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Synthesis of Liquid Hydrocarbons from Carbon Monoxide and Water with a Hybrid Catalyst

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Synopsis. Liquid hydrocarbons were produced from carbon monoxide and water at temperatures from 220 to 280 °C and under moderately pressurized conditions (3 atm), by utilizing a hybrid catalyst composed of a Co/SiO_2 catalyst and a CO shift conversion catalyst. Most of the steam, either added or formed, was converted to hydrogen in the reaction of H_2O with CO on the CO shift catalyst.

It has been known that the synthesis gas produced by modern coal gasifiers has CO/H_2 ratios between 1 and 2.[1] On the other hand the CO/H_2 ratio of feed gas for the Fischer-Tropsch (F-T) synthesis is about 0.5. In order to regulate the difference, a part of CO should be converted to CO_2 and H_2 by the reaction with added steam, and the CO_2 is removed from the product by a conventional method.[2] In this process a CO shift converter is necessary and a large amount of steam is consumed.

Koelbel et al.[3] have demonstrated that CO and H_2O are able to be directly utilized with a precipitated iron catalyst to produce a hydrocarbon mixture. Since iron catalysts are active for the $CO-H_2$ reaction as well, a synthesis gas with high CO/H_2 ratio can be used for hydrocarbon synthesis without any added steam. Because, the water produced by the $CO-H_2$ reaction could be utilized to form hydrocarbons.

$$\begin{array}{lr} CO+2H_2 \rightarrow \text{-}CH_2\text{-}+H_2O & (1)\\ 2CO+H_2O \rightarrow \text{-}CH_2\text{-}+CO_2 & (2)\\ \hline 3CO+2H_2 \rightarrow 2\text{-}CH_2\text{-}+CO_2 & (3) \end{array}$$

The present authors examined the same reaction with a fused iron catalyst and found that the catalyst is quickly carbulized by CO and oxidized by water during the reaction to lose its catalytic activity.[4]

The authors have developed a highly active supported cobalt catalyst for the Fischer-Tropsch synthesis.[5] Although the catalyst is highly resistant to oxidation with water, it has little activity for the CO shift reaction. Thus, if the cobalt catalyst mixed with a CO shift catalyst is subjected to the synthesis gas reaction, CO and H_2 should react on the cobalt catalyst to form hydrocarbons and H_2O, then the resultant water should react in situ with CO, on the CO shift catalyst to form CO_2 and H_2.

$$\begin{array}{lr} CO+2H_2 \rightarrow \text{-}CH_2\text{-}+H_2O & (4)\\ CO+H_2O \rightarrow H_2+CO_2 & (5)\\ \hline 2CO+H_2 \rightarrow \text{-}CH_2\text{-}+CO_2 & (6) \end{array}$$

Experimental

The hybrid catalyst was prepared by physically mixing the granules (20—40 mesh) of a 10 wt% Co/SiO_2 catalyst with a commercial available Cu-Cr oxide catalyst (Nikki N-201). The Co/SiO_2 catalyst was prepared by impregnating a commercially available silica gel (Fuji Davison ID gel) with cobalt nitrate from its aqueous solution, calcining in air at 450 °C for 3 h, and then reducing the catalyst precursor in hydrogen flow at 400 °C for 15 h. The reduced Co/SiO_2 catalyst was mixed with the Cu-Cr oxide catalyst under nitrogen atmosphere and packed in a tubular reactor. The hybrid catalyst was activated by reducing, in situ, in flowing hydrogen at 250 °C for 3 h.

The reaction was conducted using a fixed bed flow type reaction apparatus under pressurized conditions. The details of this apparatus has been described elsewhere.[3] Water was fed by a micro-feeder and was evaporated in a container connected to the upper part of the reactor. All products effused from the reactor were withdrawn in the gaseous states from the pressurized zone and were analyzed by gas chromatographs. The details of analysis has been described elsewhere.[6]

Results and Discussion

The catalytic activity of Nikki N-201 for the CO shift reaction was tested under conditions: 240 °C, 1—5 atm, $CO/H_2O=3/1$ (mole ratio) and was shown to keep 100% H_2O conversion for more than 24 h.

In Fig. 1 are shown the yields of hydrocarbons, CO_2, and methane over the hybrid catalyst as a function of process time. The yield of CO_2 decreased gradually from the initial value, 50% (on CO base) to 30% within about 6 h and reached a steady state. Also the yields of product hydrocarbons and methane decreased in the similar manner as that of CO_2. The decrease in CO_2 yield could be attributed most probably due to the covering of active sites on the CO shift catalyst by high-boiling hydrocarbons, because a hybrid catalyst containing a supported ruthenium catalyst, which pro-

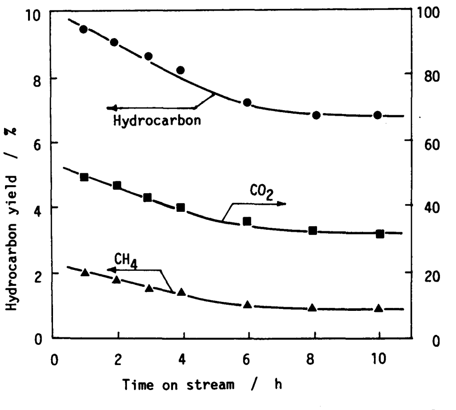

Fig. 1. Activity changes in the hybrid catalyst with time on stream CO/SiO_2+Cu-Cr (1/1 by weight), temp: 230°C, press.: 1 atm, $CO/H_2/H_2O$: 2/1/1, W/F: 20 g-cat.h mol^{-1}.

Table 1. Yield and Hydrocarbon Distribution

Run No.	1	2	3	4[a]
$CO/H_2/H_2O$ (mole ratio)	3/—/1	2/1/1	2/1/—	2/1/—
Yield (% carbon base)				
CO_2	33.9	56.0	6.0	0.1
Hydrocarbon	4.4	16.8	5.4	5.9
Distribution (C-wt%)				
C_1	4.2	8.7	6.2	5.0
C_2	1.7(29)[b]	2.6(2)	1.7(12)	1.4(64)
C_3	4.5(76)	8.1(23)	5.5(49)	5.8(82)
C_4	5.2	9.6	6.5	7.0
C_5-C_9	32.9	49.6	41.9	42.5
C_{10}-C_{14}	30.6	19.7	29.0	25.7
$C_{15}+$	20.9	1.7	9.2	12.6

10wt% Co/SiO_2 plus Cu-Cr Cat. = 1/1 (by weight). Temp: 230 °C. Press.: 3atm. W/F: 19.5 g-cat. h mol^{-1}.
a) Co/SiO_2 only. b) Olefin content (mol%).

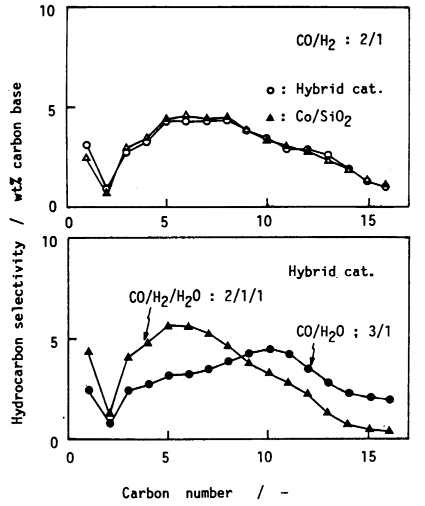

Fig. 2. Hydrocarbon distribution obtained from the reactions of water gas or synthesis gas. Temp: 230 °C, press.: 3 atm, W/F: 20 g-cat.h mol^{-1}, hybrid catalyst; 10 g-cat.h mol^{-1} (Co/SiO_2 catalyst).

duced higher hydrocarbons than the Co/SiO_2 catalyst, lost its activity more quickly. On the other hand, the decrease in the hydrocarbon formation should be attributed to the decrease in the partial pressure of hydrogen in the reaction mixture caused by the decrease in the conversion of CO and H_2O to hydrogen. All data described below were taken after the catalyst activity reached the steady state.

Some of the typical data of CO-H_2, CO-H_2O, and CO-H_2-H_2O reactions on the Co/SiO_2 catalyst or the hybrid catalyst are shown in Table 1 and Fig. 2. It is clear from the data in the table that while little CO_2 is formed on the Co/SiO_2 catalyst alone, almost all of water, irrespectively of that it is added or formed, reacted with CO to form CO_2 and hydrogen on the hybrid catalyst. For example, in experiments Nos. 2 and 3, the amount of CO_2 equal the sum of hydrocarbons (on carbon base) and added water. Since one molecule of water is formed for every one CO molecule reacted in the F-T synthesis reaction the sum of hydrocarbons and add water is the total amount of water supplied to the catalyst.

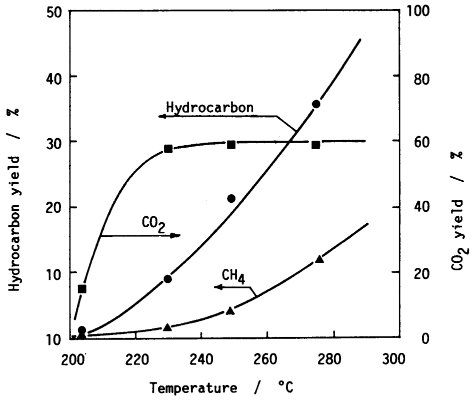

Fig. 3. Effects of temperature on the CO-H_2-H_2O reaction. Co/SiO_2+Cu-Cr (1/1 by weight), press.: 3 atm, $CO/H_2/H_2O$: 2/1/1, W/F: 20 g-cat.h mol^{-1}.

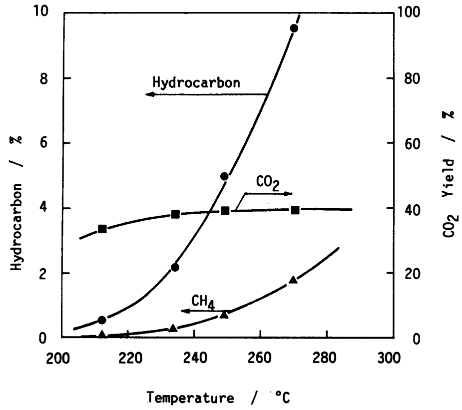

Fig. 4. Effects of temperature on the CO-H_2O reaction.
Co/SiO_2+Cu-Cr (1/1 by weight), press.: 3 atm, CO/H_2O: 3/1, W/F: 20 g-cat.h mol^{-1}.

It should be also noted that the addition of steam to the system markedly accelerates its productivity of hydrocarbons, while the hydrocarbon productivity of the Co/SiO_2 catalyst was scarcely affected by the addition of CO shift catalyst only. It should be attributed to the increase in the practical partial pressure of hydrogen caused by CO shift reaction, because the rate of hydrocarbon formation on the Co/SiO_2 catalyst is almost proportional to the partial pressure of hydrogen.[7]

The product pattern, shown in Fig. 2 and Table 1, is markedly affected by the CO shift catalyst and steam. The reaction of CO-H_2O system gave a product rich in olefins and higher hydrocarbons (C_{15+}), whereas the CO-H_2-H_2O reaction on the hybrid catalyst gave lower hydrocarbons rich in paraffins. The reaction of a synthesis gas (2CO+1 H_2) on the Co/SiO_2 and the hybrid catalysts gave products with intermediate characters as compared with other two cases mentioned above. Although the carbon number distribution of the products from the Co/SiO_2 and the hybrid catalyst systems are fairly close to each other, the hybrid catalyst gave a product which is richer in methane and paraffins than that on the Co/SiO_2 catalyst.

The characteristic features mentioned above are well interpreted by the partial pressures of CO and H_2. As it has been well known high CO/H_2 ratio in the synthesis gas is favored for the production of high molecular weight hydrocarbons and high olefin content in the F-T synthesis. The CO/H_2 ratio in the reaction mixture is in the order: Run 2>Run 3>Run 4>Run 1. The order is just the same as that of the average molecular weight and that of the olefin content in the product hydrocarbons.

Figures 3 and 4 illustrate the effects of reaction temperature on the product yields for the CO-H_2-H_2O system and the CO-H_2O system, respectively. In either system the yield of CO_2 reached the level which corresponds to 100% conversion of H_2O to H_2 and CO_2. The hydrocarbon yield increased monotonously with the increase in reaction temperature in the similar manner to that of the F-T synthesis on the same catalyst. The levels of hydrocarbon yield and space time yield were much higher for the CO-H_2-H_2O system than the CO-H_2O system because of the higher H_2 pressure and the lower CO pressure for the former system, as mentioned before.

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