Catalysis Today 71 (2002) 335–341

www.elsevier.com/locate/cattod

Application of in situ Mössbauer spectroscopy to investigate the effect of precipitating agents on precipitated iron Fischer–Tropsch catalysts

T.R. Motjope[1], H.T. Dlamini[1], G.R. Hearne, N.J. Coville*

Department of Chemistry, Schools of Chemistry and Physics, University of the Witwatersrand, Johannesburg, PO Wits 2050, South Africa

Abstract

The type of the precipitating agent used during the preparation of a precipitated iron-based Fischer–Tropsch (FT) catalyst affects the catalyst pore structure, crystallite size, phase composition and catalytic behavior. Catalysts prepared by using precipitating agents, that contain carbonate ions, have pores that are larger than those of catalysts prepared using precipitating agents that contain hydroxides. Precipitation at $\mathrm{pH} > 8$, using aqueous NH_3 solution as a precipitating agent, results in the formation of large crystallites of FeOOH, which are not observed when Na_2CO_3 and K_2CO_3 are used. Higher % CO conversion during FT synthesis was observed with the catalyst prepared by using aqueous NH_3 solution. However, this is correlated with a low selectivity for the formation of olefins. For all catalysts, in situ Mössbauer spectra recorded during FT synthesis show that the % CO conversion increases with the formation of iron carbides, viz. ε'-$Fe_{2.2}C$ and χ-$Fe_{2.5}C$.

Keywords: Fischer–Tropsch; Mössbauer spectroscopy; Precipitation; Iron carbides; In situ

1. Introduction

Although most of the Group 8–10 metals are known to be active catalysts for the Fischer–Tropsch (FT) reaction, iron-based catalysts are generally the catalysts of choice and are currently utilized in the commercial operations at SASOL. In general, iron-based catalysts have two main advantages; iron is inexpensive and iron catalysts, when operated under appropriate conditions, are very active for the formation of unbranched hydrocarbons and short chain olefins which can be oligomerized into fuels and other hydrocarbons [1,2].

There have, however, been unabated attempts to improve the performance of iron-based catalysts by increasing the catalyst lifetime, activity and selectivity for specific products, e.g. olefins, alcohols. This has often entailed changing the preparation method, preparation conditions and type of promoters and supports used during catalyst preparation.

Proper control of the preparation variables used during catalyst synthesis is the key for controlling the catalytic behavior of precipitated iron-based catalysts. Previous studies [1,3,4] have indicated that pH is the most important variable that affects the catalyst structure and the ultimate catalyst activity and selectivity. Rähse et al. [5] reported the optimal pH for the preparation of precipitated iron catalysts that are active for the conversion of CO to hydrocarbons.

Anderson [6] and Dry [1] suggested that optimal catalytic behavior was observed with precipitated iron

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* Corresponding author. Tel.: +27-11-717-6738; fax: +27-11-339-7967.
E-mail address: ncoville@aurum.chem.wits.ac.za (N.J. Coville).

[1] Present address: SASOL Technology (Pty.) Ltd., 1 Klasie Havenga Avenue, Sasolburg 9570, South Africa.

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PII: S0920-5861(01)00460-6

catalysts which were prepared with Na_2CO_3 and gave a final solution of pH between 6.8 and 8. Diffenbach and Fauth [3] observed that precipitated iron catalysts prepared at pH 3.7 and 4.7, using Na_2CO_3 as a precipitant, showed unusually high olefin selectivity and activity maintenance. These differences in catalytic activity reported by different workers could very well arise from the different experimental procedures used. The catalysts that have been reported by Anderson [6] and Dry [1] were prepared by batch precipitation, whereas the catalysts of Diffenbach and Fauth [3] were prepared by continuous precipitation.

Anderson [6] also observed that the use of potassium, sodium, or ammonium carbonates as precipitating agents resulted in a better catalyst than when hydroxides were used. Dry [1] found that the nature of the precipitating agent had an influence on the pore structure of the catalyst. The catalysts prepared by using carbonates as precipitating agents were found to have large pores when compared to those prepared using hydroxide.

In this study, we report on the application of in situ Mössbauer spectroscopy in the study of precipitated iron catalysts, which were prepared using different precipitating agents. The application of an in situ technique allows for a direct comparison of the catalyst performance during FT synthesis and its phase composition.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared via a batch precipitation procedure described by Anderson [6]. In this precipitation reaction, $Fe(NO_3)_3 \cdot 9H_2O$ was used as a metal salt precursor and either aqueous NH_3 solution, K_2CO_3 or Na_2CO_3 was used as the precipitating agent. Precipitation was performed at 75 °C over 15 min. The precipitates were aged for 18 h before washing with double distilled water. The washing step was omitted for catalysts prepared using aqueous NH_3 solution as a precipitating agent. In all the cases, the washed catalysts were dried at 393 K for 18 h in an air atmosphere. Table 1 lists the catalysts that were used in this study. For brevity, the samples are labeled according to the final pH of the precipitate and the type of precipitating agent used, e.g., 7.5 PC denotes a catalyst prepared at pH 7.5 using K_2CO_3 (PC) as the precipitating agent (AH = aqueous NH_3 solution, SC = Na_2CO_3).

Table 1
Details of the solutions used during catalyst precipitation

Sample	Fe^{3+} (g/l)	Precipitating agent (g/l)	pH
9.9 PC	2.99	80.00	9.9
9.8 AH	3.00	80.00	9.8
8.0 AH	3.00	20.00	8.0
7.5 PC	3.00	15.03	7.5
7.3 SC	3.00	10.65	7.3

2.2. Catalyst characterization

Mössbauer spectroscopy experiments were performed with a 50 mCi Co-57 source in a Rhodium matrix. The spectrometer was operated in the symmetric constant acceleration mode with 100 μs of dwell time per channel. The spectra were collected over 1024 channels in mirror image format.

Data analysis was performed using a least squares fitting routine that models the spectra as a combination of singlets, quadruple doublets and magnetic sextuplets based on a Lorenzian line shape profile. Identification of the spectral components was based on their isomeric shift (δ), quadruple splitting (Δ) and hyperfine magnetic field (H) values. All isomer shift values are reported relative to metallic iron (α-Fe). Furthermore, the catalysts were characterized using X-ray diffraction (XRD) and BET surface area measurements.

2.3. In situ Mössbauer spectroscopy and kinetic measurement

A special reactor was designed to perform in situ Mössbauer spectroscopy experiments and kinetic measurements during FT synthesis. A schematic diagram of this reactor is depicted in Fig. 1. All gases were supplied by AFROX (SA). Synthesis gas used for FT experiments comprised of a mixture of Ar, H_2 and CO in a ratio 1:6.6:3.3, respectively. The catalysts were calcined in situ in air at 427 K and thereafter reduced at 573 K and 0.4 MPa for 16 h using H_2. The FT experiments were performed at 493 K, 0.5 MPa and a gas hourly space velocity (GHSV) of 0.4 l/(g h).

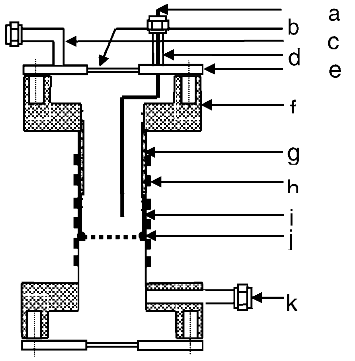

Fig. 1. Schematic diagram for the high pressure Mössbauer cell Cu gaskets have been omitted: (a) thermocouple; (b) beryllium window; (c) gas inlet; (d) thermocouple feed through; (e) 316 stainless steel flange; (f) 316 stainless steel body; (g) 316 stainless steel pressing ring; (h) heater; (i) graphite sample cup; (j) gasket; (k) gas outlet.

3. Results and discussion

3.1. Characterization of the as-prepared catalysts

The fresh catalysts, uncalcined, have surface areas ranging from 195 to 228 m^2/g. The pore volume increased from 0.31 to 0.41 m^3/g with this small increase in surface area. Preparation with Na_2CO_3 results in a catalyst with a high total pore volume and larger pores, whereas a low total pore volume is obtained when aqueous NH_3 solution is used, similar to the observations made by Dry [1]. The formation of CO_2 during precipitation with Na_2CO_3 and K_2CO_3 could be the cause of the large pores observed with catalysts prepared using these precipitating agents. The precipitation pH does not have a significant effect on the catalyst surface area and pore volume.

Fig. 2 shows the Mössbauer spectra of the fresh uncalcined precipitated catalysts. The hyperfine interaction parameters obtained from analyses of these spectra are summarized in Table 2. Mössbauer spectra were evaluated as a superposition of quadruple doublets and magnetically split components, except for the catalysts prepared in the pH range 7–8. These spectra were fitted with two quadruple doublets only. These data present the effect of: (i) the type of precipitating agent used during catalyst preparation; (ii) the precipitation pH on the catalyst phase composition and average crystallite size.

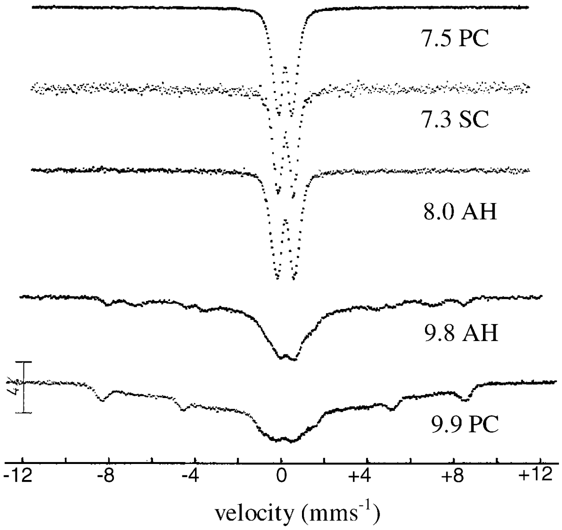

Fig. 2. Mössbauer spectra of the fresh uncalcined precipitated catalysts. Spectra recorded at 80 K.

Catalysts prepared in the pH range 7–8 consist of small crystallites of hematite irrespective of the precipitating agent used during preparation. The large and small quadruple moments used to analyze these spectra indicate the presence of two different site symmetries, which we have assigned to surface and bulk positions, respectively. Large crystallites are formed when the precipitation pH is increased to 9.8 and 9.9. Furthermore, precipitation using aqueous NH_3 solu-

Table 2
Hyperfine interaction parameters of precipitated iron catalyst (spectra recorded at 80 K)

Sample	IS ($mm\,s^{-1}$)$_{Fe}$	QS ($mm\,s^{-1}$)	B_{hf} (T)	Atomic %	Phase
9.9 PC	0.42	−0.20	51.6	78.8	α-Fe_2O_3
	0.40	0.96	–	21.2	Fe^{3+}
9.8 AH	0.43	−0.15	50.8	26.2	α-Fe_2O_3
	0.41	−0.26	43.7	47.6	α-FeOOH
	0.41	0.74	–	26.2	Fe^{3+}
8.0 AH	0.43	0.55	–	55.0	Fe^{3+}
	0.40	0.99	–	45.0	Fe^{3+}
7.5 PC	0.40	0.57	–	64.1	Fe^{3+}
	0.39	0.98	–	35.9	Fe^{3+}
7.3 SC	0.42	0.58	–	58.9	Fe^{3+}
	0.39	0.97	–	41.1	Fe^{3+}

Table 3
Phase composition of precipitated iron catalysts after reduction at 573 K for 16 h in H_2

Sample	Atomic %	Phase composition
8.0 AH	55.1	α-Fe
	35.9	Fe^{3+}
	9.0	Fe^{2+}
7.5 PC	50.0	α-Fe
	21.1	Fe_3O_4
	18.9	Fe^{3+}
	10.0	Fe^{2+}
7.3 SC	39.0	α-Fe
	24.0	Fe_3O_4
	26.8	Fe^{3+}
	10.2	Fe^{2+}

tion results in the formation of α-FeOOH that is not observed with K_2CO_3 [7,8]. The distorted baseline, reduced hyperfine magnetic fields for the sextuplets and peaks with abnormal line widths observed for the catalysts prepared at pH 9.8 and 9.9 indicate that the crystallites of α-Fe_2O_3, α-FeOOH, are still fairly small, <7 nm, and exhibit collective magnetic excitation [9].

3.2. Characterization of catalysts reduced in situ via Mössbauer spectroscopy

Table 3 shows the phase composition of samples 8.0 AH, 7.5 PC and 7.3 SC after reduction at 573 K for 16 h in H_2. The percentage reduction, which we express as 100 minus the amount of Fe^{3+} remaining after the reduction process, is higher for the catalysts prepared using precipitating agents that contain carbonate ions. The high extent of reduction correlates with the large pores observed with catalysts prepared using Na_2CO_3 and K_2CO_3. All catalysts are only partially reduced.

3.3. In situ characterization of catalysts during FT synthesis: Mössbauer spectroscopy and kinetic data

Table 4 gives a summary of the catalyst phase composition as a function of time-on-line. Fe^{3+} is further reduced to Fe_3O_4 during FT synthesis whilst α-Fe is converted to an iron carbide as well as oxidized to Fe_3O_4. Initially, α-Fe is converted to ε′-$Fe_{2.2}C$ that is further converted to χ-$Fe_{2.5}C$ at longer reaction times. The conversion of ε′-$Fe_{2.2}C$ to χ-$Fe_{2.5}C$ corresponds to the depletion of Fe^{3+} to almost zero for 8.0 AH and 7.5 PC.

Samples 8.0 AH and 7.5 PC that have high amounts of α-Fe after reduction are more carburized than 7.3 SC during FT synthesis. Only ε′-$Fe_{2.2}C$ was formed with sample 7.3 SC. For this catalyst, most of the α-Fe was oxidized to Fe_3O_4 during FT synthesis.

Fig. 3 depicts the % CO conversion as a function of time on line. There is a correlation between the % CO conversion and the degree of carburization, presented in Table 4. The % CO conversion follows a trend that is very similar to that observed for the total iron carbide content. This has led us to argue that the iron carbides, i.e. both ε′-$Fe_{2.2}C$ and χ-$Fe_{2.5}C$, are the active phase. However, the relative activity of these carbides might not be same [10].

The % CO conversion for samples 8.0 AH and 7.5 PC decreases somewhat after ∼15 h on line, whereas that of 7.3 SC remains fairly constant for the duration of the run. The decrease in conversion at longer

Table 4
Phase composition of samples 8.0 AH, 7.5 PC and 7.3 SC during FTS

Sample	Time (h)	Fe^{3+} (%)	Fe^{2+} (%)	Fe_3O_4 (%)	α-Fe (%)	ε′-$Fe_{2.2}C$ (%)	χ-$Fe_{2.5}C$ (%)
8.0 AH	7	22.0		33.0	31.9	13.1	
	14	20.6		37.3	29.0	13.1	
	26	1.9		32.0	16.1		50.0
7.5 PC	6	14.0	11.0	28.9	35.0	11.1	
	12	15.0	11.0	28.0	35.8	11.2	
	24	5.0		34.8	22.2		38.0
7.3 SC	8	16.3	7.3	47.2	21.1	5.1	
	14	19.5	8.8	49.9	16.1	5.7	
	26	16.8	9.6	52.5	14.9	6.2	

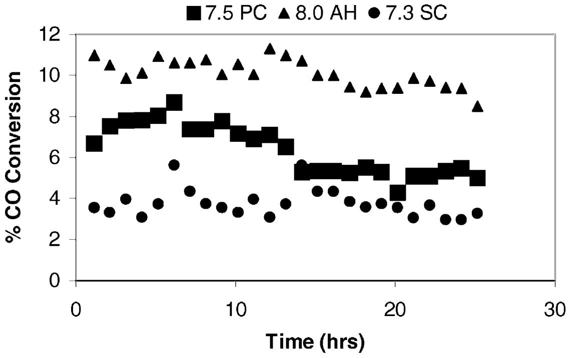

Fig. 3. % CO conversion as a function of time-on-line.

reaction times corresponds with the transformation of ε'-$Fe_{2.2}C$ to χ-$Fe_{2.5}C$ resulting in the formation of inactive carbon (C^*) on the catalyst surface:

$$2.5\varepsilon'\text{-}Fe_{2.2}C \rightarrow \chi\text{-}Fe_{2.5}C + 0.3C^*$$

Previous studies [11,12] have shown that the loss in activity with precipitated iron catalysts is primarily due to the deposition of inactive carbon on the catalyst surface.

Fig. 4 presents a correlation of catalytic activity, % α-Fe and % iron carbide, expressed in mol/(g-cat. h), with time-on-line. Initially, the activity increases with an increase in the amount of iron carbides. At longer reaction times, however, the activity drops although the amount of iron carbides still increases. This decrease in activity is similar to what was observed with the % CO conversion at longer reaction times, and is indicative of the onset of catalyst deactivation.

Comparison of the data for % CO conversion and activity indicates that although 7.5 PC has a higher % CO conversion than 7.3 SC (Fig. 3), it has a lower hydrocarbon formation rate. This indicates that most of the carbon atoms formed during CO dissociation on the surface of 7.3 SC are consumed in the production

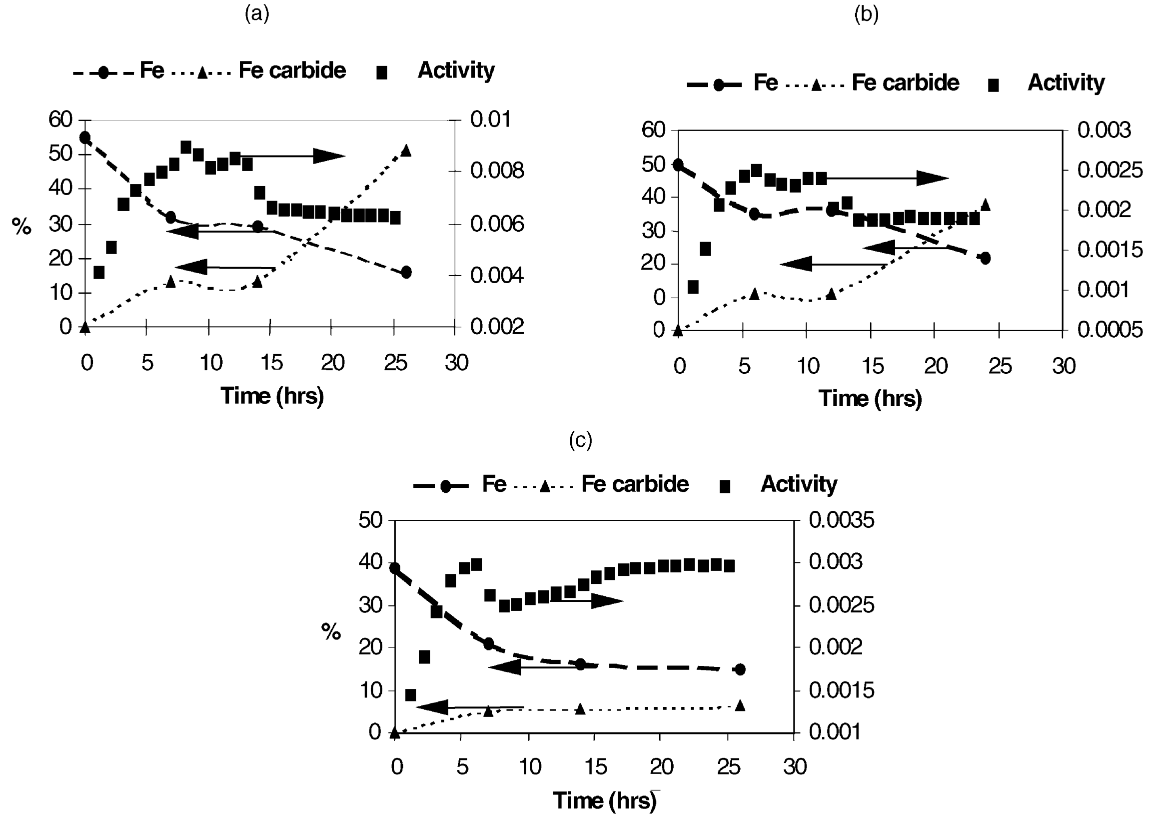

Fig. 4. Correlation of catalytic activity, % α-Fe and % iron carbide with time-on-line: (a) 8.0 AH; (b) 7.5 PC; (c) 7.3 SC.

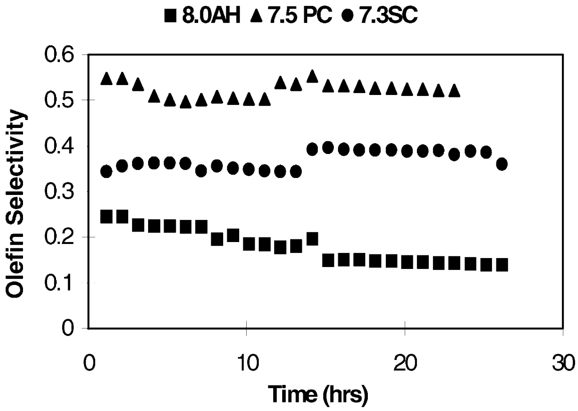

Fig. 5. Olefin selectivity as function of time-on-line.

of hydrocarbons. However, for 7.5 PC it seems that most of the carbon atoms are used for reactions other than hydrocarbon formation. This is consistent with the concept that there are a number of different types of surface carbon species present on the Fe catalysts [13].

The data found in Fig. 4 reveals that the catalytic activity increases while the % Fe decreases with time-on-line. This does not preclude some intrinsic activity being associated with Fe, but the relative activities of iron/(active iron carbide), cannot be determined presently.

The total olefin/paraffin ratios of these catalysts are presented in Fig. 5. The selectivity for the formation of olefins decreases with an increase in catalyst activity. Since olefins are generally considered to be primary products during FT synthesis [14], an increase in the catalyst activity also increases the extent of secondary reactions such as the hydrogenation of olefins to paraffins.

4. Conclusion

The nature of the precipitant used during the preparation of precipitated iron-based catalysts affects not only the physical properties of the catalysts as reflected in the different pore volume and pore diameter, but also the phase composition of the catalysts. The large pore volumes and pore diameters that are observed with catalysts prepared using K_2CO_3 and Na_2CO_3 are likely to be due to the formation of CO_2 during precipitation. It is envisaged that as CO_2 leaves the catalyst slurry, it creates voids in the structure, which result in a material with high porosity and a low density. The catalyst prepared at high pH values using aqueous NH_3 solution contains both FeOOH and α-Fe_2O_3, whereas that prepared with Na_2CO_3 contains Fe_2O_3. These phases are formed with a small average crystallite size, which resulted in reduced hyperfine field for the magnetic components. These differences were not observed for the catalysts prepared in the pH range 7–8.

The type of precipitating agent was also found to have an effect on the phase composition of the catalysts formed during reduction and FT synthesis. The in situ Mössbauer spectrum of the reduced catalyst that was prepared using aqueous NH_3 solution as a precipitating agent revealed the presence of paramagnetic Fe^{2+}, Fe^{3+} and magnetically split α-Fe only. The spectra of the catalysts prepared using Na_2CO_3 and K_2CO_3 show the presence of Fe_3O_4 in addition to the phases observed for the catalysts prepared using aqueous NH_3 solution. During the earlier stages of FT synthesis α-Fe was converted to ε'-$Fe_{2.2}C$ as well as also oxidized to Fe_3O_4 regardless of the precipitating agent used. After a long reaction time (~15 h), samples 7.5 PC and 8.0 AH reveal that ε'-$Fe_{2.2}C$ is converted to χ-$Fe_{2.5}C$. These data indicate that the evolution of the catalyst phase composition during FT depends on its composition after reduction.

Kinetic data indicate that those catalysts that contain a high amount of α-Fe after reduction give a high % CO conversion during FT synthesis. There is also a direct correlation between the % CO conversion and % iron carbide present in the catalyst. This has led to the proposal that the active phase is iron carbide. The catalyst, 8.0 AH, prepared with aqueous NH_3 solution, exhibited the highest % CO conversion. The CO conversion for samples 8.0 AH and 7.5 PC decreased somewhat after ~15 h on line, which corresponds to the transformation of ε'-$Fe_{2.2}C$ to χ-$Fe_{2.5}C$ with the formation of inactive carbon on the catalyst surface. Sample 7.3 SC was found to be the most stable catalyst during FT synthesis although its CO conversion was lower than that of 7.5 PC and 8.0 AH.

The rate of hydrocarbon formation decreased in the order 8.0 AH $>$ 7.3 SC $>$ 7.5 PC. The olefin selectivity increased in the order 8.0 AH $<$ 7.3 SC $<$ 7.5 PC. This implies that the high activity observed for 8.0 AH and 7.3 SC resulted in an increase in the secondary reactions, which included the hydrogenation of olefins.

Acknowledgements

The authors wish to thank the following companies and institutions for financial support, SASOL Technology (Pty.) Ltd., THRIP, NRF, University of the Witwatersrand and IAEA.

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