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DIRECT SYNTHESIS OF ISOPARAFFINS FROM SYNTHESIS GAS

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The product distribution of Fischer-Tropsch synthesis was drastically improved by utilizing hybrid catalysts prepared by combining F-T catalysts such as cobalt, iron and ruthenium catalysts with metal supported Y zeolite while keeping high activities. About 80% of the product was C_{4-11} hydrocarbons, most of which were isoparaffins.

Although the Fischer-Tropsch (F-T) synthesis is one of the most promising methods for producing gasoline from carbon resources other than petroleum,[1)] it has disadvantages that it is hard to produce a gasoline range product selectively and that the product hydrocarbons are composed of mostly normal paraffins,[2)] which exhibit poor octane number. Chang et al.[3)] or Bruce et al.[4)] have demonstrated that the products of CO hydrogenation over hybrid catalysts composed of iron catalysts and ZSM-5 or supported cobalt catalysts and ZSM-5 are free from C_{12}^{+} hydrocarbons and are rich in aromatics and isoparaffins. Limited carbon number distribution and modified chemical structure of products are also attainable by conducting the reaction with Co, Fe, and Ru catalysts supported on zeolites.[5-7)] Present authors have shown that isoparaffins are formed exclusively from synthesis gas with Ru-Pt bimetallic clusters supported on acid type zeolites.[8)]

In the present work, the selective synthesis of isoparaffins from synthesis gas with hybrid catalysts composed of F-T catalysts and metal supported zeolites was tried.

Hybrid catalysts were powdery mixtures composed of F-T catalysts (Co-La/SiO_2 catalyst, a fused iron catalyst and a Ru/TiO_2) and metal supported Y-type zeolites. Supported cobalt catalysts were prepared and were activated following the method which has been shown elsewhere.[9)] The content of cobalt and lanthanum was 10% and 3% by weight, respectively. Carrier materials and zeolites used were a commercially available silica gel (Fuji-Davison ID gel), a home made ZSM-5 (SiO_2/Al_2O_3=59), and a dealuminated Y type zeolite (DAY, SiO_2/Al_2O_3=8). Metal loaded zeolites were prepared by a conventional ion exchange method.[10)] They were then dried in an air oven at 120 °C and calcinated in air at 450 °C for 3 h, before mixing with the F-T catalyst.

Synthesis gas reactions were conducted under pressurized conditions, utilizing a fixed bed flow type reaction apparatus. The reactor was a stainless tube with 6mm inner diameter. Standard reaction conditions were as follows : Temperature, 220-250 °C ; Pressure 6-21 atm ; Time factor (W/F), 10 g-cat·h/mol; H_2/CO, 2/1 molar ratio; Catalyst weight, 2 g: Products were analysed by gas chromatography.

Performances of several supported Co catalysts and CoLa/SiO_2-zeolite hybrid catalysts are shown in Table 1. The ratios of isoparaffin to normal paraffin (i/n ratio) for zeolite-supported cobalt catalysts are, as expected much higher than that on silica gel-supported one. However, the methane selectivities are much higher and gasoline fractions are less with lower conversions. Thus, zeolites are concluded to be not favorable carriers for cobalt in terms of selectivity and activity. Table 1 also compares hybrid catalysts with supported catalysts. Although it is apparent that zeolite-supported catalysts are desirable in respect of i/n ratio, hybrid catalysts are more suitable concerning not only the i/n ratio but also the selectivity of gasoline fractions and the CO conversion. It should be also noted that the i/n ratio of C_4 paraffins is much higher for the hybrid catalyst containing H-DAY than that containing H-ZSM-5. It could be attributed to the shape selectivity. These results emphasize the advantage of hybrid catalysts that the activity of hydrocarbon synthesis and the product selectivity for chemical structure can be regulated independently.

Table 1. Synthesis of isoparaffins over supported catalysts and hybrid catalysts

Catalyst	CO conv. /%	Selectivity (C-wt%) CH_4	C_4-C_{12}	C_{13}^+	i/n ratio C_4H_{10}
10wt%Co/SiO_2	53.1	13.6	65.4	9.8	0
10wt%Co/ZSM-5	18.8	43.4	42.8	0	0.85
CoLa/SiO_2+fused SiO_2	32.5	16.8	59.6	10.7	0
CoLa/SiO_2+H-ZSM-5	44.5	10.1	79.8	0.7	0.43
CoLa/SiO_2+H-DAY	63.4	15.2	66.4	18.4	3.13

Standard condition : Temperature , 230 °C; Pressure , 6 atm; W/F , 10 g-cat.h/mol; H_2/CO , 2/1 molar ratio

As demonstrated in Table 2, the i/n ratios and the p/o (paraffin/olefin) ratios in C_4 and C_5 hydrocarbons are extremely high on the hybrid catalysts containing Pt-, Pd-, or Cu-DAY. This fact suggests that the hydrogenating ability of zeolite catalysts is the key step for selective synthesis of isoparaffins.

As can be seen in Fig. 1, this catalyst system clearly influences the hydrocarbon distribution. The original distribution of product hydrocarbon with the CoLa/SiO_2 catalyst is a rather flat one which distributes from C_1 to C_{20} or higher. It is worth noting for the hybrid catalyst system that C_1-C_3 hydrocarbons and C_{13}^+ products are drastically decreased and gasoline fractions are increased. This unique distribution of the product hydrocarbons could be anticipated to the acid catalysed reaction of 1-olefins, which are the primary products of F-T reaction, such as polymerization of lower olefins and cracking of higher hydrocarbons as pointed out already for the synthesis

Table 2. Effect of metal addition to dealuminated Y zeolite (DAY)

Catalyst	CO conv. /%	Selectivity (C-wt%)		i/n ratio		p/o ratio	
		CH_4	C_4-C_{12}	C_4	C_5	C_3	C_4
CoLa/SiO_2+fused SiO_2	22.2	15.0	55.8	0	0	0.2	0.3
CoLa/SiO_2+H-DAY [a)]	63.4	15.2	66.4	1.4	3.1	8.3	25.9
CoLa/SiO_2+Pt/DAY	19.2	11.2	80.5	2.1	6.3	9.0	26.2
CoLa/SiO_2+Pd/DAY	23.7	11.1	75.6	2.6	13.4	123	610
CoLa/SiO_2+Cu/DAY	38.6	9.0	86.1	4.2	40.0	91.1	136
Fe+Cu/DAY [b)]	88.5[c)]	8.5	75.5	2.6	5.8	∞[d)]	∞[d)]
Ru/TiO_2+Cu/DAY	11.5	19.0	63.6	1.4	0.7	∞[d)]	12.5

Standard condition : Temp , 220 °C; Press., 6 atm; W/F , 10 g-cat.h/mol; H_2/CO , 2/1 molar ratio; F-T catalyst/Zeolite , 1/1 by weight
Metal content : Pt , 1 wt%; Pd , 1 wt%; Cu , 6.4 wt%

a) Temp , 230 °C. b) Temp , 250 °C; Press. , 21 atm. c) H.C. Yield , 43.4% ; CO_2 Yield , 35.3%. d) Olefins are not detected.

gas reaction on Ru-Pt/Zeolite catalysts.[8)] Cracking of hydrocarbons usually requires temperatures as high as 400 °C or higher. Cracking occurs in the present system at temperatures as low as 220 °C. This could be attributed to the fact that the primary products of F-T synthesis are 1-olefins, which are easily protonated to carbenium ions, the reaction intermediates.

It is also clear from the data in Fig. 2 and Table 2 that the hybrid catalyst containing Fe and Ru based catalysts can also give products which are markedly different in their distributions from those of the parent catalysts[11)] and are rich in isoparaffins.

It should be noted that the i/n ratios of C_4 and C_5 paraffins are in excess of equilibrium values. The conventional route of acid catalyzed

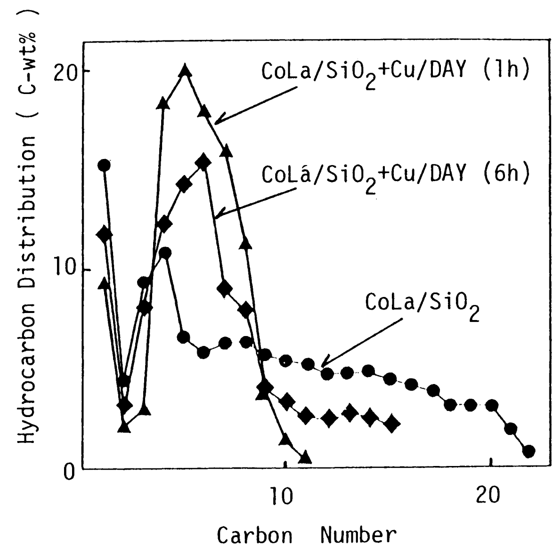

Fig. 1. Hydrocarbon product selectivity on a hybrid catalyst composed of Cu/DAY and CoLa/SiO_2 at 220 °C , 6 atm.

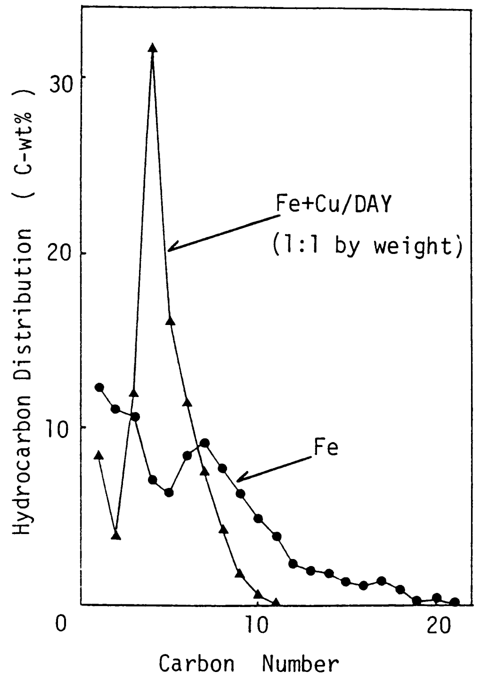

Fig. 2. Hydrocarbon product selectivity for fused Fe + Cu/DAY at 250 °C , 6 atm.

isomerization of n-olefins to iso-olefins and their successive hydrogenation, which should be ristricted by equilibrium, is hard to explain the above mentioned fact.

This paper presents a new scheme of isoparaffin synthesis as in Fig. 3: A straight chain terminal olefin, which is the primary product of F-T reaction, moves from the F-T catalyst to zeolite surface, where the olefin is protonated to secondary carbenium ion. The secondary carbenium ion is then isomerized to tertially carbenium ion because of higher stability of the latter species. The tertially carbenium ion reacts with 2 atoms of hydrogen to give an iso paraffin and a proton. The hydrogen atom should be supplied from gas phase by the spillover effect of the supported metals on the zeolite.[12)] The scheme is the same as that of transfer hydrogenation of olefins on zeolite[13)] except that the hydrogen source is not hydrocarbon but hydrogen molecule.

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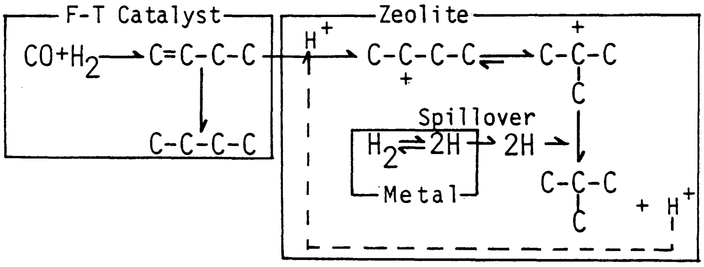

Fig. 3. Reaction scheme.

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