chromatograph, equipped with Porapak Q and capillary columns (see Chapter 2 for detailed experimental methods).

11.2.2. Effect of calcination temperature

A catalyst sulfided with 2000 ppm $(NH_4)_2S_5$ at pH 10.75 was used to investigate the effect of calcination temperature on FT activity. One 2 g sample was calcined in air at 200°C and another at 400°C (GHSV = 2000 h^{-1}) for 16 hours prior to reduction at 400°C in flowing hydrogen. Fischer-Tropsch synthesis was performed at 250°C and 8 bar pressure in a 2:1 H_2:CO mixture (GHSV = 400 h^{-1}) for a period of eight days, which included a four day mass balance. Hydrocarbon products were analysed by gas chromatography.

11.2.3. Same conversion study

The purpose of this study was to determine whether the increased olefin to paraffin ratio observed for low-level sulfided catalysts was an artifact of high CO conversion. Catalysts sulfided with 500 and 2000 ppm sulfide (Na_2S and $(NH_4)_2S_5$) were tested for FT activity at conversions comparable to that of the unsulfided catalyst (30 %). By increasing the gas hourly space velocity, the high conversions of these sulfided catalysts were reduced to between 10 and 30 %, thereby facilitating direct comparison of product selectivity.

11.3. Results and Discussion

11.3.1. Incipient Wetness as a mode of sulfidation

While investigating the effect of sulfide on the Fischer-Tropsch activity of iron catalysts, the addition of sodium sulfide by co-precipitation was preferred to exposure to H_2S owing to the experimental difficulties associated with the latter. In order not to complicate the study unnecessarily, Na_2S was added during precipitation so that practically all added sodium would be removed during washing by centrifugation. The effects of sulfidation during precipitation (herein referred to as 'co-precipitation') were dealt with in previous chapters.

However, to establish whether the stage of sulfidation is an important variable, and the possible influence of sodium, a catalyst was sulfided with 500 ppm Na_2S by impregnation of a dried precipitate using the incipient wetness technique.

In terms of morphology, the addition of sulfide by impregnation appeared to significantly increase the surface area and total pore volume of the catalyst as shown in Table 11.1. Usually the impregnation of a support by an active metal or additive, results in a decrease in surface area [208] due to pore blockage. For example, Mothebe observed that the surface areas of 10 % $Co/TiO_2/PO_4^{2-}$ catalysts decreased from 30.5 to 19.9 m^2/g as the P loading increased from 0 to 1.0 % P[208]. Therefore, the effect of the addition of sulfide in this way is rather bizarre and warrants further investigation. After calcination at 400°C, the surface areas of both impregnated and co-precipitated catalysts decrease, although the loss of area is greater for the former catalyst.

Table 11.1: Surface Areas of impregnated and co-precipitated sulfided iron catalysts

Catalyst	Pre-calcination (m^2/g)	Post-calcination (m^2/g)	Post Reaction (m^2/g)
Impregnated	152.4	42.4	3.21
Co-precipitated	97	34.8	7.88

Also, as evident from Table 11.2, is that the degree of pore collapse following calcination is minimised in the impregnated catalyst.

Table 11.2: Total pore volumes of impregnated and co-precipitated sulfided catalysts

Catalyst	Pre-calcination (cm^3/g)	Post-calcination (cm^3/g)	Post Reaction (cm^3/g)
Impregnated	0.291	0.283	0.018
Co-precipitated	0.241	0.202	0.020

The impregnated catalyst proved very active for FT synthesis, with a specific activity comparable to that of the co-precipitated low-level sulfided catalyst (Table 11.3). The lower TON however, suggests that the sites for reaction are not as active as those in the co-precipitated catalyst.

Table 11.3: Comparison of co-precipitated sulfided and impregnated catalysts in the FT reaction

Mode of sulfidation	% conversion	α-value	Specific Activity ($\mu molC/s/g_{cat}$)	TON[a] (10^{-3} s^{-1})
Impregnation	86.3	0.70	1.05	98
Co-precipitation	53.7	0.76	1.31	171

[a] TON refers to the number of CO molecules converted to product per exposed active site

A vastly different product spectrum was presented by the impregnated catalyst. The lower α-value indicates reduced propensity towards waxes and greater methane and light hydrocarbon selectivity (Figure 11.1). Moreover, the synthesis of oxygenated products was reduced; with methane (64 %) produced more selectively than ethane (36 %). The co-precipitated sulfided catalyst in turn, produced greater quantities of ethane (86 %) than methane (14 %).

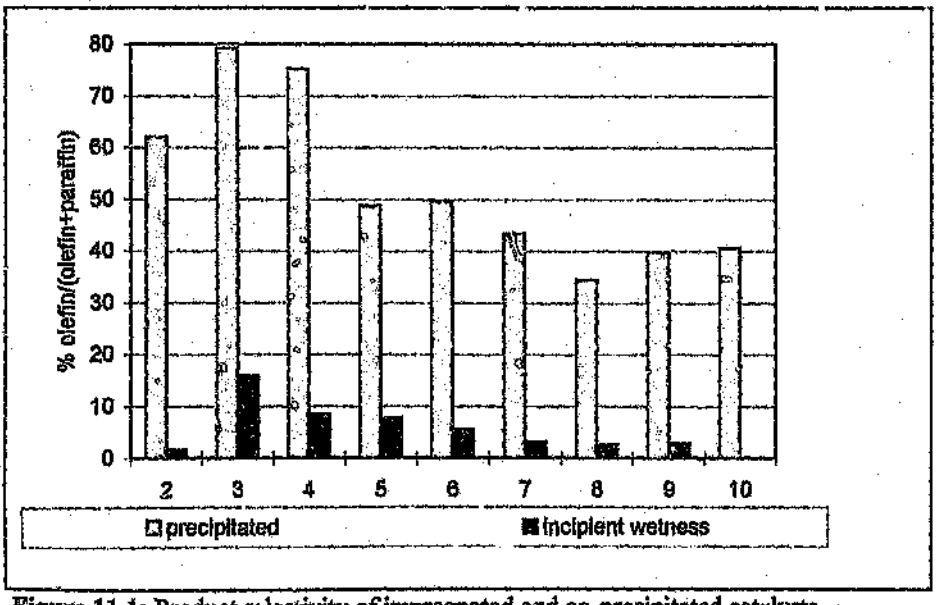


Figure 11.1: Product selectivity of impregnated and co-precipitated catalysts

As shown in Figure 11.2, The olefinity of hydrocarbons was found to be very low, even below that of the unsulfided catalyst. This indicates greater hydrogenation activity in the impregnated catalyst.

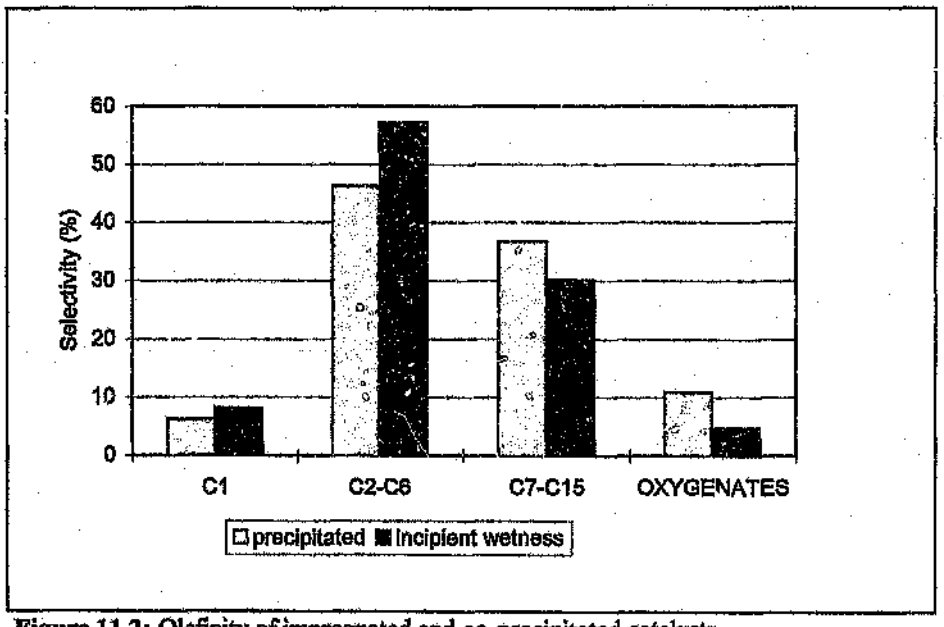


Figure 11.2: Olefinity of impregnated and co-precipitated catalysts

The effects of impregnation are difficult to rationalise, and are expected to be mutually dependent on sodium and sulfide. A further point worthy of mention is that, unlike in the co-precipitated systems, all added sulfide is present on the surface of the impregnated catalyst. This means that the surface sulfide is less well dispersed in the latter case, and hence the formation of sulfide from sulfate during reduction cannot be excluded.

The increased methane selectivity and lower olefinity are typical of sulfide-bearing surfaces. On the other hand, the high activity and lower oxygenate selectivity are features that might be attributable to sodium. The effect of sodium should be quite significant since two Na^+ ions are added for each S^{2-} ion.

11.3.1.1. Conclusion

This study was not intended to be exhaustive, but served merely to investigate the possible effect of sodium on sulfided systems. Further studies, which extend beyond the scope of this work, could involve the addition of $(NH_4)_2S$ and $(NH_4)_2S_5$ by incipient wetness to establish the exact effect of sodium. Nevertheless, this preliminary investigation into the effect of added sodium opens the way for future work. It also illustrates the effect of sulfide being present directly on the surface of iron oxide crystallites, and not being dependent on segregation mechanisms.

The addition of sulfide by the incipient wetness technique lends a new dimension to sulfided catalysts. All added sulfide is present directly on the surface, unlike in co-precipitated systems.

Even when added at the end of precipitation (pH 6.9), the sulfide is covered by precipitating iron-oxide and is thus not at the very surface of the catalyst particles. Moreover, the precise sulfide content of co-precipitated catalysts is not known, as various solution equilibria are at play.

11.3.2. Effect of calcination Temperature

The effect of calcination temperature on the activity and selectivity of sulfided catalysts was investigated using the catalyst sulfided with 2000 ppm polysulfide at pH 10.75.

Table 11.4: Reactor Data of catalysts sulfided with 2000 ppm polysulfide

T_{calc} (°C)	% CO conversion	Specific Activity (μmol C/s/g cat)	α-value	BET (m^2/g)	pore volume (cm^3/g)
200	12	0.10	0.66	4.85	0.014
400	53.5	0.64	0.71	3.20	0.020

As shown in Table 11.4, lower conversion was obtained using a calcination temperature of 200°C. This is accompanied by a decrease in α-value and olefin selectivity (Figure 11.3), as the product spectrum shifts towards gaseous light hydrocarbons. Indeed, the product slate obtained at the lower calcination temperature is very similar to that observed for highly sulfided catalysts. It is dominated by oxygenated products and methane (Figure 11.4), rather than liquid hydrocarbons as found for low-level sulfided catalysts.

The surface areas and total pore volumes after reaction are very similar. Furthermore, no difference in the pore shapes was evident, with the low temperature calcined catalyst having a pore diameter of 117 Å, and the catalyst calcined at 400°C a pore diameter of 146 Å.

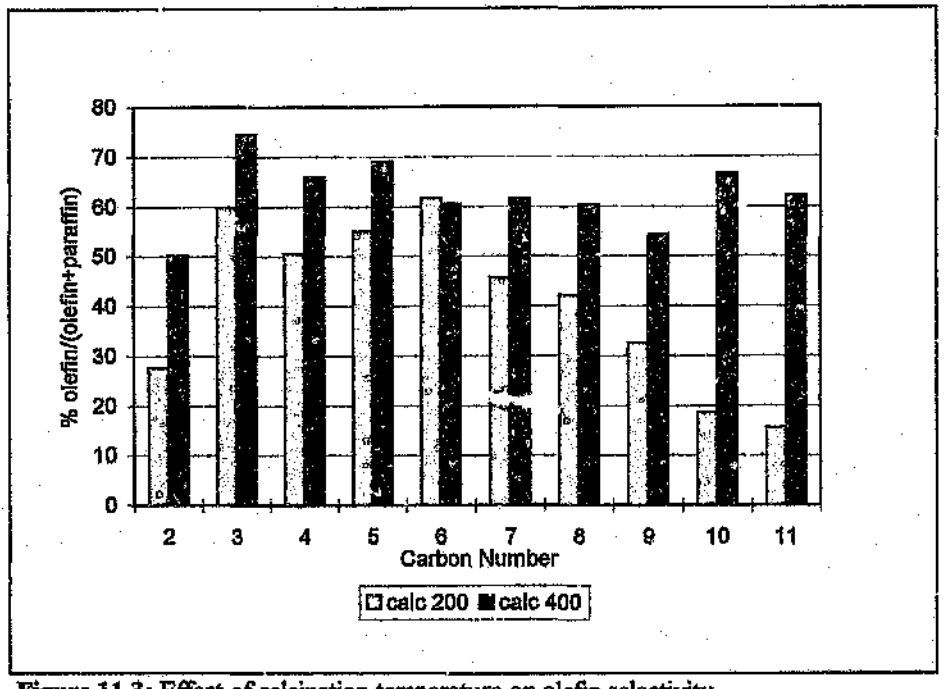


Figure 11.3: Effect of calcination temperature on olefin selectivity

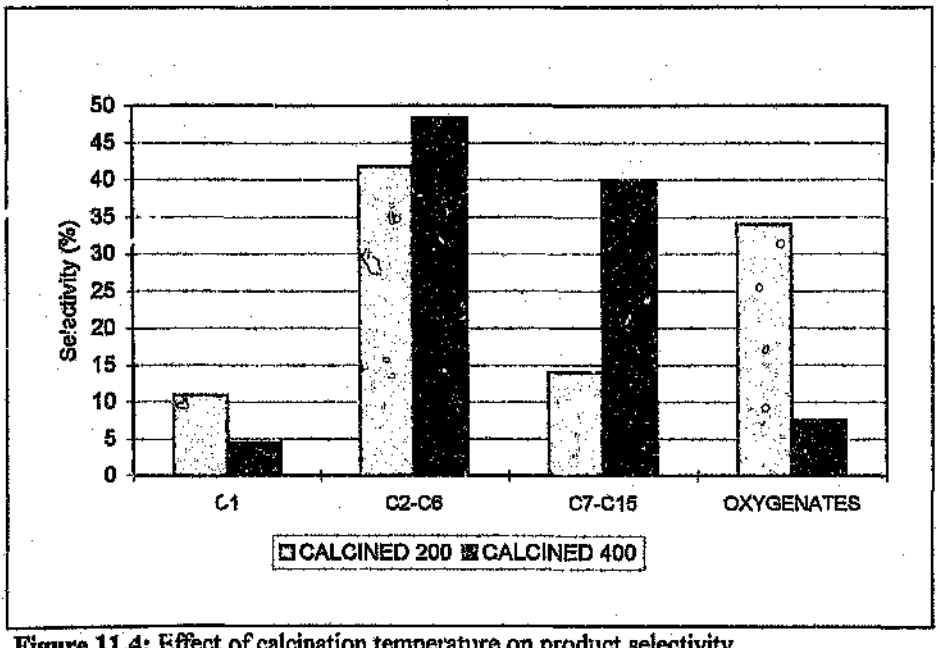


Figure 11.4: Effect of calcination temperature on product selectivity

Highly sulfided catalysts exhibited surface sulfide species in addition to sulfates following calcination and reduction at 400°C. In contrast, only sulfates were detected by XPS (Chapter 4) on the surface of low-level sulfided catalysts exposed to the same pretreatment. Calcination of these catalysts at a lower temperature results in product selectivities similar to high-level sulfided catalysts (calcined at 400°C), suggesting the existence of surface sulfides. These species have a deleterious effect on activity and shift the product spectrum from light hydrocarbons to oxygenates and methane.

Therefore, it appears that a calcination temperature of 200°C is too low to oxidise all added sulfide to sulfate. This sulfide remains on the surface after reduction and poisons catalyst activity. Certainly, it has been shown [209], that in order to convert sulfide to sulfate in Fe_2O_3-SO_4^{2-} isomerisation catalysts, calcination at 400°C or 500°C was required to fully oxidise S^{2-} to SO_4^{2-}. Moreover, calcination at 400°C may also be instrumental in establishing an active catalyst in terms of iron oxide morphology. In a study by Maiti *et al*, an exothermic peak in a Differential Thermal Analysis (DTA) curve at 380°C was ascribed to the formation of a crystalline hematite phase [201]. Changes in surface area and pore volume that followed calcination were then attributed to this phase change.

11.3.3. Is increased olefinity an artifact of high conversion?

The olefinity of hydrocarbons is known to increase at higher conversion [177]. Low-level sulfided catalysts proved more active than the unsulfided catalyst at the same GHSV and yielded a more olefinic product slate. To investigate whether the olefinity was a consequence of high activity, a study of low-level sulfided catalysts operating at

the same conversion as the unsulfided catalyst was undertaken. By adjusting the space velocity of the syngas feed to each catalyst, the conversions were reduced to between 10 and 30 %, to allow comparison of product selectivity. Although complete carbon mass balances were not performed, CO conversions were calculated (Table 11.5)

Table 11.5: CO conversions of sulfided catalysts used in olefinity study

Catalyst	% CO conversion	GHSV (h^{-1})
Unsulfided	27	400
500 ppm Na_2S	21	800
2000 ppm Na_2S	18	800
2000 ppm polysulfide	23	600

As shown in Figure 11.5, despite being slightly lower than at high conversion, the olefin to paraffin ratio is still higher for the sulfided catalysts. This confirms the effect of sulfate in creating sites that are suitable for unsaturated product formation.

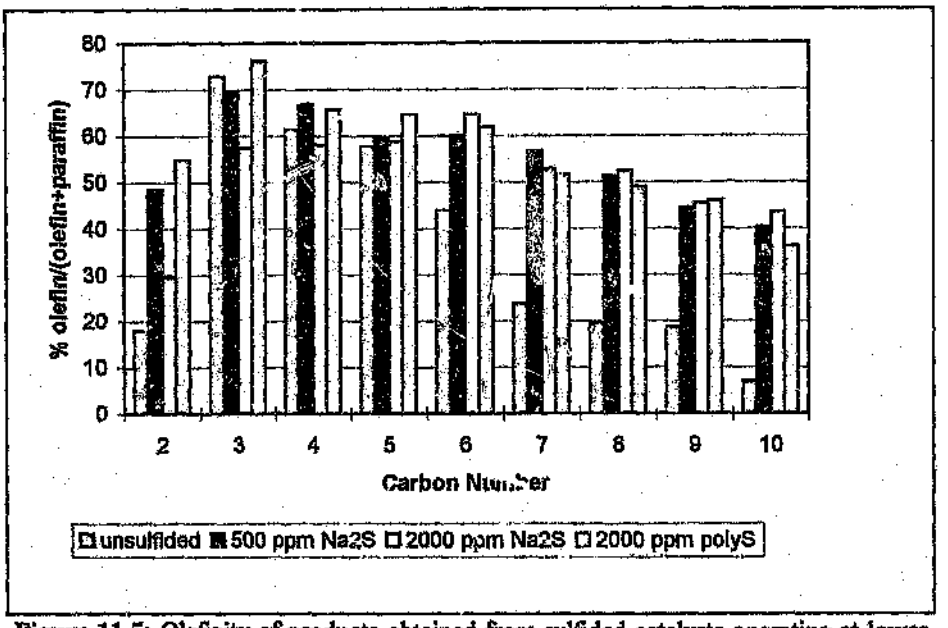


Figure 11.5: Olefinity of products obtained from sulfided catalysts operating at lower CO conversions

Sulfided catalysts were also shown to be comprised of larger crystallites than the unsulfided catalyst (see Chapters 8-10). Jones *et al* [210] have reported that steady-state activity and olefin/paraffin ratios decrease with decreasing metal crystallite size for the Fe/C system. In particular, the increase in olefin to paraffin ratio with increasing crystallite size was significant, and is purported to outweigh any effect that differences in percentage CO conversion might have had.

It has long been suspected that α-olefins are the primary products of Fischer-Tropsch synthesis, although they are thermodynamically unstable under the reaction conditions [211]. It appears that readsorption and subsequent hydrogenation occur readily, and this may be a major reaction pathway leading to the growth of hydrocarbons during FT synthesis [3]. Therefore, it is possible that sulfate species may lower the degree of readsorption of olefins, thus reducing the yield of paraffins.

11.4. Conclusion

Through the apparently unrelated studies presented in this chapter, the proposals made to rationalise the low-level sulfide promotion of precipitated-iron catalysts are confirmed. Calcination at 400°C is necessary to convert added sulfide to sulfate. This creates a highly active catalyst which is selective for olefinic products and oxygenates. High α-values also indicate good yields of wax products. In contrast, impregnation with sodium sulfide reduces the probability of chain-growth, and creates a highly active catalyst that is selective for light hydrocarbons and methane, as shown in this preliminary study.

Conclusion

The main objective of this study was to develop a fundamental understanding of the effects of sulfide addition during the preparation of precipitated-iron Fischer-Tropsch catalysts. The structural morphology of these sulfided catalysts was then correlated with their catalytic activity and product selectivity.

Having thus completed this investigation, a number of conclusions can be drawn:

i. The co-precipitation of sulfide into iron-oxyhydroxide crystallites, at various stages of precipitation, alters both the bulk morphology and surface chemistry. All sulfided catalysts exhibit enhanced surface areas and pore volumes, as well as improved crystallinity relative to a catalyst containing no extraneous sulfide. Sulfidation at the start and end of precipitation yields larger crystallites as a result of the processes of nucleation and aggregation, respectively. However, these two processes are in competition at pH 8.5 and this is reflected in the reactivity of catalysts sulfided at this pH value.

ii. Low-level sulfidation (up to 2000 ppm sulfide) at pH 10.75 and 6.9, produces catalysts which exhibit enhanced activity for the FT reaction compared to an unsulfided catalyst. This promotion correlates with the greater degree of Hägg carbide formation observed on these highly active catalysts. This may be ascribed to enhanced Fe-C interaction which weakens the C=O bond of adsorbed carbon monoxide. The product distribution obtained from low-level sulfided catalysts is also altered with respect to that obtained in the absence of sulfur. Lower methane

selectivity and improved production of C_7-C_{15} as well as higher oxygenate selectivity is observed. Furthermore, the olefinity of products is enhanced, and is independent of CO conversion.

iii. The surface segregation of sulfide is observed to occur during catalyst pretreatment. Sulfate species are formed on all sulfided catalysts following calcination at 400°C, and these species persist on the surfaces of low-level sulfided catalysts (168 eV) after reduction in hydrogen at 400°C. At higher levels of sulfidation, sulfate species are reduced to sulfides (161 eV). Therefore, the chemical modification of the catalytic surface is a further consequence of sulfide addition. The presence of sulfur-containing species lowers the temperature of reduction of $Fe_2O_3 \rightarrow Fe_3O_4$, and this effect is enhanced at higher levels of sulfidation. Highly sulfided catalysts are therefore reduced to metallic iron more easily than low-level sulfided catalysts.

iv. The poor Fischer-Tropsch activity of high-level sulfided catalysts may be ascribed to the presence of sulfide species. The electron-withdrawing tendency of sulfide reduces the iron-carbon interaction, preventing CO dissociation. This precludes the formation of χ-carbide, rendering the catalysts inactive. However, the selectivity of oxygenate production is enhanced through reduced CO dissociation. This is accompanied by higher yields of methane and light hydrocarbons.

v. Highly active catalysts are those which are not completely reduced to metallic iron in the presence of sulfur, since this is noted to bring about deactivation. The presence of some residual oxygen appears to be imperative in resisting sulfur poisoning, and in conserving sulfate species at the surface.

vi. The addition of sulfide between 2000 and 5000 ppm at pH 8.5 produces an effect analogous to that observed at high sulfide content (20000 ppm). Poor FT activity, and a shift in product distribution towards gaseous products, lower olefinity and higher yields of oxygenates indicates sulfide poisoning. This leads to the conclusion that catalysts sulfided midway through precipitation exhibit a greater surface concentration of sulfide species that those sulfided at pH 10.75 or 6.9. This may be attributed to the competing processes of nucleation and aggregation that occurred during precipitation.

vii. The source of sulfide has no effect on the activity of catalysts. This correlates with aqueous HS^- concentrations which appear to be the pivotal species governing the formation of FeS. This ferrous sulfide is proposed to be responsible for the modifications in the processes of nucleation and aggregation that give rise to sulfided precipitated-iron catalysts with high activity. Furthermore, the identity of the sulfide cation (sodium or ammonium) does not appreciably affect catalytic behaviour.

viii. The temperature of calcination is one of the most important variables in determining catalyst activity. Although too high a temperature may induce severe loss of surface area due to pore collapse, the oxidation of sulfide to sulfate must be complete to avoid catalyst poisoning by sulfide. Furthermore, the oxidative desorption of nitrates and other such contaminants requires the temperature to be greater than 300°C.

ix. The addition of a promoter such as sodium to low-level sulfided catalysts could provide a range of highly active catalysts with unique properties. This has been demonstrated uisng a preliminary study of a catalyst sulfided by low-level impregnation of sodium sulfide. Results suggest that such catalysts exhibit high selectivity for light hydrocarbons, and reduced propensity towards oxygenates.

References

[1] Mellor, J.W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Volume X, Longmans, Green and Co., (1930), 1

[2] Gv 19:24

[3] The Faerie Queene, book 1 c VIII, (1599), pg xiii

[4] Bailor, J.C., Emeleus, H.J., Nyholm, R. (Sir), Trotman-Dickenson, A.F. (eds) " Comprehensive Inorganic Chemistry", Volume 2, Pergamon Press, Oxford (1973), 795

[5] Nickless, G. (ed), "Inorganic Sulphur Chemistry", Elsevier Publishing Company, Amsterdam, (1968)

[6] Wells, A.F., "Structural Inorganic Chemistry", 5th edition, Clarendon Press, Oxford, (1984)

[7] Cotton, F.A; Wilkinson, G. and Gaus, P.L., "Basic Inorganic Chemistry" second edition, John Wiley and Sons, New York, (1987), 216

[8] Bartholomew, C.H., and Agrawal, P.K., *Adv. Catal.*, **31**, (1982), 135

[9] Watertek Report, CSIR, (1995)

[10] Sato, M., *Geochim Cosmochim. Acta.*, **56**, (1992), 3133

[11] Müller, A. and Diemann, E., *Advances in Inorganic Chemistry*, Vol 31, (1987), 89

[12] Clarke, E.T., Solouki, T., Russell, D.H., Martell A.E. and McManus, D., *Analytica Chimica Acta*, 299 (1994) 97

[13] Dubois, P., Lelieur, J.P., and Lepoutre, G., *Inorg. Chem.*, **27**, (1988), 1883

[14] Sonne, K. and Dasgupta, P.K., *Anal.Chem.*, **63**, (1991), 427

[15] Giggenbach, W., *Inorg. Chem.*, **11**, (1972), 1201

[16] Müller, A., *Polyhedron*, **5**, (1986), *12*, 323

[17] Draganjac, M. and Rauchfuss, T.B., *Angew. Chem. Int. Ed. Engl.* **24**, (1985), 742

[18] Murray, R.C, Jr. and Cubicciotti, D., *J. Electrochem. Soc.*, **130**, (1983), *4*, 868

[19] Giggenbach, W.F., *Inorg. Chem.*, **13**, (1974), *7*, 1724

[20] Anderson, R.B. "The Fischer-Tropsch Synthesis", Academic Press, Inc., New York, (1984)

[21] Kölbel, H., and Ralek, M., *Catal. Rev.-Sci. Eng.*, **21**, (1980), *2*, 225

[22] Dry, M.E., *Appl. Catal. A: General*, **138**, (1996), 319

[23] Jager, B. and Espinoza, R., *Catalysis Today*, **23**, (1995), 17

[24] Dry, M.E., *Catalysis Today*, **6**, (1990), 183

[25] Adesina, A.A., *Appl. Catal. A: General*, **138**, (1996), 345

[26] Bartholomew, C.H., in "New Trends in CO Activation", Volume 64, Elsevier, Amsterdam, (1991), 158

[27] de Bruijn, D.P. and Kuipers, H.P.C.E., *Catalysis Today*, **10**, (1991), 131

[28] Bukur, D.B., Mukesh, D. and Patel, S.A., *Ind. Eng. Chem. Res.*, **29**, (1990), 194

[29] Xu, L., Bao, S., O'Brien, R., Houpt, D.J. and Davis, B.H., *Fuel Science and Technology Int'l.*, **12**, (1994), *10*, 1323

[30] Diffenbach, R.A. and Fauth, D.J., *J. Catal.*, **100**, (1986), 466

[31] Dry, M.E., in "Catalysis-Science and Technology", Anderson, J.R. and Boudart, M. (eds.), Springer-Verlag, Berlin, (1981), 159

[32] Wesner, D.A., Coenen, F.P. and Bonzel, H.P., *Langmuir*, **1**, (1985), 478

[33] Leith, I.R. and McCormack, C.G., *CHEMSA*, March 1982, 2

[34] McCandlish, L.E., *J. Catal.*, **83**, (1983), 362

[35] Leith, I.R. and Howden, M.G., *Appl. Catal.*, **37**, (1988), 75

[36] Madon, R.J., and Taylor, W.F., *Am. Chem. Soc. Adv. Chem. Ser.*, **178**, (1979), 93

[37] Bartholomew, C.H. and Bowman, R.M. *Appl. Catal.* **15**, (1985), 59

[38] Somorjai, G.A., in "Studies in Surface Science and Catalysis" Kiskinova, M.P. (ed), Volume 70, Elsevier, Amsterdam, (1992)

[39] Bartholomew, C.H. and Bowman, R.M. *Appl. Catal.* **15**, (1985), 67

[40] Oades, R.D., Morris, S.R., Moyes, R.B., Parkyns, N.D., Komodromos, C. and Bradshaw, D.I., *Appl. Catal.*, **25**, (1986), 77

[41] Merrick, D., "Coal Combustion and Conversion Technology", Macmillan, London, (1984), 129

[42] Madon, R.J. and Shaw., *Catal. Rev.-Sci. Eng.*, **15**, (1977), *1*, 69

[43] Shultz, J.F., Hofer, L.J.E., Karn, F.S. and Anderson, R.B., *J. Phys. Chem.*, **66**, (1962), 501

[44] Chaffee, A.L., Campbell, I. and Valentine, N., *Appl. Catal.*, **47**, (1989), 253

[45] Stenger, H.G., Jr. and Satterfield, C. N., *Ind. Eng. Chem. Process Des. Dev.*, **24**, (1985), 415

[46] van Dijk, W.L., Niemandtsverdriet, J.W., van der Kraan, A.M. and van der Baan, H.S., *Appl. Catal.*, **2**, (1982), 273

[47] Smith, G.V., Hinckley, C.C., Zahraa, O., Nishizawa, T., Saporoschenko, M. and Shiley, R.H., *J. Catal.*, **78**, (1982), 262

[48] Barbier, J., Lamy-Pitara, E., Marecot, P., Boitiaux, J.P., Cosyns, J. and Verna, F., *Adv. Catal.*, **37**, (1991), 279

[49] Nowotny, J. and Dufour, L.C., eds, "Surface and Near-Surface Chemistry of Oxide Materials", Elsevier Science Publishers, Amsterdam, (1988)

[50] Fackler, J.P., Jr., (ed) "Inorganic Syntheses" Volume 21, John Wiley and Sons, New York, (1982), 12

[51] JCPDS Powder Diffraction File, Published by the International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, Pennsylvania, (1989)

[52] Niemandtsverdriet, J.W., "Spectroscopy in Catalysis - An Introduction" VCH, Weinheim, (1995)

[53] Smith, D.M., Hua, D. and Earl, W.L., *MRS Bulletin*, April 1994, 44

[54] Lecloux, A.J., in "Catalysis-Science and Technology", Volume 2, Anderson, J.R. and Boudart, M. (eds.), Springer-Verlag, Berlin, (1981), 179

[55] Allen, T. (ed), "Particle Size Measurement", Chapman and Hall, London, (1981)

[56] Yunes, S. Micromeritics Seminar (1996)

[57] Maboka, S., Msc Thesis (1994), 52

[58] Barrett, E.P., Joyner, L.G. and Halenda, P.P., *J. Am. Chem. Soc.*, **73**, (1951), 373

[59] Termes, S.C., Buckley, A.N. and Gillard, R.D., *Inorg. Chim. Acta.*, **126**, (1987), 79

[60] MINTEQA2 Version 3.0 User's Manual (1990)

[61] Brookins, D.G., "Eh-pH Diagrams for Geochemistry", Springer-Verlag, Berlin, (1988)

[62] Duffield, J.R., Johns, J.R., Marsicano, F. and Williams, D.R., *Polyhedron*, **10**, (1991), *10*, 1121

[63] Duvenhage, D.J., PhD Thesis: The Preparation, Characterisation and Evaluation of Titania supported Fe:Co Bimetallic Catalysts for the Hydrogenation of CO, University of the Witwatersrand, South Africa, (1993)

[64] Brunauer, S. and Emmet, P.H., *J. Am. Chem. Soc.*, **59** (1937), 1553

[65] Hess, D., Pepp, H. and Baerns, M., *Ber. Bunsenges. Phys. Chem.*, 90, (1986), 1234

[66] Price, J.G., PhD Thesis: An Investigation into novel bimetallic catalysts for use in the Fischer-Tropsch reaction, University of the Witwatersrand, South Africa, (1994)

[67] Dietz, W.A., *J. of G.C.*, February 1967, 79

[68] von Weimarn, P.P., *Chemical Reviews*, 2, (1925), 217

[69] Haberman, N. and Gordon, L., *Anal. Chem.*, 33, (1961), *12*, 1801

[70] Benedetti-Pichler, A.A., *Anal. Chem.*, 27, (1955), *9*, 1505

[71] Schwertmann, U. and Cornell, R.M., "Iron Oxides in the Laboratory - Preparation and Characterisation", VCH, Weinheim, (1991)

[72] Nielsen, A.E., "Kinetics of Precipitation", Pergamon Press, Oxford, (1964)

[73] Dunning, W.J., in "Particle Growth in Suspensions", Smith, A.L. (ed), Academic Press, London, (1973)

[74] Bye, G.C. and Sing, K.S.W., in "Particle Growth in Suspensions", Smith, A.L. (ed), Academic Press, London, (1973)

[75] Milburn, D.R., O'Brien, R., Chary, K. and Davis, B.H., "Characterisation of Porous Solids III" in "Studies in Surface Science and Catalysis", Volume 87, Rouquerol, J., Rodriguez-Reinoso, F., Sing, K.S.W. and Unger, K.K. (eds), Elsevier Science, Amsterdam, (1994)

[76] Kung, H.H., in "Studies in Surface Science and Catalysis", Volume 45, Delmon, B. and Yates, J.T. (eds), Elsevier, Science, Amsterdam, (1989)

[77] Andreeva, D., Tabakova, T., Mitov, I. and Andreev, A., *J. Mater. Sci.*, 2, (1991), 199

[78] Anderson, R.B., in "Catalysis" Volume IV, Emmet, P.H. (ed), Reinhold, New York, (1956)

[79] Morales, M.P., Gonzales-Carreno, T. and Serna, C.J., *J. Mater. Res.*, 7, (1992), 9, 2538

[80] Reed-Hill, R.E. and Abbaschian, R., "Physical Metallurgy Principles", third edition, PWS Publishing Company, New York, (1994)

[81] Baba-Kishi, K.Z., *Scanning*, 18, (1996), 315

[82] Woodruff, D.P., "The Solid-Liquid Interface", Cambridge University Press, New York, (1973)

[83] Avner, S.H., "Introduction to Physical Metallurgy", McGraw-Hill, Inc, Singapore, (1985)

[84] Klug, H.P. and Alexander, L.E., "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials", second edition, John Wiley and Sons, New York, (1974), 491

[85] JCPDS PDF database card number 330664

[86] Wang, D., Cheng, X., Huang, Z., Wang, X. and Peng, S., *Appl. Catal.*, 77, (1991), 109

[87] Jung, H. and Thomson, W.J., *J. Catal.*, 134, (1992), 654

[88] Jung, H. and Thomson, W.J., *J. Catal.*, 139, (1993), 375

[89] Mellor, J.W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Volume XII, Longmans, Green and Co., (1932), 768

[90] Yunes, S., "Explanation and Application of the Physisorption and the Chemisorption Techniques in the Characterisation of solids in General and Catalysts in Particular" Micromeritics (1996)

[91] Briggs, D. and Seah, M.P. (eds) "Practical Surface Analysis" second edition, Volume 1, John Wiley and Sons, New York, (1990)

[92] Dwyer D.J., in "Catalyst Characterization Science", chapter 11, American Chemical Society, USA, (1985)

[93] Fiedor, J.N., Proctor, A., Houalla, M. and Hercules, D.M., *Surf. Interface. Anal.*, **23**, (1995), 204

[94] Lin, J., May, J.A., Didziulis, S.V. and Solomon, E.I., *J. Am. Chem. Soc.*, **114**, (1992), 4718

[95] Baltrus, J.P., Diehl, J.R., McDonald, M.A. and Zarochak, M.F., *Appl. Catal.*, **48**, (1989), 199

[96] Loggenberg, P.M. and Copperthwaite, R.G., *Appl. Surf. Sci.*, **31**, (1988), 327

[97] Benziger, J.B and Madix, R.J., *J. Catal.*, **65**, (1980), 49

[98] Ott, G.L., Delgass, W.N., Winograd, N. and Baitinger, W.E., *J. Catal.*, **56**, (1979), 174

[99] Ott, G.L., Fleisch, T. and Delgass, W.N., *J. Catal.*, **65**, (1980), 253

[100] Ott, G.L., Fleisch, T. and Delgass, W.N., *J. Catal.*, **60**, (1979), 394

[101] Galtayries, A. and Bonnelle, J-P., *Surf. Interface. Anal.*, **23**, (1995), 171

[102] Grimal, J.M. and Marcus, P., *Surf. Sci.*, **249**, (1991), 171

[103] Sault, A.G. and Datye, A.K., *J. Catal.*, **140**, (1993), 136

[104] Silverman, D.C. and Boudart, M. *J. Catal.*, **77**, (1982), 208

[105] Lichtman, D., Craig, J.H, Jr., Sailer, V. and Drinkwine, M., *Appl. Surf. Sci.*, **7**, (1981), 325

[106] Matsumoto, Y., Soma, M., Onishi, T. and Tamaru, K., *J. Chem. Soc. Faraday Trans. 1*, **76**, (1980), 1122

[107] Sault, A.G., *J. Catal.*, **140**, (1993), 121

[108] Brion, D., *Appl. Surf. Sci.*, **5**, (1980), 133

[109] Johansson, G., *Acta. Chem. Scand.*, **16**, (1962), 1234

[110] Kyotani, T., Kawashima, H. and Tomita, A., *Environ. Sci. Technol.*, **23**, (1989), 218

[111] Brundle, C.R., Chuang, T.J. and Wandelt, K., *Surf. Sci.*, **68**, (1977), 459

[112] Madon, R.J. and Taylor, W.F., *J. Catal.*, **69**, (1981), 32

[113] Anderson, A.B. and Hong, S.Y., *Surf. Sci.*, **204**, (1988), L708

[114] Seah, M.P., in "Practical Surface Analysis", Briggs, D. and Seah, M.P. (eds), Second edition, Volume 1, John Wiley and Sons, Chichester, (1990), 357

[115] Bernasik, A., Janowski, J., Hirschwald, W., Stolze, F. and Nowotny, J., *J.Mater. Sci.* **26**, (1991), 2527

[116] van Gestel, J., Leglise, T. and Duchet, J-C., *J. Catal.*, **145**, (1994), 429

[117] Coucouvanis, D., Swenson, D., Stremple, P. and Baenziger, N.C., *J. Am. Chem. Soc.*, **101**, (1979), 3392

[118] Buckley, A.N., Wouterlood, H.J., Cartwright, P.S. and Gillard, R.D., *Inorg. Chim. Acta.*, **143**, (1988), 77

[119] Briggs, D. and Seah, M.P. (eds) "Practical Surface Analysis" second edition, Volume 1, John Wiley and Sons, Chichester, (1990), 491

[120] Muller, A., *Polyhedron*, **5**, (1986), *12*, 323

[121] Griffiths, P.R. and de Haseth, J.A.," Fourier Transform Infrared Spectrometry", Chapter 17, John Wiley, New York, (1986)

[122] Hamedeh, I. M., King, D., and Griffiths, P. R., *J. Catal*, **88**, (1984), 264

[123] Davydov, A.A., " Infrared Spectroscopy of adsorbed species on the surface of Transition Metal Oxides" John Wiley and Sons, Chichester, (1984)

[124] Heal, M.J., PhD Thesis: Infrared Studies of Carbon Monoxide and Hydrogen Adsorbed on Silica Supported Metal Catalysts, University of Cape Town, (1976)

[125] Jorgensen, N and Rochester, C.H., *Appl. Catal.*, **25**, (1986), 69

[126] Johnston, C., Jorgensen, N. and Rochester, C., *J. Chem. Soc. Faraday Trans. I.*, **84**, (1988), 309

[127] Blyholder, G. and Neff, L.D., *J. Phys. Chem.*, **66**, (1962), 1464

[128] Rewick, R.T and Wise, H., *J. Phys. Chem.*, **82**, (1978), 751

[129] Kroeker, R.M., Kaska, W.C. and Hansma, P.K., *J. Catal*, **63**, (1980), 487

[130] Kazansky, V.B., Zaitsev, A.V., Borovkov, V.YU. and Lapidus, A.L., *Appl. Catal.*, **40**, (1988), 17

[131] McDonald, M.A., Storm, D.A. and Boudart, M., *J. Catal*, **102**, (1986), 386

[132] Kishi, K. and Roberts, M.W., *J. Chem. Soc. Faraday. Trans. I.*, **71**, (1975), 1715

[133] Davydov, A.A., " Infrared Spectroscopy of adsorbed species on the surface of Transition Metal Oxides" John Wiley and Sons, Chichester, (1984)

[134] Al-Mashta, F., Sheppard, N., Lorenzelli, V. and Busca, G., *J. Chem. Soc. Faraday. Trans. I.*, **78**, (1982), 979

[135] Rochester, C.H. and Topham, S.A., *J. Chem. Soc. Faraday Trans. I.*, **75**, (1979), 1073

[136] Nakamoto, K., " Infrared spectra of inorganic and coordination compounds", Wiley, New York, (1970)

[137] Saur, O., Bensitel, M., Mohammed Saad, A.B, Lavalley, J.C., Tripp, C.P. and Morrow, B.A., *J. Catal.*, **99**, (1986), 104

[138] Kayo, A., Yamaguchi. T. and Tanabe, K., *J. Catal.*, **83**, (1983), 99

[139] Jin, T., Machida, M., Yamaguchi, T. and Tanabe, K., *Inorg. Chem.*, **23**, (1984), 4396

[140] Miao, C., Hua, W., Chen, J. and Gao, Z., *Catalysis Letters*, **37**, (1996), 187

[141] Kellner, C.S. and Bell, A.T., *J. Catal.*, **71**, (1981), 288

[142] McQuire, M.W. and Rochester, C.H., *J. Catal.*, **141**, (1993), 355

[143] Nakanishi, K., " Infrared adsorption Spectroscopy (Practical)", Holden-Day, San Fransisco, (1962)

[144] Benziger, J.B. and Larson, L.R., *J. Catal*, **77**, (1982), 550

[145] Unmuth, E.E., Schwartz, L.H. and Butt, J.B., *J. Catal*, **63**, (1980), 404

[146] Colthup, N.B., Daly, L. and Wiberley, S.E., " Intrroduction to Infrared and Raman Spectroscopy", Academic Press, New York, (1964)

[147] Blyholder, G., in " Experimental Methods in Catalytic Research", Anderson, R.B. (ed), Academic Press, New York, 1968

[148] Benziger, J. B. and Madix, R. J., *J. Catal*, **65**, (1980), 36

[149] Jackson, S. D., Brandreth, B. J. and Winstanley, D., *J. Catal.*, **129**, (1991), 540

[150] Loek, T., Favre, F., van der Lee, G. and Ponec, V., *J. Chem. Soc. Chem. Commun.*, (1985), 230

[151] Wang, C.J. and Ekerdt, J.G., *J. Catal*, **86**, (1984), 239

[152] Galuska, J., Sano, T. and Sawicki, J.A., *J. Catal.*, **136**, (1992), 96

[153] Jones, R.N., *Spectrochim. Acta*, **9**, (1957), 235

[154] Topsoe, H., Clausen, B.S. and Morup, S., *Hyperfine Interactions*, **27**, (1986), 231

[155] Weilers, A.F.H., Kock, A.J.H.M., Hop, C.E.C.A., Geus, J.W. and van der Kraan, A.M., *J. Catal.*, **117**, (1989), 1

[156] Vertes, A., Korecz, L. and Burger, K., "Mössbauer Spectroscopy", in "Studies in Physical and Theoretical chemistry", Volume 5, Elesevier Scientific Publishing Company, Amsterdam, (1979)

[157] van der Kraan, A.M., Nonnekens, R.C.H. and Niemandtsverdriet, J.W., *Hyperfine Interactions*, **28**, (1986), 899

[158] Rao, K.R.P.M., Huggins, F.E., Mahajan, V., Huffman, G.P., Bukur, D.B. and Rao, V.U.S., *Hyperfine Interactions*, **93**, (1994), 1751

[159] Rao, K.R.P.M., Huggins, F.E., Ganguly, B., Mahajan, V., Huffman, G.P., Davis, B., O'Brien, R.J., Xu, L. and Rao, V.U.S., *Hyperfine Interactions*, **93**, (1994), 1755

[160] Lazar, K., Reiff, W.M. and Guczi, L., *Hyperfine Interactions*, **28**, (1996), 871

[161] Greenwood, N.N. and Gibb, T.C., in "Mössbauer Spectroscopy" Chapter 10, Chapman and Hall, London, (1971)

[162] Kolk, B., Albers, A., Leith, I.R. and Howden, M.G., *Appl. Catal.*, **37**, (1988), 57

[163] Long, G.J. (ed) "Mossbauer Spectroscopy Applied to inorganic chemistry" Volume 2, Plenum Press, New York, (1987)

[164] Olowe, A.A., Marie. Y., Refait, P.H. and Genir, J-M.R., *Hyperfine Interactions*, **93**, (1994), 1783

[165] Jorgensen, C.K., *Structure and Bonding*, **1**, (1966), 3

[166] Duffield, J.R., Marsicano, F. and Williams, D.R., *Polyhedron*, **10**, (1991), *10*, 1105

[167] Duffield, J.R. and Williams, D.R., *Chem. Soc. Rev.*, **15**, (1986), 291

[168] Duffield, J.R., Marsicano, F., Waters, M. and Williams, D.R., *Polyhedron*, **10**, (1991), *10*, 1113

[169] Giggenbach, W., *Inorg. Chem.*, **11**, (1972), *6*, 1201

[170] King, E.J., "Qualitative Analysis and Electrolytic Solutions" Harcourt, Brace and World, Inc, New York (1959)

[171] Giggenbach, W.F., *Inorg. Chem.*, **13**, (1974), *7*, 1730

[172] Jensen, K.B. and Massoth, F.E., *J. Catal.*, **92**, (1985), 98

[173] Abbot, J., Clark, N.J. and Baker, B.G., *Appl. Catal.*, **26**, (1986), 141

[174] Rao, V.U.S., Stiegel, G.J., Cinquegrane, G.J. and Srivastava, R.D., *Fuel Processing Technology*, **30**, (1992), 83

[175] Schliebs, B. and Gaube, J., *Ber. Bunsenges. Phys. Chem.*, **89**, (1985), 68

[176] Donnelly, T.J. and Satterfield, C.N., *Appl. Catal.*, **52**, (1989), 93

[177] Lox, E. S. and Froment, G.F., *Ind. Eng. Chem. Res.*, **32**, (1993), 71

[178] Dictor, R.A. and Bell, A.T., *Appl. Catal.*, **20**, (1986), 145

[179] Dry, M.E., Shingles, T., Boshoff, L.J. and Oosthuizen, G.J., *J. Catal.*, **15**, (1969), 190

[180] Sano, T., Yanagisawa, H., Saitio, K., Okabe, K Okado, H., Takaya, H. and Bando, K., *Appl. Catal.*, **19**, (1985), 247

[181] Liu, Z., Zhou, J. and Zhang, B., *J. Molec. Catal.*, **94**, (1994), 255

[182] Duvenhage, D.J. and Coville, N.J., *Catalysis and Catalytic Proceedings*, Cape Town SA (1993)

[183] Kiskinova, M.P., "Poisoning and Promotion in catalysis based on surface science concepts and experiments", Elesevier Press, Amsterdam, (1992)

[184] Bayer, J., Stein, K.C., Hofer, L.J.E. and Anderson, R.B., *J. Catal.*, **3**, (1964), 145

[185] Lox, E.S. and Froment, G.F., *Ind. Eng. Chem. Res.*, **32**, (1993), 61

[186] Kim, M.S., Rodriguez, N.M. and Baker, R.T.K., *J. Catal.*, **143**, (1993), 449

[187] Orita, H., Shuichi, N. and Tamaru, K., J. Chem. Soc. Chem. Commun, (1984), 150

[188] Smith, K.J. and Anderson, R.B., *J. Catal.*, **85**, (1984), 428

[189] van der Kraan, A.M., Ramselaar, W.L.T.M. and de Beer, V.H.J. in "Mössbauer spectroscopy applied to inorganic chemistry" Volume 3, Long, G.J. and Grandjean F. (eds), Plenum Press, New York, (1989), 376

[190] Wimmers, O.J., Arnoldy, P. and Moulijn, J.A., *J. Phys. Chem.*, **90**, (1986), 1331

[191] Mangnus, P.J., Riezebos, A., van Langeveld, A.D. and Moulijn, J.A., *J. Catal.*, **151**, (1995), 178

[192] Inamura, K., Takyu, T., Okamoto, Y., Nagata, K. and Imanaka, T., *J. Catal.*, **133**, (1992), 498

[193] Plint, N.D., personal communication

[194] Reymond, J.P., Meriaudeau, P. and Teichner, S.J., *J. Catal.*, **75**, (1992), 39

[195] Shroff, M.D., Kalakkad, D.S., Coulter, K.E., Kohler, S.D., Harrington, M.S., Jackson, N.B., Sault, A.G. and Datye, A.K., *J. Catal.*, **156**, (1995), 185

[196] Shashkin, D.P., Shiryaev, P.A., Chichagov, A.V. , Morozova, O.S. and Krylov, O.V., *Kinetics and Catalysis*, **33**, (1992), 744

[197] Grzybek, T., Papp, H. and Baerns, M., *Appl. Catal.*, **29**, (1987), 335

[198] Matumoto, H., *J. Catal.*, **86**, (1984), 201

[199] Raup, G.B. and Delgass, W.N., *J. Catal.*, **58**, (1979), 348

[200] Niemandtsverdriet, J.W., van der Kraan, A.M., van Dijk, W.L. and van der Baan, H.S. *J. Phys. Chem.*, **84**,(1980), 3363

[201] Maiti, G.C., Malessa, R. and Baerns, M., *Appl. Catal.*, 5, (1983), 51

[202] Jolly, W.L., "The Inorganic Chemistry of Nitrogen", W.A. Benjamin, Inc., New York, (1964)

[203] Somorjai, G.A., *J. Catal.*, 27, (1972), 453

[204] Pourbaix, M. and Pourbaix, A., *Geochimica et Cosmochimica Acta*, 56, (1992), 3157

[205] Rickard, D., *Chemical Geology*, 78, (1989), 315

[206] Wang, T., Vazquez, A., Kato, A. and Schmidt, L.D., *J. Catal.*, 78, (1982), 306

[207] Yang, B.L., Lee., S.B., Cheng, D.S. and Chang, W.S., *J.Catal.*, 141, (1993), 161

[208] Mothebe, B.L., MSc Dissertation, University of the Witwatersrand, (1995)

[209] Nagase, Y., Jin, T., Hattori, H., Yamaguchi, T. and Tanabe, K., *Bull. Chem. Soc. Jpn.* , 58, (1985), 916

[210] Jones, V.K., Neubauer, L.R. and Bartholomew, C.H., *J. Phys. Chem.*, 90 (1986), 4832

[211] Somorjai, G.A., "Introduction to Surface Chemistry and Catalysis", John Wiley, New York, (1994)

Appendix I

A summary of some of the calculations performed by MINTEQA2 (version 3.10) in order to model the solution speciation of sulfided precipitated-iron catalysts is given.

Mathematical concepts

A system of *n* independent components that can combine to form *m* species, is represented by a set of mass action expressions:

$$K_i = (S_i)\prod_j X_j^{-a_{ij}} \quad \text{..... (A.1)}$$

where K_i = equilibrium constant for the formation of species i

(S_i) = activity of species i

X_j = activity of component j

a_{ij} = stoichiometric coefficient of component j in species i

Π = indicates the product over all components in species i

In addition to equation A.1 above, the set of *n* independent components is governed by *n* mass balance equations of the form:

$$Y_j = \sum_i a_{ij} C_i - T_j \quad \text{..... (A.2)}$$

where: T_j = total dissolved concentration of component j

Y_j = the difference between the *calculated* total dissolved concentration of component j and the known *analytical* total dissolved concentration of component j

The mathematical problem (or the speciation model) is solved when the matrix set of component activities which results in the set of concentrations, C, such that each individual of the set of mass balance differences, Y, is equal to zero.

Correction of Equilibrium Constants

Equilibrium constants contained in the MINTEQA2 database have generally been determined at 25°C. Since the precipitation of iron oxide was modelled at 75°C, the equilibrium constants were adjusted for temperature using the van't Hoff equation:

$$\log K_T = \log K_{Tr} - \frac{\Delta H_r^\circ}{2.303R}\left[\frac{1}{T} - \frac{1}{T_r}\right] \quad \text{.....(A.3)}$$

where: T_r = reference temperature, 298.16 K

$\log K_{Tr}$ = logarithm of the equilibrium constant at the reference temperature

R = molar gas constant

T = temperature of the system to be modelled (Kelvin)

ΔH_r° = standard enthalpy change of the reaction

This method is limited to temperatures of up to 100°C, since the van't Hoff equation implicitly assumes reaction enthalpies to be independent of temperature (and this is generally not true at high temperatures).

Computation of Activity Coefficients

The Davies equation (A.4) was used to compute activity coefficients (γ) for charged species:

$$\log\gamma_i = -AZ_i^2\left[\frac{I^{1/2}}{1+I^{1/2}} - 0.24I\right] \quad \text{.....(A.4)}$$

where: A = constant that depends on the dielectric constant and temperature

Z_i = the charge on each species i

I = solution iomc strength

Precipitation of solids

In order to decide which species would precipitate first, a priority sequence of thermodynamic stabilities of each solid was established. This was done by comparing the appropriate ion activity products (IAP) with the corresponding formation constant after the aqueous phase had been equilibrated. The saturation index (A.5) so determined was calculated and used to establish the stability order for precipitation or dissolution of solids.

$$\text{saturation index} = \log\frac{IAP}{K} \quad \text{.. ..... (A.5)}$$

A negative saturation index implies undersaturation of the solution in that particular species.

Redox Reactions

The reduction of Fe^{3+} to Fe^{2+} was inserted as a thermodynamic redox reaction from the MINTEQA2 database:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad \log K = 13.0320$$

Table A.1: Formation constants of components participating in the precipitation of iron-oxide in the presence of sulfide

Component	log K[a]	new log K[b]
Fe^{2+}/Fe^{3+}	13.0320	11.979
E^{-1}	1.4477	4.053
FeS precipitate	3.9150	3.915
$Fe_4(OH)_{12}$ (Ferrihydrite)	-4.8910	-4.891
Fe_2O_3 (Hematite)	4.0080	7.225
S_5^{2-}	4.4150	12.076

[a] According to MINTEQA2 database
[b] Value predicted by model

Table A.2: Parameters of input datafile created in PRODEFA2

Parameter	
Temperature	75°C
Units of concentration	Molal
Ionic strength	Computed: Davies Equatic
Maximum number of iterations	200
Terminate if charge imbalance exceeds 30 %	NO
Precipitation is allowed only for those solids specified	YES

Appendix II

The Mössbauer spectra of uncalcined catalysts sulfided with 2000 and 5000 ppm polysulfide (referred to in Table 6.1) are shown below:

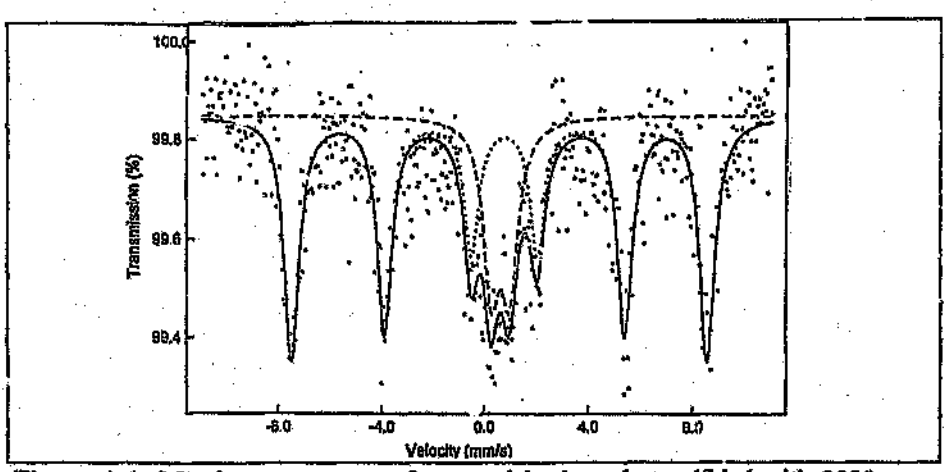


Figure A.1: Mössbauer spectrum of an uncalcined catalyst sulfided with 2000 ppm polysulfide

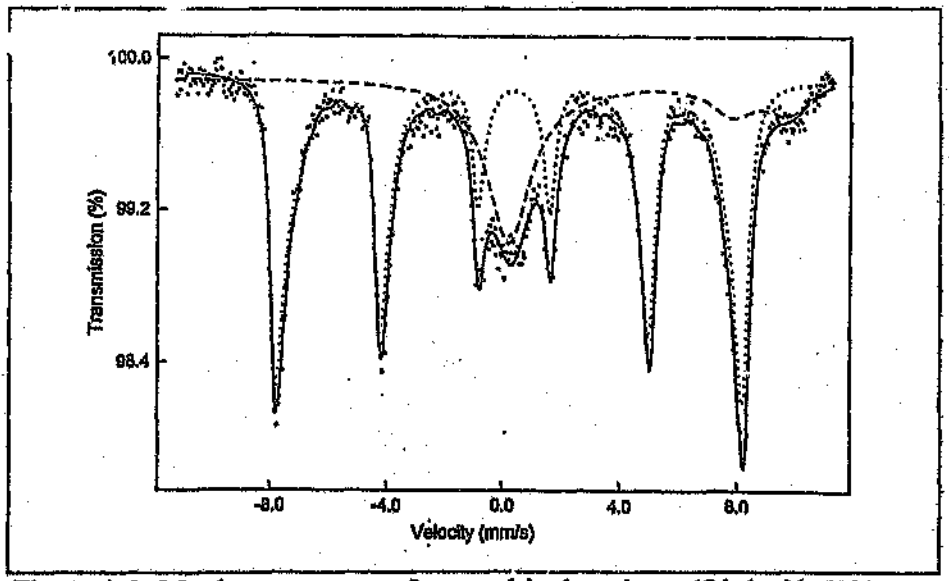


Figure A.2: Mössbauer spectrum of an uncalcined catalyst sulfided with 5000 ppm polysulfide

"What you can do, or dream you can, begin it. Boldness has genius, power and magic in it"

Goethe

Author: Bromfield, Tracy Carolyn.
Name of thesis: The effect of low-level sulfide addition on the performance of precipitated-iron Fischer-Tropsch catalysts.

PUBLISHER:
University of the Witwatersrand, Johannesburg
©2015

LEGALNOTICES:

Copyright Notice: All materials on the University of the Witwatersrand, Johannesburg Library website are protected by South African copyright law and may not be distributed, transmitted, displayed or otherwise published in any format, without the prior written permission of the copyright owner.

Disclaimer and Terms of Use: Provided that you maintain all copyright and other notices contained therein, you may download material (one machine readable copy and one print copy per page)for your personal and/or educational non-commercial use only.

The University of the Witwatersrand, Johannesburg, is not responsible for any errors or omissions and excludes any and all liability for any errors in or omissions from the information on the Library website.