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Study on the Precursor Phase Composition of Fused Iron Catalyst for Fischer-Tropsch Synthesis

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Abstract: The effect of the precursor composition of fused iron catalyst on the performance of Fischer-Tropsch synthesis was investigated. XRD, BET and CO_2 adsorption experiments were carried out to provide better insight into the relationship therein. The results showed that the selectivity of C_{5+} hydrocarbon products was dependent on the mole ratio of Fe^{2+}/Fe^{3+}, which was represented by a hump-shaped curve. Catalysts with precursors containing Fe_3O_4 phase favored the magnetite spinal formation during F-T reaction, while $Fe_{1-x}O$-based catalysts were more likely to favor the formation and growth of the iron carbide crystals.

Keywords: Fischer-Tropsch synthesis, fused iron catalyst, precursor, selectivity.

The Fischer-Tropsch (F-T) process can be operated at high temperatures (HTFT) to produce a light syncrude and olefins. In practice, only fused iron catalysts are used for HTFT process. This technology is practiced on commercial scale at SASOL plants in South Africa, but the composition of the catalyst used is not known[1]. In recent years a substantial amount of data has been presented on the performance of alkali promoted fused magnetite catalyst by Satterfield and coworkers[2] and others[3].

Liu *et al.*[4, 5] have noted that, with the change of the precursor phase composition, a hump curve was detected for the fused iron catalyst activity for ammonia synthesis. A similar line may exist in the catalyst performance for Fischer-Tropsch synthesis.

Dry has already noticed that the relative amounts of wustite (FeO) and of magnetite (Fe_3O_4) present in the fused catalyst influence the final surface area[6]. Recently, Steynberg *et al.*[7] reported that the mole ratio of ($Fe^{3+}/2Fe^{2+}$) has an effect on catalyst parameters such as mechanical strength and surface area. So far, the effect of the precursor phase composition of fused iron catalyst on the performance of Fischer-Tropsch synthesis has not been reported.

In this study, the effect of the precursor composition of fused iron catalyst on the performance of Fischer-Tropsch synthesis was investigated. XRD, BET and CO_2 adsorption experiments were carried out to provide better insight into the relationship therein.

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Experimental

The catalysts were prepared by steps including melting iron oxides together with the required amount of promoters, cooling the melt and crushing the solid. The final mole ratio of Fe^{2+}/Fe^{3+} was controlled by addition of iron powder which acts as a reducing agent. The promoters in the samples were identical, including Al_2O_3, K_2O, CaO and other metal oxides, and the total content of the promoters was 6.3 wt%. The mole ratio of Fe^{2+}/Fe^{3+} was determined according to HG 1-1430-81. The catalysts, designated as F**1**-F**8**, had a mole ratio of $Fe^{2+}/Fe^{3+}$of 0.41, 0.56, 1.24, 2.05, 3.46, 5.74, 7.04 and 8.43 respectively.

About 0.5 mL of catalyst (20-40 mesh) was charged into the fixed bed reactor. The Fischer-Tropsch reaction was carried out under conditions of $n(H_2)/n(CO) = 2.0$, $T = 578$ K, $p = 1.4$ MPa and GHSV = 12600 h^{-1}. The products obtained over a period of 6 h were analyzed by gas chromatography.

The XRD patterns of the catalyst samples before reduction and after catalytic reaction were performed on a Thermo ARL X'TRA X-ray diffractometer (Cu K_α radiation). The BET surface areas of the reduced catalyst samples were obtained by N_2 adsorption at liquid nitrogen temperatures after degassing at 473 K using a Micromeritics ASAP 2010 apparatus. The CO_2-adsorpion studies of the reduced catalyst samples were carried out at 323 K in a Micromeritics Autochem 2910 system.

Results and Discussion

The XRD patterns of the catalyst samples with different precursor phase composition are shown in **Figure 1**. It can be seen that the precursor phase of sample F**1** is $Fe_{3-x}O_4$ and Fe_2O_3 is not detected, while sample F**2** is virtually a conventional Fe_3O_4-based catalyst. In the case of samples F**3**- F**5**, Fe_3O_4 phase coexisted with FeO phase where the relative intensity was different. The precursor phase of samples F**6**- F**8** was only FeO.

Table 1 shows that when $n(Fe^{2+})/n(Fe^{3+}) \geqslant 0.56$, the BET surface area of the reduced catalyst decreased and ranged between 9-10 m^2/g. A comparable study has been given by Steynberg *et al*[7]. The carbon dioxide adsorption results are also presented in **Table 1**. It is seen that the surface basicity of the reduced catalyst decreased when the mole ratio of Fe^{2+}/Fe^{3+} increased from 0.41 to 5.74, and then increased slightly when $n(Fe^{2+})/n(Fe^{3+})$ further increased from 5.74 to 8.43. We can attribute the observed changes to the fluctuant distribution of the promoters on the catalyst surface brought about by their various precursor phases[5].

Table 1 BET area and CO_2 adsorption of reduced catalyst samples

Catalyst	F**1**	F**2**	F**3**	F**4**	F**5**	F**6**	F**7**	F**8**
$n(Fe^{2+})/n(Fe^{3+})$	0.41	0.56	1.24	2.05	3.46	5.74	7.04	8.43
BET area after reduction(m^2/g)	15.13	11.69	9.94	10.51	9.18	9.94	8.92	10.18
Volume of CO_2 adsorbed(ml/g)	1.84	1.69	1.53	1.50	1.39	1.24	1.52	1.46

Figure 1 XRD patterns of fused iron catalyst with various $n(Fe^{2+})$ /$n(Fe^{3+})$ before reduction

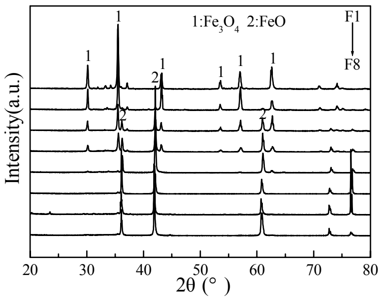
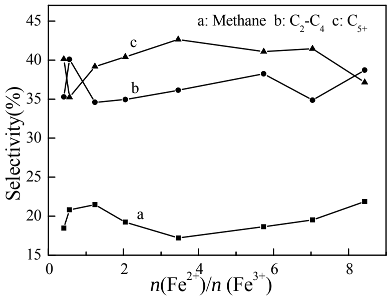


Figure 2 F-T selectivity as a function of $n(Fe^{2+})/n(Fe^{3+})$ of fused iron catalysts



The reaction data for the F-T synthesis over the catalysts with different precursor phase composition is presented in **Table 2**. It is seen that the precursor phase seems to have no significant effect on the catalytic activity for the F-T synthesis. Among the catalysts herein, F**2** exhibited the lowest syngas conversion and the lowest H_2/CO usage ratio accordingly. It is obvious that a higher area will result in a higher rate of reaction for the catalyst[7], but direct relationship between catalytic activity and surface area has not been found from this study.

Hydrocarbon selectivities, as a function of the mole ratio of Fe^{2+}/Fe^{3+}, are shown in **Figure 2**. As $n(Fe^{2+})/n(Fe^{3+})$ changes, no discernible trend was found in C_2-C_4 hydrocarbons and oxygenates seletivities. However, the selectivity of C_{5+} hydrocarbon products was dependent on the mole ratio of Fe^{2+}/Fe^{3+}, which was represented by a hump-shaped curve. The order of the selectivity of C_{5+} hydrocarbon products was as follows: $Fe_{1-x}O > Fe_{3-x}O_4 > Fe_3O_4$. For the samples F**1,** F**2** and F**5,** the selectivity of C_{5+} hydrocarbon products was 40.13, 35.25 and 42.64 % respectively. The opposite trend was observed for the dependence of the selectivity of methane products on the mole ratio of Fe^{2+}/Fe^{3+}. The above experimental results indicate that the wustite $Fe_{1-x}O$ system can not only improve the performance of ammonia synthesis[4, 5], but also improve that of F-T synthesis.

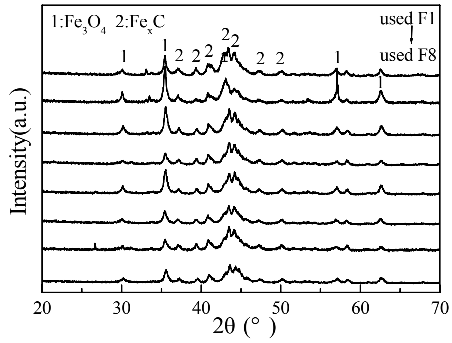
Table 2 The performance of F-T synthesis over fused iron catalysts of different precursor phase[a]

Catalyst	$X(CO+H_2)$ (%)	H_2/CO usage ratio	Product distribution/*wt* %				$Y(C_{5+})$ (g/m^3)
			Methane	C_2-C_4	C_{5+}	WSO[b]	
F**1**(0.41)	71.65	1.212	18.47	35.28	40.13	6.13	44.12
F**2**(0.56)	66.63	1.067	20.81	40.09	35.25	3.87	38.83
F**3**(1.24)	69.49	1.182	21.47	34.58	39.18	4.78	39.31
F**4**(2.05)	70.60	1.178	19.23	34.95	40.41	5.42	42.19
F**5**(3.46)	69.90	1.157	17.21	36.14	42.64	4.02	45.11
F**6**(5.74)	72.52	1.237	18.64	38.24	41.08	2.03	42.78
F**7**(7.04)	71.55	1.201	19.52	34.87	41.45	4.17	44.91
F**8**(8.43)	70.33	1.183	21.88	38.71	37.16	2.25	39.31

a: Reaction conditions: $n(H_2)/n(CO) = 2.0$, $T = 578$ K, $p = 1.4$ MPa, GHSV = 12600 h^{-1}.

b: Refers to water soluble oxygenates. *X*: Conversion, *Y*: Yield.

Figure 3 XRD patterns of fused iron catalyst with various $n(\mathrm{Fe}^{2+})/n(\mathrm{Fe}^{3+})$ after F-T reaction



The XRD patterns of the used catalysts are shown in **Figure 3**. Catalysts with precursors containing Fe_3O_4 phase favored the magnetite spinal in stead of the iron carbide formation during F-T reaction, and that might account for the exceptional F-T activity and selectivity behavior of F**2**, although it possesses relatively strong surface basicity that should suppress the formation of methane[8]. On the other hand, $Fe_{1-x}O$-based catalysts are more likely to favor the formation and growth of the iron carbide crystals, resulting in a better environment for carbon-containing monomers to contact each other and propagate[9]. The used F**8** showed a decrease in the carbide phase formation compared with other wustite-rich catalysts, which suggested that further increase in $n(\mathrm{Fe}^{2+})/n(\mathrm{Fe}^{3+})$ of the precursor catalyst will result in deterioration of its F-T performance.

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