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FISCHER-TROPSCH SYNTHESIS OF LIGHT OLEFINS CATALYZED BY $Fe_3(CO)_{12}$-MOH-HYZEOLITE AND $Fe_3(CO)_{12}$-MZSM5 (M=K OR Cs)$^{1)}$

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Fischer-Tropsch syntheses by two catalyst systems (A)$Fe_3(CO)_{12}$-MOH-HYZeolite and (B) $Fe_3(CO)_{12}$-MZSM5 (M=K or Cs) were performed using a pressurized fixed-bed flow reactor at 260-320 °C (CO/H_2=1-1.5, 14 atm). On the catalyst (A), especially when M was Cs, the activity was very high (conversion of carbon monoxide was up to 75%) and stable. On both catalysts the main product was propylene.

A number of attempts have been made to synthesize lower molecular weight olefins from synthesis gas by selective Fischer-Tropsch (F-T) reaction.$^{2-9)}$ It has been found that catalysts prepared from low valent transition metal complexes such as iron carbonyls supported on metal oxides exhibited a high selectivity for light olefins.$^{4-9)}$ For example, McVicker and Vannice have reported that a catalyst derived from $K_2Fe(CO)_4$-Al_2O_3 exhibited a high selectivity for lower olefins with low activity (conversion of CO, up to 3.5%).$^{5)}$ In most cases, disadvantages of these catalysts are rather low activity$^{4-8)}$ and/or rapid deactivation of the catalysts.$^{5-8)}$ We now report that the F-T catalysts derived from (A) $Fe_3(CO)_{12}$-MOH-HYZeolite and (B) $Fe_3(CO)_{12}$-MZSM5, where M is potassium or cesium, give propylene as a main product with a high and stable catalytic activity.

Typical preparation of the catalysts is as follows. (A) $Fe_3(CO)_{12}$-4MOH-HYZeolite: To a KOH or CsOH (2.0 mmol) solution in 5 ml of methanol was added $Fe_3(CO)_{12}$ (0.5 mmol, 252 mg) and the mixture was stirred at 25 °C under an atmosphere of argon for 2 h. Into a suspension of HYZeolite (0.30 g) in 5 ml of methanol, 2.0 ml of the methanol solution of $Fe_3(CO)_{12}$-MOH was added and the mixture was stirred at 25 °C for 3 h. Removal of the solvent in vacuo gave a deep red solid$^{10)}$ (Fe/HY, 10 wt%, K/HY, 9.4 or Cs/HY, 32wt%). $Fe(CO)_5$-MOH-HY was prepared similarly. (B) $Fe_3(CO)_{12}$-CsZSM5: To a suspension of HZSM5 (0.30 g) in methanol (20 ml) was added 0.017 g of CsOH and the mixture was refluxed for 2 h. Then 0.090 g of $Fe_3(CO)_{12}$ was added to the suspension and it was refluxed for

Table 1. Fischer-Tropsch Synthesis Catalyzed by Iron Carbonyls-Cs or K-Zeolite Systems[a)]

Run	Catalyst	React. temp / °C	Conv. of CO/%	Effect.[c)] conv./%	Distribution of hydrocarbons (C-%)[b)]						
					C_1	C_2	C_3	C_4	C_5	C_6	C_7^+
1	$Fe(CO)_5$-3KOH-HY	300	18	9.5	26	18(10)	24(43)	16	8	5	5
2	$Fe(CO)_5$-3CsOH-HY	300	26	13	15	13(85)	18(82)	14	11	10	19
3	$Fe_3(CO)_{12}$-4KOH-HY	300	58	26	18	12(28)	21(77)	17	11	8	13
4	$Fe_3(CO)_{12}$-4CsOH-HY	300	62	29	18	12(45)	21(84)	17	12	9	11
5	$Fe_3(CO)_{12}$-4CsOH-HY[d)]	300	75	34	15	11(51)	20(89)	15	11	9	19
6	$Fe_3(CO)_{12}$-3CsOH-HY	320	75	31	24	11(34)	20(81)	15	10	8	11
7	$Fe_3(CO)_{12}$-3CsOH-γ-Al_2O_3[g)]	320	11	3.6	23	17(87)	16(89)	11	8	8	18
8	$Fe_3(CO)_{12}$-3CsOH-HZSM5[e)]	300	11	6.7	12	10(80)	14(82)	11	9	12	31
9	$Fe_3(CO)_{12}$-KZSM5[e)]	300	9.3	3.8	10	17(89)	23(93)	17	11	10	12
10	$Fe_3(CO)_{12}$-CsZSM5[e)]	300	8.9	5.0	10	13(88)	20(87)	15	11	10	21
11	$Fe_3(CO)_{12}$-CsZSM5[e)]	320	12	6.3	14	16(80)	22(90)	18	11	9	10
12	$Fe_3(CO)_{12}$-CSZSM5[f)]	300	13	7.9	13	14(74)	22(89)	18	11	10	12
13	$Fe_3(CO)_{12}$-CsZSM5[f)]	320	16	7.5	18	15(24)	23(65)	20	11	7	5

a)P(total)=14 atm, $CO/H_2=1$, SV=2000 h^{-1}. b)Selectivities for olefins are given in the parentheses. c)Carbon monoxide converted into hydrocarbons based on the charged CO. d) $CO/H_2=1.5$. e)$SiO_2/Al_2O_3=400$. f)$SiO_2/Al_2O_3=50$. g)JRC-ALO-4. Deactivated in 10 h.

additional 2 h and the solvent was removed in vacuo (Fe, 10 wt%, Cs, 5 wt%).

The F-T reaction was performed in a conventional pressurized fixed-bed flow reactor (4.0 mm$^{\phi}$x100 mm. $CO/H_2=1-1.5$, 14 atm, SV=2000 h^{-1}). Each catalyst was activated in a flow of H_2 at 260 °C for 2 h.

Both catalysts A and B were active for the production of light olefins with a trace amount of methanol. Results are summarized in Table 1. The data in the table were taken after 6 h on stream.

In the reaction on $Fe(CO)_5$-3KOH-HY (Method A) at 300 °C (Run 1), the conversion of carbon monoxide was 18% and 9.5% of the charged carbon monoxide was converted into low molecular weight hydrocarbons with low olefin content. When CsOH was used instead of KOH, both the activity (conversion 26%, effective conversion (see the footnote of the Table 1, c) 13%) and the selectivity of olefins were markedly improved (Run 2). When trinuclear iron carbonyl, $Fe_3(CO)_{12}$, was used, the catalysts were more active (Runs 3 and 4) and when CO/H_2 was 3/2 (Run 5) 75% of CO was converted. In this case, the main product was propylene with a stable catalytic activity kept for more than 40 h. The distribution profile in these runs except for Run 1 followed the Schulz-Flory (S-F) law (an α-value for Run 5 was 0.63). HZSM5 and γ-alumina were less favorable supports for the production of light olefins (Runs 7 and 8).

The catalyst system $Fe_3(CO)_{12}$-MZSM5 (Method B; M=K or Cs) was also effective for selective production of lower olefins (Runs 9-13). Although the activities were lower than those of $Fe_3(CO)_{12}$-MOH-HY, the product distribution did not follow the

S-F law (Fig. 1). The chain growth probability sharply dropped down at C_7 and hydrocarbons above C_{10} were not produced. Through these runs, the main product was propylene and the selectivities for methane can be controlled to less than 14%. In the catalyst B, cesium showed slightly larger effective conversion than potassium.

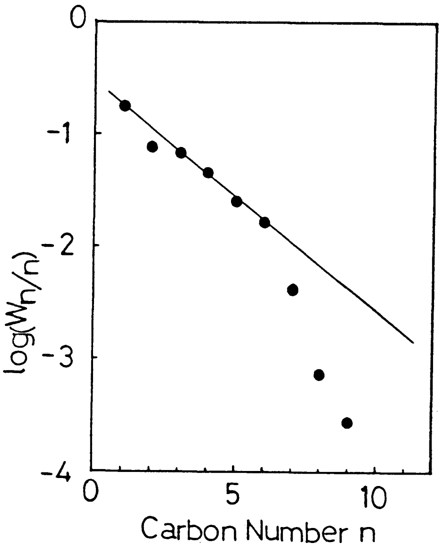

Fig. 1. Schulz-Flory plot (Run 11).

It is well known that highly dispersed iron cluster with a size less than 1.4 nm, which is an active catalyst for selective production of propylene, is formed by the thermal decompsition of $Fe_3(CO)_{12}$[11] supported on Al_2O_3 or MgO.[7] However, the particle size increased to 20-30 nm by sintering of the iron under the prolonged F-T reaction losing the selectivity.[7] Although the characterization of the present catalysts has not been performed yet, the characteristics feature of the catalysts that the product distributions with the maximum at propylene is kept for long time may be partly due to the "cage effect"[12] of the zeolites to prevent the complete sintering of the formed well-dispersed iron/alkali metal particles.[5,13]

In conclusion novel catalyst systems, $Fe_3(CO)_{12}$-MOH-HY and $Fe_3(CO)_{12}$-MZSM5,[14] especially when M is Cs, are found to be active and stable for production of light olefins.

References

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10) The IR spectrum of the deep red solid exhibited ν C=O at 2071(w), 2002(vs, br), 1962(s), 1946(m), 1937(m), 1656(m) cm^{-1} strongly suggesting the formation of supported $HFe_3(CO)_{11}^-$ (Ref.11). The activated catalyst had no νC=O band.

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13) The following additional two factors should be noted to explain the deviation from the S-F law in Runs 9-13: i) Secondary cracking of longer hydrocarbons. ii) Capture of the longer chain hydrocarbons in the pores of zeolites. The former is unlikely because the acidic site of HZSM5 is replaced by the alkali metal and iso-hydrocarbons were not detected in the product at all. The latter would be ruled out since in the reaction on $Fe_3(CO)_{12}$-CsOH-HZSM5, which is expected to have the similar pore size as $Fe_3(CO)_{12}$-CsZSM5, the product distribution followed the S-F law; over C_{20} was detected after 30 min on stream.

14) $Fe_3(CO)_{12}$-CsY was inactive.

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