Fischer–Tropsch synthesis on Fe–Mn ultrafine catalysts

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The Fischer–Tropsch (FT) synthesis on Fe–Mn ultrafine catalysts prepared by a special degradation method of Fe–Mn complexes is presented. The effects of preparation method and Mn content on the FT performance are examined and the active phases and the role of Mn are elucidated.

Keywords: Fe–Mn catalyst; ultrafine particle; FT synthesis; active phase; role of Mn

1. Introduction

Iron based catalysts have been used in commercial Fischer–Tropsch (FT) synthesis, and manganese has been regarded as one of the most effective promoters for enhancing selectivity for light olefins [1], although the interpretations of its role still remain controversial. The catalysts were conventionally prepared by coprecipitation of the corresponding nitrates in alkali or by decarbonylation of the corresponding metal carbonyl compounds. In this paper, a special degradation method of Fe–Mn complexes is used to obtain Fe–Mn ultrafine particle (UFP) catalysts and the effects of preparation method and manganese content on FT performance are studied. The active phases and the role of manganese are elucidated.

2. Experimental

2.1. PREPARATION AND PROPERTIES OF THE CATALYSTS

Fe–Mn oxalate precursors were prepared by coprecipitation of the corresponding metal acetate solutions with aqueous oxalic acid solution followed by filtration and extensive wash with water. Fe–Mn acetate or hydroxide precursors were prepared by coprecipitation of the corresponding metal nitrate solutions with acetic acid solution or $NH_8 \cdot H_2O$ respectively followed by filtration and wash. Subsequently, the precursors were fast or gently degraded in air at 773 K, denoted as D or C respectively, followed by impregnation with KNO_3 solution and drying in air at 393 K to obtain Fe–Mn UFP catalysts.

The catalysts and some of their properties are listed in table 1. Each catalyst contains about 1 wt% of K_2O. The average particle size of all catalysts is much less than 0.1 μm, which falls within the range of ultrafine particles, as is evidenced by TEM [2] and by small angle X-ray scattering (SAXS).

The physical mixed catalyst was prepared by mixing Fe UFP (prepared by fast degradation of FeC_2O_4) and $MnCO_3$ with Fe/Mn atomic ratio of 3 followed by impregnation with KNO_3 solution and drying in air at 393 K. BET surface area of this catalyst is 30.2 m^2/g. The average particle size measured by TEM is about 0.1 μm.

2.2. FT SYNTHESIS AND XRD EXAMINATION

FT synthesis was carried out in a continuous down-flow 1.5 cm i.d. tube microreactor, in which pelleted catalyst sample of 5 ml was employed. The catalyst was first reduced and carburized in syngas ($H_2/CO = 2$) at 553 K, 0.2 MPa for 36 h. Then the pressure and temperature were progressively increased to the indicated reaction condition. After 72 h on stream allowing to get a steady performance, the daily averaged FT performance was measured. The results were presented in terms of activity as CO conversion (X_{CO}), light olefin selectivity as olefin to paraffin (O/P) ratio in the C_2–C_4 fraction, methane selectivity as weight percentage in total hydrocarbons and CO_2 selectivity as molar percentage of CO converted to CO_2 in total CO converted.

XRD was performed on a Rigaku D/max-rA diffractometer using Cu K_α radiation in combination with a graphite monochromator. Measures were taken to protect treated syngas and reacted catalysts from oxidation before XRD examination.

Table 1
Catalysts and some of their properties

Catalyst	Precursor	Fe/Mn molar ratio	Degradation method	BET surf. area (m^2/g)	D[a] (nm)
OFe3Mn1(C)	oxalate	3	C	30.5	17.7
OFe3Mn1(D)	oxalate	3	D	117.8	9.9
HFe3Mn1(D)	hydroxide	3	D	136.8	8.8
AFe3Mn1(D)	acetate	3	D	89.2	7.2
OFe(D)	oxalate	no Mn	D	31.8	12.8
OFe2Mn1(D)	oxalate	2	D	83.2	11.5
OFe1Mn3(D)	oxalate	1/3	D	50.2	11.2
OMn(D)	oxalate	0	D	–	13.7

[a] Average particle size as measured by SAXS.

3. Results and discussion

3.1. FT SYNTHESIS

Table 2 shows the effects of degradation method and precursor on the FT performance. Among the four catalysts, OFe3Mn1(C) has the lowest activity. This indicates quite clearly that fast degradation of Fe–Mn complex is preferable for the preparation of Fe–Mn UFP catalyst with much higher FT activity. On the other hand, among the catalysts from different precursors, the order of activity is HFe3Mn1(D) > OFe3Mn1(D) > AFe3Mn1(D), which is consistent with that of the BET surface area as listed in table 1, implying that the number of active sites increases with specific surface area of the catalysts.

Since the O/P ratio depends not only on the catalyst and reaction conditions but also on the degree of CO conversion, this influence must be taken into account when light olefin selectivity is concerned. Usually, the O/P ratio is only slightly affected by X_{CO} as long as it does not exceed 60%, and markedly decreases with X_{CO} when it is higher than 60% [3]. The light olefin yield of OFe3Mn1(D) is much higher than that of OFe3Mn1(C) taking CO conversion into consideration (see table 2). This indicates that the catalyst from fast degradation gives more light olefins than that from gentle decomposition. The light olefin selectivity of OFe3Mn1(D) is much higher than that of HFe3Mn1(D) and AFe3Mn1(D), showing the effect of precursor on light olefin selectivity.

The changing trend of CO_2 selectivity is much like that of the activity, i.e., the higher the activity, the higher is the CO_2 selectivity.

The effect of catalyst composition on FT performance has also been examined for catalysts from fast degradation of Fe–Mn oxalates. Fig. 1 gives the relation between FT performance and Mn content showing that with increasing Mn content:

(a) CO conversion slightly decreases at first and then declines sharply. The activity of OMn(D) is very low;

(b) light olefin selectivity increases remarkably at the beginning and then remains virtually constant but rises sharply when the catalyst contains no iron;

Table 2
FT performance of Fe–Mn UFP catalysts prepared by different methods and from different precursors. ($T = 573$ K, $P = 2.4$ MPa, VHSV = 550 h^{-1}, $H_2/CO = 2$)

Catalyst	CO conv. (%)	HC distribution (wt%)					O/P ratio in C_2–C_4	S_{CO_2} (%)	H_2/CO usage
		CH_4	C_2	C_3	C_4	C_{5+}			
OFe3Mn1(C)	70.2	9.3	7.7	9.8	7.5	65.7	3.80	34.3	0.89
OFe3Mn1(D)	92.4	12.7	9.1	11.6	8.0	58.6	4.04	42.3	1.09
HFe3Mn1(D)	96.2	15.9	11.8	15.0	9.9	47.4	2.00	42.8	1.15
AFe3Mn1(D)	71.6	10.8	8.2	10.7	8.6	61.7	3.58	34.9	1.09

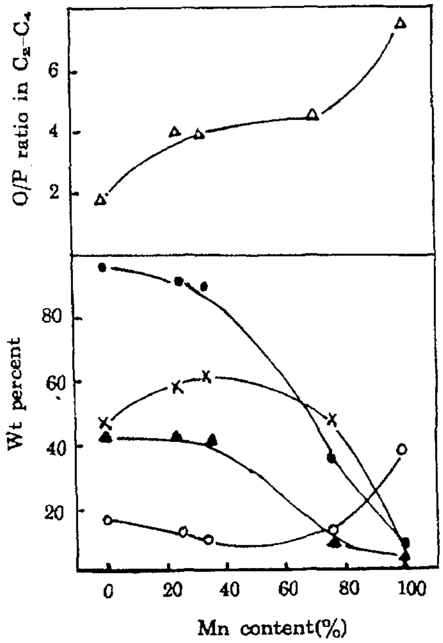

Fig. 1. Effects of catalyst composition. (●) CO conversion, (○) CH_4 selectivity, (×) C_{5+} selectivity, (▲) CO_2 selectivity. ($T = 573$ K, $P = 2.4$ MPa, VHSV $= 550\ h^{-1}$, $H_2/CO = 2$.)

(c) the weight percentage of C_{5+} hydrocarbons increases distinctly but drops sharply when the catalyst is manganese-rich, and tends to zero for OMn(D);

(d) methane selectivity considerably decreases but goes up again when the catalyst is rich in Mn. The methane selectivity of OMn(D) is very high.

(e) CO_2 selectivity slightly decreases at the beginning but goes sharply down when the catalyst is rich in manganese.

The above results suggest that the addition of an appropriate amount of manganese can remarkably improve the light olefin selectivity of iron based UFP catalyst and depress in certain extent the formation of methane and CO_2 without impairing the stability of the catalyst.

3.2. THE ACTIVE PHASES AND THE ROLE OF MANGANESE

The bulk phases of the syngas pretreated and the reacted catalyst were determined by XRD for catalyst OFe3Mn1(D). It is shown that the syngas pretreated catalyst consists of χ-Fe_5C_2 and FeO–MnO, independently of the temperature and time of pretreatment. It reveals that the starting phases of the catalyst for FT synthesis are χ-Fe_5C_2 and FeO–MnO. It is also indicated from XRD that after 120 h on stream the catalyst is composed of mixed spinel-like phase $Mn_xFe_{3-x}O_4$ and $MnCO_3$. The cell parameter (a) of the spinel-like phase is about 0.844 nm, which is between that of Fe_3O_4 ($a = 0.840$ nm) and of $MnFe_2O_4$ ($a = 0.855$ nm) but nearer to that of Fe_3O_4. The remainder is $MnCO_3$. These results suggest that the active phases of the catalyst are continuously changed during the conditioning period. At the beginning, the active phase is χ-Fe_5C_2 or the oxide of Fe^{2+} and its solid solution with MnO. But they are unstable and converted to $Mn_xFe_{3-x}O_4$ via osmosis and migration with each other and reoxidized by CO_2 and H_2O in the reaction medium. That is to say, the mixed spinel-like $Mn_xFe_{3-x}O_4$ phase is the stable active phase of Fe–Mn UFP catalyst at the steady-state of reaction.

Fig. 2 shows the activity and selectivity of the catalyst as a function of reaction time during the conditioning period. It indicates that the continuous change of active phases will result in gradual alteration of activity and selectivity, and reach the stable form at the steady-state after about 100 h on stream. It is also indicated that the catalyst does not deactivate after 120 h on stream.

The role of Mn was extensively discussed previously [3]. It is recognized that Mn has both electronic (chemical) and geometric effects on iron based UFP catalyst. It has been mentioned above that Mn is mainly presented as $MnCO_3$ under reaction condition. In order to probe further the effect of $MnCO_3$, the FT performance of a mixture of Fe UFP catalyst and $MnCO_3$ with Fe/Mn atomic ratio of 3, as listed in table 3, was examined.

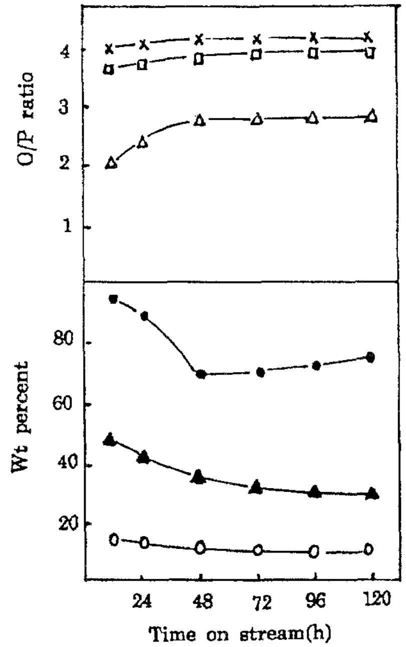

Fig. 2. FT performance of catalyst OFe3Mn1(D) as a function of reaction time during the conditioning period. (●) CO conversion, (○) CH_4 selectivity, (▲) CO_2 selectivity, (△) $C_2^=/C_2^0$, (×) $C_3^=/C_3^0$, (□) $C_4^=/C_4^0$. ($T = 553$ K, $P = 2.4$ MPa, VHSV $= 550$ h^{-1}, $H_2/CO = 2$.)

Table 3
FT performance of a mixture of Fe UFP and $MnCO_3$ with Fe/Mn atomic ratio of 3. ($T = 573$ K, $P = 2.4$ MPa, VHSV $= 550\ h^{-1}$, $H_2/CO = 2$)

CO conv. (%)	HC distribution (wt%)					O/P ratio in C_2–C_4	S_{CO_2} (%)	H_2/CO usage
	CH_4	C_2	C_3	C_4	C_{5+}			
90.1	30.4	15.5	16.3	9.3	28.5	0.34	47.0	1.02

It is very clear, from the comparison of the FT performance of catalyst OFe3Mn1(D) (see table 2) with that of the mixture, that the mixture gives a lower FT activity and a much lower selectivity to light olefins but a much higher selectivity to methane and CO_2 even though its composition is identical to that of OFe3Mn1(D). This implies that only when $MnCO_3$ is intimately contacted with iron-containing phase can it improve the light olefin selectivity remarkably and depress the formation of CH_4 and CO_2, and this efficacy cannot be achieved by physical mixing of $MnCO_3$ with iron catalyst. It is very likely that only when intimate contact is attained can appropriate coordination and interaction between iron and manganese be obtained, and give full play to their synergistic catalytic action.

4. Conclusions

Fe–Mn UFP catalysts prepared by the degradation of Fe–Mn complexes are active for FT synthesis and with high yield to light olefins, among which the catalysts with Fe/Mn atomic ratio of 3 from fast degradation of Fe–Mn oxalate exhibits the best FT performance.

The FT active phases of Fe–Mn UFP catalyst are continuously changed during the conditioning period, from χ-Fe_5C_2 or/and FeO–MnO at the beginning to $Mn_xFe_{3-x}O_4$ at steady-state of reaction. $MnCO_3$ at the steady-state is the active species for improving light olefin selectivity and impressing the formation of methane and CO_2 by intimately contacting or coordinating with iron-containing phase.

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